The formation of para-benzoquinone and the mechanism of the hydroxylation of phenol by hydrogen peroxide over solid acids

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The transient formation of para-benzoquinone during the hydroxylation of phenol by hydrogen peroxide over solid acids is investigated. Formed by overoxidation of hydroquinone, para-benzoquinone is involved in an acid catalysed redox process responsible for the autocatalysis of the reaction and for a partial decomposition of hydrogen peroxide into oxygen and water.

Keywords: hydroxylation; phenol; hydrogen peroxide; benzoquinone; redox catalysis; heterogeneous catalysis; solid acids

1. Introduction

The heterogeneous hydroxylation of phenol with hydrogen peroxide has shown important expansion since the discovery of titanium silicalites [1]. Good to excellent selectivity in ortho- and para-dihydroxybenzenes (catechol and hydroquinone) were obtained. However, some authors have also observed the formation of para-benzoquinone, as a transient intermediate at the initial stage of the reaction [2–6]. Recently, it was suggested that this quinone would not be a product of the reaction, but would be generated by oxidation of hydroquinone, with the excess of hydrogen peroxide, during the gas-chromatographic analysis of the reaction mixture [7]. Thus, para-benzoquinone would be detected as long as hydrogen peroxide would be present in the solution. An other explanation of the transient nature of the quinone is to assume this product to be an intermediate in the formation of tars [4,6].

In a recent communication, we described the hydroxylation of phenol over acid solids [8]. In most of the cases, an induction period is observed and catechol is the first dihydroxybenzene obtained. The induction period is considerably reduced by initial addition of catechol or hydroquinone. The transitory formation of para-

benzoquinone is also detected, particularly when hydroquinone is added. More-over, the initial addition of para-benzoquinone also removes the induction period.

In this paper, we will attempt to demonstrate that para-benzoquinone is not a by-product, but a reactive intermediate in the hydroxylation of phenol by hydrogen peroxide over solid acid catalysts.

2. Experimental

Silica–alumina containing 13 wt% alumina was obtained from Ketjen. The fau-jasite ($Si/Al = 2.5$) was the Linde type Y molecular sieve SK-41, purchased from Alfa-Products.

Phenol, a Gen-Apex chemical, and hydrogen peroxide 30%, stabilized by sodium stannate (5 ppm), were purchased from Prolabo. Hydroquinone, catechol, resorcinol, para-benzoquinone, 1,2,4-trihydroxybenzene, veratrol (1,2-dimethoxy-benzene) and N,N,N',N'-tetramethyl-1,4-phenylenediamine dihydrochloride (TMPDH) were obtained from Aldrich.

The reactions were carried out batchwise in air, in a thermostated glass reactor, closed with a septum. Hydrogen peroxide was added at time zero to the magneti-cally stirred suspension of the catalyst in the solution of phenol in water. The course of the reaction was followed by taking periodically small samples (50 mm^3) with a microlitre seringe, through the septum. Each sample was poured in methanolic solution (2 cm^3) of fluorophenol used as external standard. After filtration, prod-ucts were analysed by HPLC (Shimadzu) using a C-8 column, with methanol/water as eluent and UV detection operating at a wavelength of 280 nm. During the reaction, the emission of oxygen was determined by gas volumetry.

3. Results and discussion

An example of the reaction catalyzed by silica–alumina (13 wt% alumina) is shown fig. 1. The yields (%) are relative to the initial hydrogen peroxide concentra-tion. Hydrogen peroxide was added at once at the initial time. Besides the forma-tion of the dihydroxybenzenes – hydroquinone (HYD) and catechol (CAT) – the transitory observation of para-benzoquinone (PBQ) and the evolution of oxygen (O_2) were also presented as a function of time. Resorcinol was not detected ($<0.5\%$). The organic products are determined by high-performance liquid chro-matography (HPLC), at room temperature, after dilution. Thus, para-benzoqui-none cannot be the product of the oxidation of hydroquinone during the analysis.

As previously noticed [8], the reaction occurs with a delay and catechol is the first dihydroxybenzene obtained. However, para-benzoquinone is also formed as soon as the reaction starts. In fact, the lack of hydroquinone is counterbalanced by
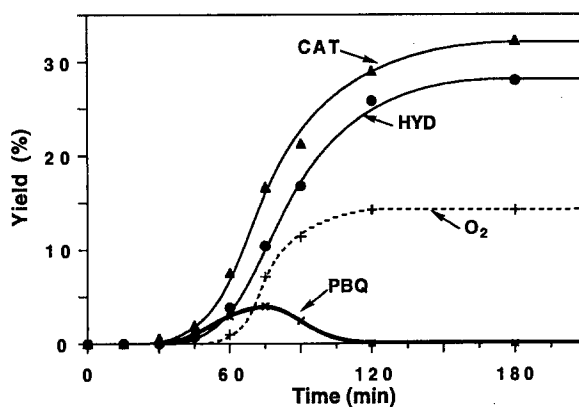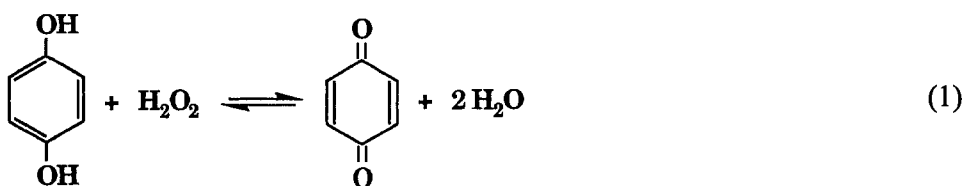
Fig. 1. Formation of dihydroxybenzenes, para-benzoquinone and oxygen (%H_2O_2) as a function of time over silica–alumina. Phenol: 21 mmol; H_2O_2 (30%): 9.4 mmol; silica–alumina (13 wt%): 100 mg; H_2O: 10 cm^3; 60°C.

the formation of para-benzoquinone. This is demonstrated by the study of the para-selectivity as a function of the reaction time (fig. 2). Whereas the selectivity to hydroquinone in the dihydroxybenzenes (HYD/(HYD + CAT)) is increasing at the beginning of the reaction, the para-selectivity in whole di-oxygenated products ((HYD + PBQ)/(HYD + CAT + PBQ)) is constant. Thus, the most probable explanation of the formation of para-benzoquinone is a fast overoxidation of hydroquinone in the reaction medium by the large concentration of hydrogen peroxide at the beginning of the reaction,

$$\text{(structure: OH–C}_6\text{H}_4\text{–OH)} + H_2O_2 \rightleftharpoons \text{(structure: O=C}_6\text{H}_4\text{=O)} + 2\,H_2O \qquad (1)$$

Effectively, as shown in table 1, hydroquinone is rapidly oxidized by hydrogen peroxide, using the same catalyst: almost half of hydroquinone disappears in 15 min. Under these conditions, with a large excess of hydrogen peroxide, but without phenol, the decomposition of hydroquinone and/or para-benzoquinone is important. Without catalyst, the oxidation of hydroquinone is negligible.

The formation of para-benzoquinone in the first stage of the oxidation of phenol by hydrogen peroxide, was also observed very recently, under mixed La–Eu cuprates [9]. The authors proposed that hydroquinone was quickly oxidized to the black quinhydrone, which is the equimolecular complex of hydroquinone and para-benzoquinone, and the latter was oxidized more easily than hydroquinone itself. The absence of ortho-benzoquinone can be ascribed to the highest oxidation potential of catechol [10] and the lowest stability of the related quinone.
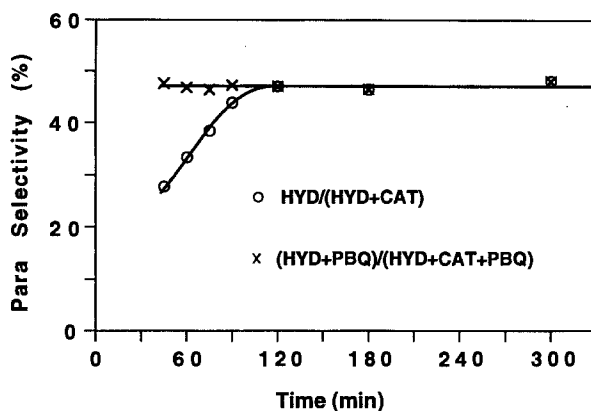
Fig. 2. Para-selectivity as a function of the reaction time, taking, or not, the transitory formation of para-benzoquinone into account. Same conditions as fig. 1.

Concerning the subsequent disappearance of para-benzoquinone, several explanations can be suggested:

– The decomposition of the quinone into "tars" or degradation products, as already proposed [4,6]. It is known, and confirmed by the results of table 1, that dihydroxybenzenes are easily decomposed in presence of an excess of hydrogen peroxide. It is not excluded that quinones would participate in such reactions. However, according to fig. 1, para-benzoquinone does not behave like an intermediate in the decomposition of hydroquinone, but, on the contrary, like an intermediate in the formation of hydroquinone: it appears before hydroquinone, and disappears while hydroquinone is always growing. Thus, para-benzoquinone, at least in large part, is transformed into hydroquinone.

– The oxidation of phenol by the quinone, when the concentration in hydrogen peroxide becomes low. The oxidation potential of phenol, higher than the one of hydroquinone [10], is not in favour of such a reaction. Nevertheless, we have examined this possibility. The reaction would lead to a new formation of dihydroxybenzenes, according to the following equation:

Table 1
Reaction of hydroquinone and para-benzoquinone with hydrogen peroxide over silica–alumina (15%). H_2O_2: 9.4 mmol; silica–alumina: 100 mg; H_2O: 10 cm^3; 60°C

| Time (min)	HYD (mmol)	PBQ (mmol)
0	1	0
15	0.52	0.10
0	0	1
15	0.42	0.27

$$(2)$$
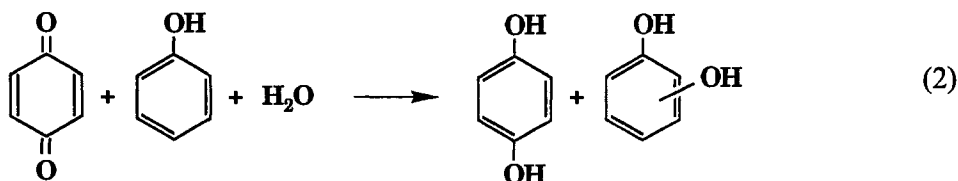
In fact, in the presence of phenol (21 mmol) and catalyst (silica–alumina: 100 mg), but without hydrogen peroxide, para-benzoquinone (1 mmol) does not lead to the formation of catechol, nor resorcinol. Only a low formation of hydroquinone, at the expense of the quinone, is observed. This reaction also occurs in absence of phenol. This is ascribed to the slow reduction of the quinone in reaction medium. Thus, the oxidation of phenol by para-benzoquinone is unlikely in the present conditions.

– The oxidation of hydrogen peroxide into oxygen and water. The evolution of oxygen, shown in fig. 1, is expressed in hydrogen peroxide decomposition (%), according to the equation:

$$2H_2O_2 \rightarrow 2H_2O + O_2 .\qquad(3)$$

It is noteworthy that oxygen emission is not immediate. Moreover, it was checked that the decomposition of hydrogen peroxide by the catalyst alone is very low ($\sim 1\%$ per hour). Thus, the emission of oxygen is not due to a parallel reaction of hydrogen peroxide on the catalyst, but seems in relation with a consecutive reaction involved in the formation of products. It is proposed that the production of oxygen would be due to the oxidation of hydrogen peroxide by para-benzoquinone, according to the following reaction:

$$(4)$$
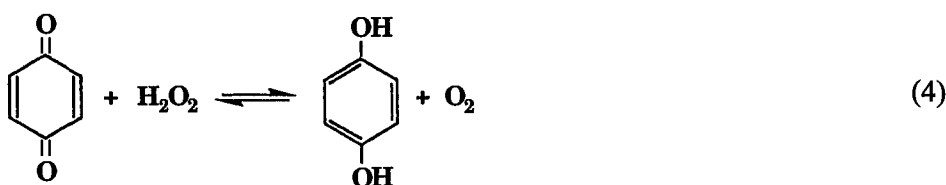
From a thermodynamic point of view, this reaction is possible: the potential of reduction of oxygen into hydrogen peroxide in acid medium (0.695 V) is slightly lower than the potential of reduction of para-benzoquinone into hydroquinone (0.699 V) in the same medium [11], and the evolution of oxygen shifts the equilibrium to the right. It was effectively verified (see table 1) that para-benzoquinone reacts rapidly with hydrogen peroxide in presence of catalyst, giving hydroquinone and oxygen.

In association with the oxidation of hydroquinone (eq. (1)), this reduction of para-benzoquinone (eq. (4)), constitutes a cycle of decomposition of hydrogen per-

Table 2
Effect of additives on the induction time of the hydroxylation of phenol over protonic faujasite
(Si/Al = 2.5). Phenol: 21 mmol; H_2O_2: 9.4 mmol; FAU 2.5: 250 mg; H_2O: 10 cm^3; 60°C

Additive (1 mmol)	Induction time (min)
none	90
catechol	2
hydroquinone	3
para-benzoquinone	5
1,2,4-trihydroxybenzene	1
resorcinol	120
veratrol	105
TMPDH[a]	0

[a] TMPDH: N,N,N',N'- tetramethyl-1,4-phenylenediamine dihydrochloride.

oxide into oxygen and water, similar to the Haber–Weiss cycle, which is catalysed by the couple Fe(II)/Fe(III) [12]. Thus, dihydroxybenzenes and benzoquinones constitute redox couples that catalyse the decomposition of hydrogen peroxide. Concurrently, as in the Fenton reaction [13], the intermediate formation of hydroxyl radicals participates in the hydroxylation of phenol, thereby generating the autocatalysis.

Confirmation that a redox mechanism involving quinone is responsible for the autocatalysis is given by the study of the effect of various additives on the induction time (see table 2). In these experiments the catalyst is a protonic faujasite with Si/Al = 2.5 (FAU 2.5), the behaviour of which is similar to silica–alumina [8]. As already noticed, the induction time is considerably reduced by addition of catechol, hydroquinone and para-benzoquinone. In the absence of catalyst, these additives have no effect. 1,2,4-trihydroxybenzene, which is a potential secondary product of the reaction of hydroxylation of phenol, also reduces the induction period of the catalyzed reaction. By contrast, resorcinol and veratrol have a negative effect. The oxidation of these aromatics cannot produce quinone: the former because meta-benzoquinone does not exist, the later because it is the O,O'-dimethylated derivative of catechol. Thus, to be efficient, an additive must be one of the components of a quinonic redox couple.

The addition of N,N,N',N'-tetramethyl-1,4-phenylenediamine dihydrochloride (TMPDH) gives further evidence of the redox mechanism. This additive, which is a very powerful electron transfer agent, induces the instantaneous formation of the dihydroxybenzenes in 63% yield.

4. Conclusion

Unlike previous assignments, we conclude that the observation of the transitory formation of para-benzoquinone, at the first step of the hydroxylation of phenol,

cannot be the result of an artefact during the analysis of the products. Likewise, if para-benzoquinone can be effectively decomposed in the reaction media, it is not only an intermediate in the formation of tars. The present results show that para-benzoquinone participates in the autocatalysis of the reaction over solid acid catalysts. A redox catalysis (involving the couple: hydroquinone/para-benzoquinone) is suggested. In return, this acid catalysed redox mechanism also participates in the decomposition of hydrogen peroxide into oxygen and water. This undesireable reaction decreases the efficiency of hydrogen peroxide. The necessity of acid sites for this reaction explains why it does not occur over pure titanosilicalites, despite the overoxidation of hydroquinone into para-benzoquinone. By contrast, when aluminium is also present in titanosilicalites the partial decomposition of hydrogen peroxide, according to the mechanism presented here, explains part of the reduction in yield.

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