

Quinone-mediated synthesis of hydrogen peroxide from carbon monoxide, water and oxygen

Cecilia Querci, Rino D'Aloisio, Rossella Bortolo, Marco Ricci, Daniele Bianchi*

EniChem S.p.A., Istituto G. Donegani, Centro Ricerche Novara, Via Fauser 4, I-28100 Novara, Italy

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Abstract

An improved method for the synthesis of hydrogen peroxide from carbon monoxide, water and oxygen catalyzed by palladium complexes in presence of a quinone co-catalyst is described.

Even if the reaction balance is formally the same, the mechanism of formation of hydrogen peroxide in the new process is totally different to that proposed for the reaction carried out in absence of quinones. Using 1,10-phenanthroline as a palladium ligand in a water/organic biphasic reaction medium, a dramatic enhancement of the catalyst stability was obtained operating in presence of 1,4-naphthoquinone, which prevented the formation of inactive binuclear palladium species. Additional improvements, with respect to the reaction carried out in absence of quinone, are the use of cheaper palladium ligands and the safer process conditions, since air can be used as a reagent instead of pure oxygen. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; N-ligands; Quinones; Hydrogen peroxide

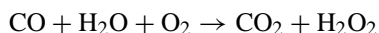
1. Introduction

Hydrogen peroxide is a chemical used in large volumes for chlorine free bleaching and in a wide variety of chemical processes as environmentally friendly oxidant, mainly due to its unique feature of producing water as the only by-product [1].

Industrially, hydrogen peroxide is almost universally produced by the alternate hydrogenation and oxidation with air of an alkylanthraquinone [2]. Although the process is efficient from a yield standpoint, it is quite complex and is carried out in two separate steps, using a stoichiometric amount of expensive high molecular weight quinones (e.g. 2-ethylanthraquinone).

Recently, we have reported a new process for the direct synthesis of hydrogen peroxide from carbon

monoxide, water and oxygen, catalyzed by palladium complexes with bidentate nitrogen ligands in a biphasic system [3]



The selected catalyst showed high efficiency and stability, making the process promising for a possible industrial application [4].

In this paper, we describe an improvement of the above mentioned process, obtained by operating in the presence of a suitable quinone, acting as a co-catalyst. This new process differs from the classical quinones alternate reduction and oxidation since the quinone is used in catalytic amount and the reduction and oxidation steps are carried out simultaneously in a single reactor.

The main advantages obtained by the new method are: (i) the use of a cheaper catalyst (the most effective

* Corresponding author.

E-mail address: daniele.bianchi@enichem.it (D. Bianchi).

palladium ligand is now 1,10-phenanthroline, instead of the expensive 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), (ii) an even improved catalyst stability, and (iii) safer process conditions (air can be used instead of pure oxygen in the gas mixture with carbon monoxide).

2. Experimental

The following ligands were used: 1,10-phenanthroline (phen) (**1**); 2,2'-bipyridine (bipy) (**2**); 4,7-diphenyl-1,10-phenanthroline (4,7-dpphen) (**3**); 5-nitro-1,10-phenanthroline (5-NO₂phen) (**4**); 2,9-dimethyl-1,10-phenanthroline (2,9-dmphen) (**5**); 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (2,9-dm-4,7-dpphen) (**6**).

The following quinones were used: 1,4-benzoquinone (**7**); phenyl-1,4-benzoquinone (**8**); 1,4-naphthoquinone (**9**); 2-methyl-1,4-naphthoquinone (**10**); tetramethyl-1,4-benzoquinone (**11**); 2-ethylanthraquinone (**12**).

All these chemicals were purchased from Aldrich.

2.1. Palladium catalyzed reduction 1,4-naphthoquinone (**9**)

Pd(OAc)₂ (5.6 mg, 0.025 mmol), 1,10-phenanthroline (22.5 mg, 0.125 mmol), and C₇F₁₅COOH (207 mg, 0.5 mmol) were dissolved in a mixture of chlorobenzene (3 ml) and 1-butanol (7 ml), and stirred for 6 h at 25°C. The resulting complex solution was added to water (10 ml) to form a biphasic system. The 1,4-naphthoquinone (**9**) (395 mg, 2.50 mmol) was then added and the reaction was carried out by stirring under CO atmosphere for 2 h at 50°C. At the end of the reaction, the products composition was quinone **9**, 0.23 mmol, and 1,4-dihydroxynaphthalene (**9a**), 2.27 mmol, corresponding to 91% conversion (determined by HPLC analysis).

2.2. Isolation of the red inactive palladium/1,10-phenanthroline complex

Pre-formed Pd(1,10-phenanthroline)(OAc)₂ complex [5] (510 mg, 1.25 mmol) and (1.42 g, 12.5 mmol) of CF₃COOH, were dissolved in a mixture of toluene (15 ml) and 1-butanol (35 ml). After the addition of

50 ml of water, the resulting biphasic system was stirred under carbon monoxide atmosphere for 2 h at 25°C. The solution was filtered off and vacuum dried, affording 480 mg of a red powder. ¹H NMR: δ -15.72 (s, 1H, hydride); ¹³C NMR: δ 215.1 (C=O); IR: ν(C=O) 1830 cm⁻¹; ESI-MS: *m/z* 603 (*M*⁺). The *m/z* value represents the most intense peak in a cluster, the pattern of which is consistent with the presence of two palladium atoms.

2.3. General procedure for the synthesis of hydrogen peroxide

Pd(OAc)₂ (5.6 mg, 0.025 mmol), 1,10-phenanthroline (67.5 mg, 0.375 mmol), and C₇F₁₅COOH (414 mg, 1 mmol) were dissolved in a mixture of toluene (3 ml) and 1-butanol (7 ml), and stirred for 6 h at 25°C. The resulting complex solution was added to water (10 ml) to form a biphasic system.

1,4-Naphthoquinone (**9**) (198 mg, 1.25 mmol) was added and the mixture was poured into an autoclave containing a glass liner. The reactor was then pressured to 64 atm partial pressure of O₂ and 6 atm partial pressure of CO in order to form a non-flammable gas mixture and reaction was carried out for 1 h at 70°C. At the end of the reaction, the hydrogen peroxide concentration was evaluated by titration with potassium permanganate.

3. Results and discussion

In the synthesis of hydrogen peroxide from CO/H₂O/O₂ catalyzed by homogeneous palladium complexes with phenanthroline ligands, the palladium complex with 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (**6**) turned out to be the most efficient catalyst [3]. We suggested [4] that the formation of hydrogen peroxide occurred through: (i) reduction of a Pd(II) complex by carbon monoxide and water, via hydride intermediate, affording carbon dioxide and Pd(0) species; (ii) oxidation of this Pd(0) species by oxygen with formation of a Pd(II) peroxy-complex; (iii) reaction of the latter species with an acid, producing hydrogen peroxide and restoring the initial Pd(II) complex.

However, ligand **6** is quite expensive, and the use of a simpler and cheaper ligand, such as 1,10-phenanthroline (**1**), was highly desirable for the

development of an industrial process. But, in the absence of the methyl substitution in the positions 2 and 9 of the phenanthroline, red palladium complexes formed, which were stable under the reaction conditions and were responsible of the fast irreversible deactivation of the catalyst. Thus, using 1,10-phenanthroline (**1**) as the ligand, a red solid was isolated which, on the basis of MS and ^1H NMR results (see Section 2), turned out to be a multinuclear hydride species (possibly, a binuclear one), the formation of which was prevented by the steric hindrance of 2,9-substituted ligands. Since it is likely that reduced palladium species are involved in the formation of such inactive complexes, a possible way to prevent the catalyst deactivation appeared to be the addition to the reaction media of suitable ligands, other than carbon monoxide, effective in the stabilization of Pd(0). At this purpose, we explored the use of quinones [6].

In order to evaluate the effect of quinones on our system, we tested the series of compounds **7–12** using the complex $\text{Pd}(\text{phen})\text{X}_2$ as a catalyst, operating under reducing reaction conditions ($\text{CO}/\text{H}_2\text{O}$, in absence of O_2) which favors the formation of red, inactive complexes.

The reaction was carried out in the biphasic system previously selected for the synthesis of hydrogen

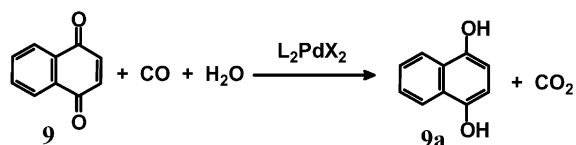


Fig. 1. Palladium catalyzed reduction of 1,4-naphthoquinone.

peroxide (1-butanol/chlorobenzene/water). Since the hydrophilic ligand phenanthroline **1** afforded a complex soluble in the aqueous phase, the catalyst was moved into the organic phase by using a highly hydrophobic acid co-catalyst (perfluorooctanoic acid) acting as a phase transfer anion (the partition of the complex in the organic layer was <1 and $>99\%$ with trifluoroacetate and perfluorooctanoate anion, respectively).

Operating under these conditions, we found that quinones **7–10**, added in excess with respect to the palladium (quinone/Pd molar ratio = 100) not only prevented the formation of red, inactive species, but were also reduced in a catalytic way to the corresponding hydroquinones [7]. Fig. 1 shows the reaction of quinone **9** that is reduced to 1,4-dihydroxynaphthalene (**9a**) in the presence of $\text{Pd}(\text{phen})(\text{C}_7\text{H}_{15}\text{COO})_2$ catalyst.

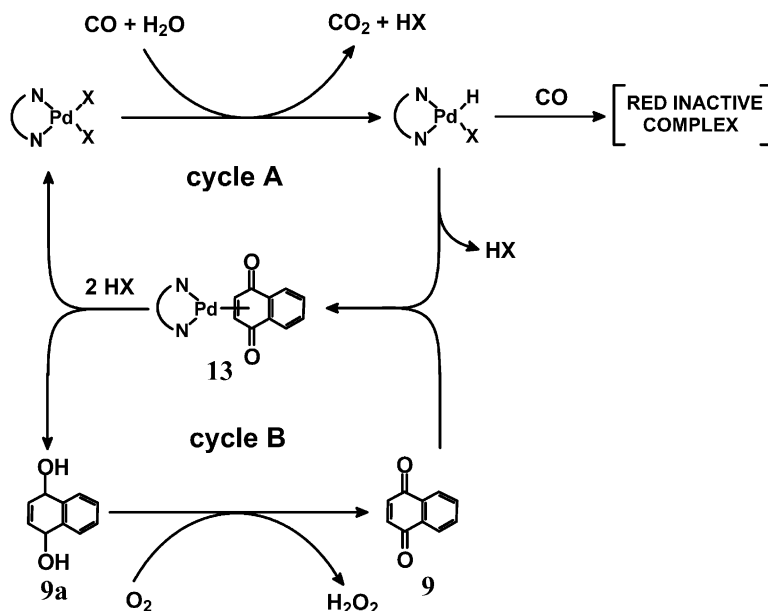


Fig. 2. Quinone-mediated palladium catalyzed synthesis of hydrogen peroxide. N–N: bidentate nitrogen ligand; X: CF_3COO^- , $\text{C}_7\text{F}_{15}\text{COO}^-$.

In a possible reaction mechanism, the intermediate complex $L_2Pd(0)$ -quinone **13** is formed instead of the red inactive species [8,9]. Complex **13** is not stable under the reaction conditions and, in presence of the acid co-catalyst, forms the hydroquinone **9a**, with regeneration of the starting Pd(II) complex (Fig. 2, cycle A).

On the contrary, quinones **11** and **12** did not bind to the reduced palladium (probably because of their steric hindrance) and failed in preventing the formation of the red inactive species.

The same quinones series was tested in the presence of oxygen ($CO/H_2O/O_2$) under the reaction conditions suitable for the synthesis of hydrogen peroxide. As reported in Table 1, the only quinone really effective in promoting the formation of hydrogen peroxide was the 1,4-naphthoquinone **9**. In all the other cases, we

observed the fast formation of the red inactive species. The analysis of the final reaction mixtures showed that the quinones **7** and **8** were quantitatively reduced to the corresponding hydroquinones, not effective in the stabilization of reduced palladium species. Quinones **11** and **12** were not transformed, confirming the results obtained operating under reducing conditions in absence of oxygen. Also the quinone **9** was recovered unaltered, but in this case we observed the vigorous formation of hydrogen peroxide and the maintenance of the palladium catalyst in the active form.

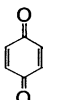
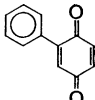
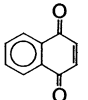
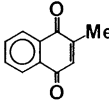
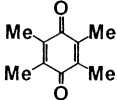
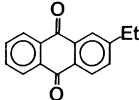
These findings can be explained by the ability of 1,4-dihydroxynaphthalene (**9a**), resulting from the first reduction step (Fig. 2, cycle A), to react with oxygen to give hydrogen peroxide, thus, regenerating the starting quinone **9** which can re-enter into the catalytic cycle (Fig. 2, cycle B). Conversely, hydroquinone and phenylhydroquinone arising from the reduction of quinones **7** and **8**, respectively, have a too high reduction potential (E^0) and cannot undergo the oxidation process.

2-Methyl-1,4-dihydroxynaphthalene, coming from the reduction of 2-methylnaphthoquinone (**10**), was easily oxidized, but due to the steric hindrance of its methyl group, quinone **10** showed a low binding capability towards the Pd(0) species and failed in preventing the formation of the inactive complex.

So, despite the same overall stoichiometry, processes run in the absence [3] and in the presence of a suitable quinone are likely to have completely different mechanisms. In the former case, Pd(0) species are likely to be oxidized by oxygen, and hydrogen peroxide is formed upon hydrolysis of the resulting peroxo-complex. On the contrary, in the presence of the quinone, Pd(0) species are oxidized by the quinone itself, and hydrogen peroxide is formed upon auto-oxidation of the resulting hydroquinone.

The different mechanism was confirmed by studying the ligand effect on the reaction carried out in absence and in presence of quinones. Table 2 reports the catalytic activities of a series of palladium complexes with the bidentate nitrogen ligands **1–6** in the synthesis of hydrogen peroxide carried out in presence or in absence of the selected quinone **9** (used in catalytic amount). Trifluoroacetic acid and perfluorooctanoic acid were used as acid co-catalysts for hydrophobic and hydrophilic ligands, respectively, in order to ensure the segregation of the catalysts into the

Table 1
Effect of the quinone^a

Quinone	E^0 (V) ^b	TOF (h^{-1}) ^c
7 	0.712	5 ^d
8 	0.698	13 ^d
9 	0.484	263
10 	0.422	20 ^d
11 	0.466	0 ^d
12 	0.150	0 ^d

^a Phenanthroline/ $C_7F_{15}COOH$ /quinone/Pd molar ratio: 5:20:50:1; solvent: 1-butanol/chloro benzene/water 35:15:50 (v/v/v); temperature: 70°C; P_{CO} : 6 atm; P_{O_2} : 64 atm.

^b Reduction potential.

^c Turnover frequency (calculated as moles of hydrogen peroxide per mole of palladium per hour).

^d Formation of red inactive complexes was observed.

Table 2
Effect of the ligand^a

Entry	Ligand	Acid	Quinone	TOF (h ⁻¹) ^b
1	phen (1)	C ₇ F ₁₅ COOH	None	0 ^c
2	phen (1)	C ₇ F ₁₅ COOH	1,4-Naphthoquinone	263
3	bipy (2)	C ₇ F ₁₅ COOH	None	0 ^c
4	bipy (2)	C ₇ F ₁₅ COOH	1,4-Naphthoquinone	225
5	4,7-dpphen (3)	CF ₃ COOH	1,4-Naphthoquinone	185
6	5-NO ₂ phen (4)	CF ₃ COOH	1,4-Naphthoquinone	180
7	2,9-dmphen (5)	C ₇ F ₁₅ COOH	None	434 ^d
8	2,9-dmphen (5)	C ₇ F ₁₅ COOH	1,4-Naphthoquinone	90
9	2,9-dm-4,7-dpphen (6)	CF ₃ COOH	None	528 ^d
10	2,9-dm-4,7-dpphen (6)	CF ₃ COOH	1,4-Naphthoquinone	75

^a Ligand/acid/quinone/Pd molar ratio: 5:20:50:1; solvent: 1-butanol/chlorobenzene/water 35:15:50 (v/v/v); temperature: 70°C; *P*_{CO}: 6 atm; *P*_{O₂}: 64 atm.

^b Turnover frequency (calculated as moles of hydrogen peroxide per mole of palladium per hour).

^c The formation of red inactive complexes was observed.

^d The fraction of 1-butanol ratio was reduced 1-butanol/chlorobenzene/water 25:25:50 (v/v/v) in order to prevent the precipitation of reduced palladium.

organic layer of the biphasic system. The complexes with 2,9-unsubstituted ligands **1–4** resulted inactive in absence of quinones ([3] and entries 1, 3), due to the formation of red inactive species, but became active in presence of **9**. Conversely, the complexes with ligands **5** and **6**, which were strongly effective in absence of quinones (entries 7, 9), displayed a lower activity in presence of **9**. Thus, this behavior seems to confirm the presence of two different reaction pathways, and consequently different reaction rates, if palladium is oxidized by the oxygen or the quinone.

After selection of **1** as the most effective ligand, the reaction conditions were optimized in order to improve the catalyst efficiency and stability. The ligand **1**/perfluorooctanoic acid/quinone **9**/Pd(OAc)₂ molar ratio was tuned to 15:40:50:1, achieving an increase of turnover frequency (TOF) higher than 500 moles of hydrogen peroxide per mole of palladium per hour. The best catalyst stability was obtained operating in a chlorine free reaction medium (1-butanol/toluene/water) [10].

In the case of the process carried out in the absence of quinone, the use of a large excess of oxygen in the gas phase was necessary in order to prevent the precipitation of reduced palladium, which becomes predominant under reducing conditions (operating with pure oxygen, the maximum allowed CO fraction was 8.5%) [4]. In the new process, the strong stabilizing effect of the quinone allowed to use air instead of oxygen and

to increase the CO fraction up to 14%. As reported in Fig. 3, this resulted in a higher catalytic activity (TOF = 680) and in safer reaction conditions, being the lower explosion limit (LEL) of carbon monoxide in air (17.5%) higher than that in pure oxygen (12.5%).

In a preliminary study, the stability of the catalytic system was evaluated by running a series of reaction cycles in a discontinuous operation mode. At the end of each cycle, the aqueous phase, containing

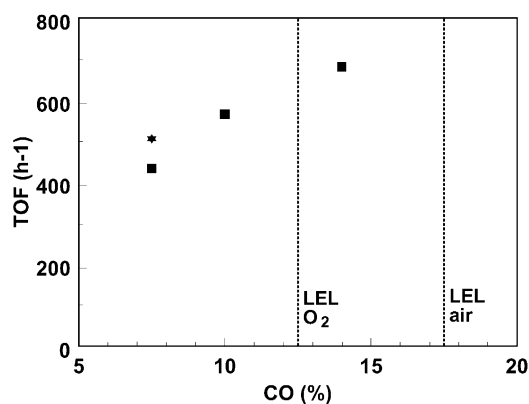


Fig. 3. Effect of the gas phase composition. Phenanthroline/C₇F₁₅COOH/1,4-naphthoquinone/Pd(OAc)₂ molar ratio: 15:40:50:1; solvent: 1-butanol/toluene/water 35:15:50 (v/v/v); temperature: 70°C; total pressure: 70 atm. LEL: lower explosion limit for carbon monoxide in mixture with oxygen or air; (★) oxygen; (■) air.

the produced hydrogen peroxide, was removed by decantation and replaced with pure water. The organic layer, containing the catalyst, the quinone and the acid co-catalyst, was then reused in a following cycle. After 10 consecutive cycles (carried out in 10 h), an overall turnover number (TON) of 4150 moles of hydrogen peroxide per mole of palladium was achieved and the catalyst did not show any appreciable loss of activity. However, in the aqueous phase we detected traces of phthalic acid, produced by the partial oxidation of the quinone **9**: thus, quinones more stable under oxidizing conditions are highly desirable.

4. Conclusions

The use of palladium complexes with bidentate nitrogen ligands in the presence of a catalytic amount of a suitable quinone, provides an efficient catalyst for the synthesis of hydrogen peroxide from carbon monoxide, oxygen and water. The improvements with respect to the reaction carried out in absence of quinone are the use of a cheap palladium ligand such as phenanthroline, an improved catalyst stability, and the safer process conditions.

The features of an effective quinone co-catalyst should be: (i) a reduction potential value (E^0) ranging between 0.4 and 0.5 V, to make possible both the reduction and oxidation processes; (ii) the absence of substituents in positions 2 and 3 on the ring to allow an efficient Pd(0) binding and stabilization; (iii) the presence of hydrophobic substituents to ensure a selective partition of the quinone in the organic layer of the biphasic system; (iv) its high stability toward oxidation.

The development of a continuous process, based on the above reported improvement, is presently under consideration.

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