

Catalytic effects of metal(IV) phosphates on the oxidation of phenol and 2-naphthol

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Abstract

Tetravalent metal phosphates form highly insoluble inorganic polymers and act as catalysts in some oxidative reactions. In the present work, α -amorphous zirconium, tin, titanium, zirconium tungstate (acidic and basic form), crystalline vanadyl, fibrous crystalline cerium and pellicular zirconium phosphates, were prepared and evaluated as catalysts, for the hydroxylation of phenol and 2-naphthol by hydrogen peroxide, in acetic acid. Oxidation of phenol yielded hydroquinone, catechol, *cis,cis*-muconic and *cis,trans*-muconic acids, depending on the catalyst. All oxidations of 2-naphthol produced 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone but reaction with crystalline vanadyl phosphate also resulted in the formation of 1,1'-bi(2-naphthol).

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1. Introduction

The development of ecologically friendly technologies is a major goal of present research in chemistry. This is especially true in the field of oxidation of organic compounds, where there is an urgent need to replace highly effective but wasteful and toxic stoichiometric oxidants, such as chromates. A possible solution to this problem consists in using technology based on catalytic oxygen transfer from “clean” oxygen donors, such as hydrogen peroxide (H₂O₂).

Organic compounds such as phenols and phenolic derivatives are amongst the most common chemicals found in regular commercial manufacturing processes.

They occur in wastewater from major industrial operations, in cooking, oil refining, chemicals, resin and steel manufacture. An abundance of other commercial activities, including paint stripping, foundry work and disinfection regimes, also give rise to phenolic discharges.

Some of the most important products of phenol oxidation are hydroquinone, catechol and resorcinol. The main uses of hydroquinone are as photographic developer, polymerisation inhibitor and antioxidant. It is also an important intermediate for production of numerous dyes. Commercially, important derivatives include the mono- and di-ethers of hydroquinone, the alkyhydroquinones and their ethers. Catechol is a starting material for a series of important fine chemicals used for pest control, pharmaceuticals, flavours and aromas. Resorcinol is also used as an intermediate

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for dyes and for ultraviolet stabilisers of polyolefins and pharmaceutical products.

The oxidation of a number of naphthols by oxygen has been carried out, with copper–collidine and copper–pyridine complexes as catalysts [1]. More recently [2], it was shown that phenols can be specifically oxygenated to give *ortho*-quinones by a combination of the transition metal complexes $\text{Ti}(\text{O}i\text{Pr})_4$, $\text{VO}(\text{acac})_2$, $\text{Zr}(\text{acac})_4$, $\text{Zr}(\text{OnPr})_4$ and *tert*-butylhydroperoxide (TBHP) or by $(\text{Mo}(\text{O}_2)_2 \cdot \text{Py} \cdot \text{HMPT})$. By using the same method, naphthols, anthranols, phenanthrols and mononuclear phenols are readily converted into the corresponding 1,2-quinones. However, unhindered *ortho*-naphthoquinones can yield binaphthyls from unreacted starting material by Michael addition. This type of C–C coupling, with the formation of a binaphthyl system, has been observed also in the autoxidation of naphthols [3,4] as well as in molybdenum-catalysed oxidations [5]. Dimerisation of 2-naphthol can also lead to the formation of 1,1'-bi(2-naphthol) [5].

Direct oxidation of aromatics with H_2O_2 can be accomplished by increasing the electrophilicity of the oxidant through the use of Lewis acids as, for example, with aluminium chloride (AlCl_3) or boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$) or by carrying out the reaction in superacidic media. However, these systems are not catalytic, often requiring a large excess of the activating agent [6].

For over 100 years, clays and clay-like minerals have been used as catalysts and absorbents. A wide range of natural clays exists, ranging from the relatively simple bentonite to more complex minerals such as zeolites and other silicate complexes. However, a common feature of these natural structures is that they are very difficult to modify. The use of synthetic inorganic polymers provides a good alternative to clays. Indeed, catalysts such as acids, transition metal redox and titanium zeolites, are all known to be effective for phenol oxidation [7–13].

Recently, the use of metal(IV) phosphates as acid catalysts in various reactions, such as dehydration, isomerisation, polymerisation, oxidation and alkylation, has received considerable attention [14–17]. These materials can be considered as solid strong inorganic acids and much of the catalytic activity so far observed in the literature, has been justified by their acidic nature, which is attributed to the Brønsted acidity of the

hydroxyl groups in the interlayers and to the Lewis acidity of the metal centre.

Given the properties described above, the present work was undertaken to examine the application of tetravalent metal phosphates for the activation of hydrogen peroxide, as an electrophilic source of oxygen, in oxidation of phenol and 2-naphthol. The main advantages of these polymeric phosphates include a simple procedure for their use in oxidation reactions, easy work-up and reuse without loss of activity. Oxidation of phenol was found to give the corresponding *ortho* and *para* hydroxylated compounds, catechol and hydroquinone. With particular tetravalent metal phosphates, formation of muconic acids was observed. In the case of 2-naphthol, 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone and 1,1'-bi(2-naphthol) were formed. Direct hydroxylation of 2-naphthol was not observed. The catalysts used in these studies were α -amorphous zirconium phosphate (α -ZrPA), pellicular zirconium phosphate (ZrPP), amorphous tin phosphate (SnPA), amorphous titanium phosphate (TiPA), crystalline vanadyl phosphate (VOPC), fibrous crystalline cerium phosphate (CePFC), amorphous zirconium tungstate phosphate (ZrWPA) (basic form) and ZrWPA (acidic form).

2. Experimental

2.1. Characterisation of catalysts and reaction products

For metal(IV) phosphates already described in the literature, sufficient spectroscopic data were obtained for their identification. Unknown compounds, obtained in the oxidation reactions, were identified by comparison with authentic samples and by elemental analysis.

High-pressure liquid chromatography (HPLC) was performed on a Varian 2000 chromatograph, with a Hypersil ODS column (25 cm \times 5 μm). Infrared spectra were recorded on a Perkin-Elmer 1720-X Infrared Fourier-Transform Spectrometer, liquid compounds as films and solids as KBr disks. Ultraviolet/visible spectra (UV/Vis) were recorded on a Hewlett Packard 8452A diode array spectrometer. Mass spectra were obtained on a VG 7070E spectrometer using electron ionisation at 70 eV. ^1H nuclear magnetic

resonance spectra were produced on a Bruker AMX300 (300 MHz) instrument. Melting points were determined on a Gallenkamp melting point apparatus.

Authentic samples of catechol, hydroquinone, *trans,trans*-muconic acid and 1,1'-bi(2-naphthol) were purchased (Aldrich, Fluka) and used without further purification.

2.2. Synthesis of metal(IV) phosphates

α -ZrPA [18], crystalline zirconium phosphate (direct precipitation method) [19,20], ZrPP [21], SnPA [22], TiPA [23], VOPC [24] and CePFC [25], were prepared as previously described in the literature.

2.2.1. Amorphous zirconium tungstate phosphate (basic form) [26]

A solution of zirconylchloride (10.52 g, 32.65 mmol) in water (20.0 ml), was added slowly to a solution of disodium hydrogen phosphate (14.68 g, 82.50 mmol) and sodium tungstate dihydrate (2.67 g, 8.1 mmol) in water (100 ml), at room temperature and with stirring. The initially clear solution, produced a precipitate after 15 min and this suspension was warmed to 80 °C during 4 h, with stirring. After cooling the mixture, the precipitate was filtered off and washed with distilled water until pH = 8 of the filtrate. The residual white solid was air-dried at room temperature for 48 h; ν_{\max} (cm⁻¹) 3468, 2371 (OH); 1646 (P–O); 1137 (P–O); 985 (P–O). Found: Zr, 21.0%, W, 2.9%, P, 13.4%.

2.2.2. Amorphous zirconium tungstate phosphate (acidic form) [26]

Basic zirconium tungstate phosphate, prepared by the method described above, was suspended in aqueous hydrochloric acid (24%, 40 ml) and, after stirring the mixture for 3 h at room temperature, the solid was filtered off and washed with distilled water until pH = 2 of the filtrate. The white solid was air-dried at room temperature for 48 h; ν_{\max} (cm⁻¹) 3461 (OH); 2366 (OH); 1630 (P–O); 1050 (P–O). Found: Zr, 22.1%, W, 5.2%, P, 16.0%.

2.3. Oxidation of phenol with H₂O₂ in the absence of metal(IV) phosphates

In a typical reaction, phenol (0.94 g, 0.01 mol) was dissolved in glacial acetic acid (5 ml) and heated to

60 °C. Aqueous hydrogen peroxide solution (35%, w/w; 0.5 g, 5 mmol) was added slowly via a peristaltic pump over a period of about 30 min. The reaction mixture was maintained at this temperature for a total of 6 h and then analysed by HPLC, which revealed the formation of hydroquinone (12.1% yield) and catechol (32.4% yield), based on a phenol conversion of 20.7% (w/w). The reaction was repeated in methanol, acetonitrile or *tert*-butyl alcohol as solvent, but no significant oxidation was observed.

2.4. Oxidation of phenol with H₂O₂ in the presence of metal(IV) phosphates

To study the effect of tetravalent metal phosphates on the rate of oxidation and the product range, phenol (0.94 g, 0.01 mol) was dissolved in glacial acetic acid (5 ml) with catalyst added (0.05 g) and the mixture was heated to 60 °C. Aqueous hydrogen peroxide solution (35%, w/w; 0.5 g, 5 mmol) was slowly added via a peristaltic pump. The reaction mixture was maintained at this temperature for a total of 6 h. The formation of hydroquinone, catechol, *cis,cis*-muconic and *cis,trans*-muconic acids was quantified by HPLC and results are listed in Table 1. *cis,cis*-Muconic and the *cis,trans* isomer were identified by comparison with authentic specimens [27,28].

This reaction was also repeated in methanol, acetonitrile or *tert*-butyl alcohol as solvent but, again, no significant oxidation was observed. Because of the many potential variables in these systems, the oxidation of phenol was examined by use of the Simplex method [29]. After a series of reactions with α -ZrPA, the optimum reaction conditions for best yields of hydroquinone and catechol were found to depend mostly on temperature (60 °C), time (6 h), concentration of H₂O₂ (35%, w/w) and amount of H₂O₂ oxidant (2 mol to each mol of phenol). These define the standard conditions, used in all subsequent oxidations with other metal phosphates.

2.5. Oxidation of 2-naphthol with H₂O₂ in the absence of metal(IV) phosphates

In a typical reaction, 2-naphthol (1.44 g, 0.01 mol) was dissolved in glacial acetic acid (5 ml) and heated to 60 °C. Aqueous hydrogen peroxide solution (35%,

Table 1

Distribution of products from oxidation of phenol in the presence of different tetravalent metal phosphates^a

Phosphates	α -ZrPA (%)	SnPA (%)	CePFC (%)	TiPA (%)	VOPC (%)	ZrPP (%)	ZrWPA basic (%)	ZrWPA acidic (%)	No catalyst (%)
Yield of hydroquinone based on phenol conversion	37.3	31.0	31.0	1.4	–	–	–	–	12.1
Yield of catechol based on phenol conversion	44.0	46.8	63.7	5.5	–	–	–	–	32.4
Yield of <i>cis,cis</i> -muconic acid based on phenol conversion	–	–	–	–	–	16.3	5.5	5.3	–
Yield of <i>cis,trans</i> -muconic acid based on phenol conversion	–	–	–	–	–	–	13.8	3.3	–
Phenol conversion (w/w)	20.9	17.1	16.8	29.2	–	24.6	28.9	30.3	20.7

^a Reaction conditions were all similar and are described in Section 2. In all cases, acetic acid was used as solvent.

w/w; 0.5 g, 5 mmol) was slowly added via a peristaltic pump. The reaction mixture was maintained at this temperature for a total of 6 h and then analysed by HPLC. The main reaction product was isolated from the reaction mixture by preparative HPLC and was identified by comparison with an authentic sample of 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone [30].

2.6. Oxidation of 2-naphthol with H₂O₂ in the presence of metal(IV) phosphates

To evaluate the impact of metal phosphates on the oxidation reaction, 2-naphthol (1.44 g, 0.01 mol) was dissolved in glacial acetic acid (5 ml) and oxidised as above (Section 2.5) but with added catalyst (0.05 g). The reaction mixture was maintained at this temperature for a total of 6 h and then analysed by HPLC. Formation of 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone and 1,1'-bi(2-naphthol) was confirmed by

their isolation and identification. The 1,1'-bi(2-naphthol) produced with vanadyl phosphate was isolated by preparative scale TLC. Results are shown in Table 2.

2.7. Preparation of *cis,cis*-muconic acid [27]

With use of a Teflon stirrer, phenol (5.00 g, 0.0532 mol) and basic ferric acetate (0.0104 g, 0.0544×10^{-3} mol) were dissolved in glacial acetic acid (20.0 g) in a glass-stoppered flask. After the ferric acetate had dissolved, a mixture of 10.5 g of acetic acid and 30.5 g of aqueous peroxyacetic acid solution (40%, w/w; 12.2 g, 0.161 mol AcOOH) was added over a period of 5 min. Colourless *cis,cis*-muconic acid precipitated from the solution as the reaction proceeded. After stirring at 25 °C for 5 days, the mixture was cooled to about 10 °C and the product was filtered off, washed with cold water (1 ml), and air-dried to

Table 2

Distribution of products from oxidation of 2-naphthol in the presence of different tetravalent metal phosphates^a

Phosphates	α -ZrPA (%)	SnPA (%)	CePFC (%)	TiPA (%)	VOPC (%)	ZrPP (%)	No catalyst (%)
Yield of 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone based on 2-naphthol conversion	43.8	49.6	29.2	51.5	12.4	53.9	21.6
Yield of 1,1'-bi(2-naphthol) based on 2-naphthol conversion	–	–	–	–	31.4	–	–
2-Naphthol conversion (w/w)	25.6	30.4	29.1	23.3	47.7	24.5	22.2

^a Reaction conditions were all similar and are described in Section 2. In all cases, acetic acid was used as solvent.

give *cis,cis*-muconic acid, m.p. 194–195.5 °C (from methanol; lit., 194–195 °C) [28]; λ_{\max} (0.1 M NaOH) 251 nm ($\epsilon=15\,600$), 258 nm ($\epsilon = 17\,000$) and 264 nm ($\epsilon=15\,300$); ν_{\max} 1250, 830 cm^{-1} ; MS, m/z 142 (29%) $[\text{M}]^+$, 124 (54%), 97 (100%), 79 (27%) and 69 (27%).

2.8. Preparation of *cis,trans*-muconic acid [28]

cis,cis-Muconic acid (2.00 g), produced as described above, was heated to boiling, during 1 h, with just sufficient distilled water to effect solution. When the filtrate was cooled, small prismatic needles of *cis,trans*-muconic acid separated, m.p. 188–189.5 °C (lit., 190–191 °C) [28]; λ_{\max} (0.1 M NaOH) 251 nm ($\epsilon = 23\,400$), 259 nm ($\epsilon = 25\,600$) and 265 nm ($\epsilon = 23\,400$); ν_{\max} 890, 750 cm^{-1} .

2.9. Preparation of 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone [30]

2-Naphthol (150 mg) was adsorbed onto silica gel (Kieselgel 60 GF₂₅₄; Merck; 15 g; from acetone or methanol), and the mixture was spread onto a sheet of paper as a thin layer, and left exposed to air. After 24 h, the silica was extracted with cold acetone or methanol, which after filtration, was evaporated to give a crude product. The latter was purified by preparative TLC, using chloroform as eluent. The isolated 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone was crystallised from benzene as dark red needles, m.p. 149–150 °C (lit., 148–149 °C) [31]; λ_{\max} (methanol) 230 nm ($\log \epsilon = 4.86$), 252.5 nm ($\log \epsilon = 4.42$), 274.5 nm ($\log \epsilon = 3.92$), 288 nm ($\log \epsilon = 3.78$), 332.5 nm ($\log \epsilon = 3.70$) and 405 nm ($\log \epsilon = 3.37$); MS, m/z 302 (2%) $[\text{M}]^+$, 300 (5%), 272 (100%), 255 (4%), 243 (14%), 215 (8%), 213 (8%), 189 (1%); ν_{\max} (KBr disk) 3100–3500, 1650, 1695 cm^{-1} ; $^1\text{H NMR}$, $\delta(\text{DMSO})$: 6.55 (s, 1H, 3H), 6.87–6.95 (m, 1H), 7.5 (d, $J = 8.0$ Hz, 1H), 7.51–7.57 (m, 2H), 7.7–7.6 (m, 2H), 7.9–7.95 (m, 1H), 8.06–8.09 (m, 1H), 8.14 (d, $J = 8.0$ Hz, 1H), 8.24–8.28 (m, 1H) and 10.05 (s, 1H, OH).

2.10. Isolation of 1,1'-bi(2-naphthol) from a typical reaction mixture

1,1'-Bi(2-naphthol) was isolated from the oxidation of 2-naphthol by preparative TLC on silica gel

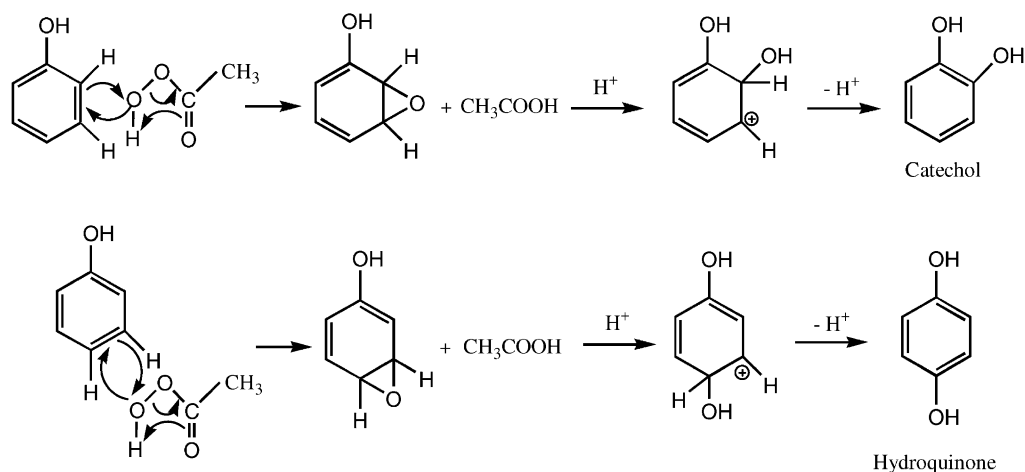
(Kieselgel 60 GF₂₅₄; Merck) and a mixture of chloroform (50 ml) and methanol (1 ml) as eluent. The isolated compound was crystallised from ethanol, m.p. 206–207.5 °C (lit., 206–207 °C) [32]; MS, m/z 286 (100%) $[\text{M}]^+$, 268 (14%), 257 (26%), 239 (28%), 226 (17%), 120 (52%), 115 (27%); ν_{\max} (KBr disk) 3705–3125, 1390–1315, 1335–1165 cm^{-1} ; $^1\text{H NMR}$, $\delta(\text{CDCl}_3)$: 7.16 (d, $J = 8.0$ Hz, 1H), 7.31 (ddd, $J = 8.0$; 7.3 and 1.5 Hz, 1H), 7.38 (ddd, $J = 8.0$; 7.3 and 1.5 Hz, 1H), 7.40 (d, $J = 8.8$ Hz, 1H), 7.90 (d, $J = 7.8$ Hz, 1H) and 7.99 (d, $J = 8.8$ Hz, 1H). The isolated compound was also characterised by comparison with an authentic sample (Fluka).

3. Results and discussion

The object of the present work was to study the catalytic activity of several metal(IV) phosphates, on the oxidation of phenol and 2-naphthol. Metal(IV) phosphates are relatively cheap, easy to synthesise, non-toxic and extremely resistant to extremes of temperature and radiation and hydrogen peroxide is an efficient, cheap and “clean” oxidant. Individual oxidations are described below.

3.1. Oxidation of phenol

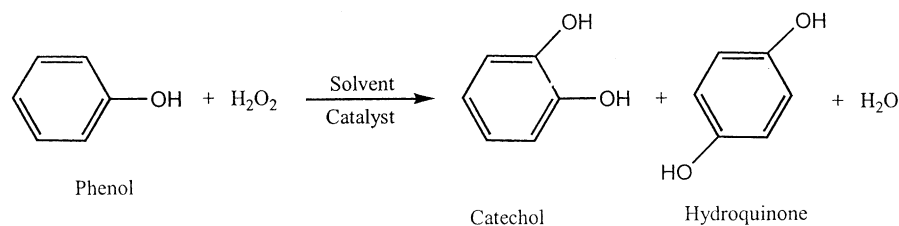
A start has been made in this area by examining the oxidation of phenol in the absence and the presence of metal(IV) phosphates, with aqueous H_2O_2 as oxidant, in a range of solvents. It was quickly apparent that in solvents such as acetonitrile, methanol or *tert*-butyl alcohol, no significant oxidation occurred. In glacial acetic acid, oxidation proceeded to give various products. This solvent effect suggested that peroxyacetic acid was being formed and was likely to be the effective oxidant rather than H_2O_2 itself. To investigate this possibility, in further work to be reported, the rate of formation of peroxyacetic acid was examined in the absence and presence of metal(IV) phosphates, in addition to the effect of the latter on phenol oxidation. The results clearly indicate that peroxyacetic acid is formed with most of the phosphates, but the latter have no catalytic effect on its formation. However, it was found that other phosphate catalyst did significantly accelerate the production of peroxyacetic acid.



Scheme 1.

Although, some of the studied phosphates did not catalyse the formation of peroxyacetic acid, they did influence the nature of the oxidation products obtained from phenol. Thus, the effect of these metal phosphates in phenol oxidation appears to lie in their influence on the mechanism of oxidation. Indeed, additional studies with ZrPA suggest that H₂O₂ penetrates right inside the phosphate structure and is possibly held there by hydrogen bonding. This indicates that any effect of the phosphates on oxidation of phenol with H₂O₂, could occur by affecting selectivity towards product formation in their pores and not by catalysing effects.

The stages of oxidation of phenol may be summarised as initial formation of a dihydroxy compound (hydroquinone and catechol; Eq. (1)), followed by aromatic ring cleavage to give *cis,cis*-muconic acid, which may or may not be isomerised to *cis,trans*-muconic acid.

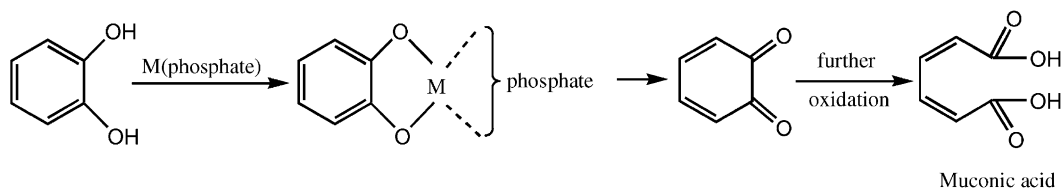


Formally, these reactions may be regarded as proceeding through radical mechanisms but, in view of the

formation of peroxyacetic acid in the systems used here, it is likely that the reactions follow an acid catalysed “ionic” mechanism, similar to that shown in Scheme 1. Formation of muconic acids requires further oxidation of the catechol (Scheme 2).

As shown in Table 1, in the absence of a metal(IV) phosphate, it was found a 21% conversion of phenol to products, of which 12% is hydroquinone and 32% is catechol. When Zr, Sn and Ce phosphates are added, the overall conversion remains approximately the same but the yields of hydroquinone and catechol increase considerably and the ratios of the two products change. Phenol conversion variations with phosphate type can be explained by differences in shape selectivity (the true role of the phosphates) due to the heterogeneous lamellar nature of the phosphates. The different effects on the phenol conversion for the various phosphates could be due to different mechanisms

of trapping and removing peroxyacetic acid from the reaction products.



Scheme 2.

Titration during the reactions showed that no peroxyacetic acid is formed in the presence of VOPC. This result suggests that H_2O_2 was decomposed by the VOPC before there was any chance to form substantial amounts of peroxyacetic acid. Then, under our assumption of peroxyacetic acid as the true oxidant, the VOPC result of no phenol conversion is expected.

Remarkably, for ZrPP and ZrWPA (acidic and basic), only muconic acids are observed and none of hydroquinone or catechol, the rational precursor to the muconic acids. This suggests that formation of the latter proceeds through a different mechanism to that for oxidation to hydroquinone and catechol.

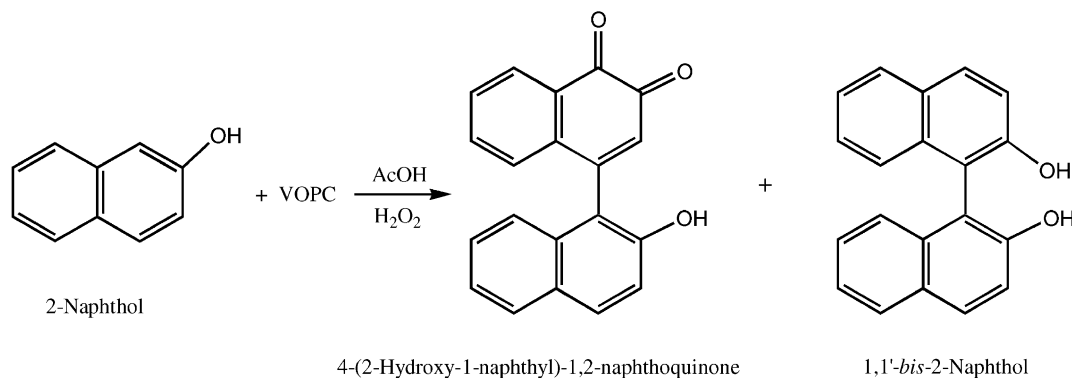
Various methods for the synthesis of muconic acids are described in the literature [33,34]. Oxidation of phenol by peroxyacetic acid, catalysed by basic Fe(III) acetate [27] gives the *cis,cis*-isomer. Catechol, in the presence of Fe(III) or Cu(II) acetate forms a complex with the metal which is quickly oxidised to *cis,cis*-muconic acid. There are several mechanisms possible for the proposed oxidation of the metal–catechol complex [27]. The postulation of a metal–catechol complex as an intermediate in phenol oxidation is reasonable, in the light of the observation

that phenol is not oxidised to *cis,cis*-muconic acid in the absence of Fe(III) or Cu(II), in spite of the formation of catechol. It appears that the role of the metals is to provide a reaction path whereby catechol can be oxidised to *cis,cis*-muconic acid, with little or no side reaction. In the absence of these metals, catechol is probably oxidised to products other than *cis,cis*-muconic acid since the “directing” effect of the metal is absent.

3.2. Oxidation of 2-naphthol

Oxidation of 2-naphthol was studied with α -ZrPA, SnPA, CePFC, TiPA, VOPC and ZrPP, as catalysts and also without any catalyst. The reactions were performed following the procedures described above in the experimental section.

Oxidation reactions of 2-naphthol were controlled by HPLC. The analysis of the reaction mixtures revealed the presence of a main product, as well as the starting material. Because this reaction was not published under the conditions used in this work, the main product was considered unknown until its identification. This compound was isolated by preparative

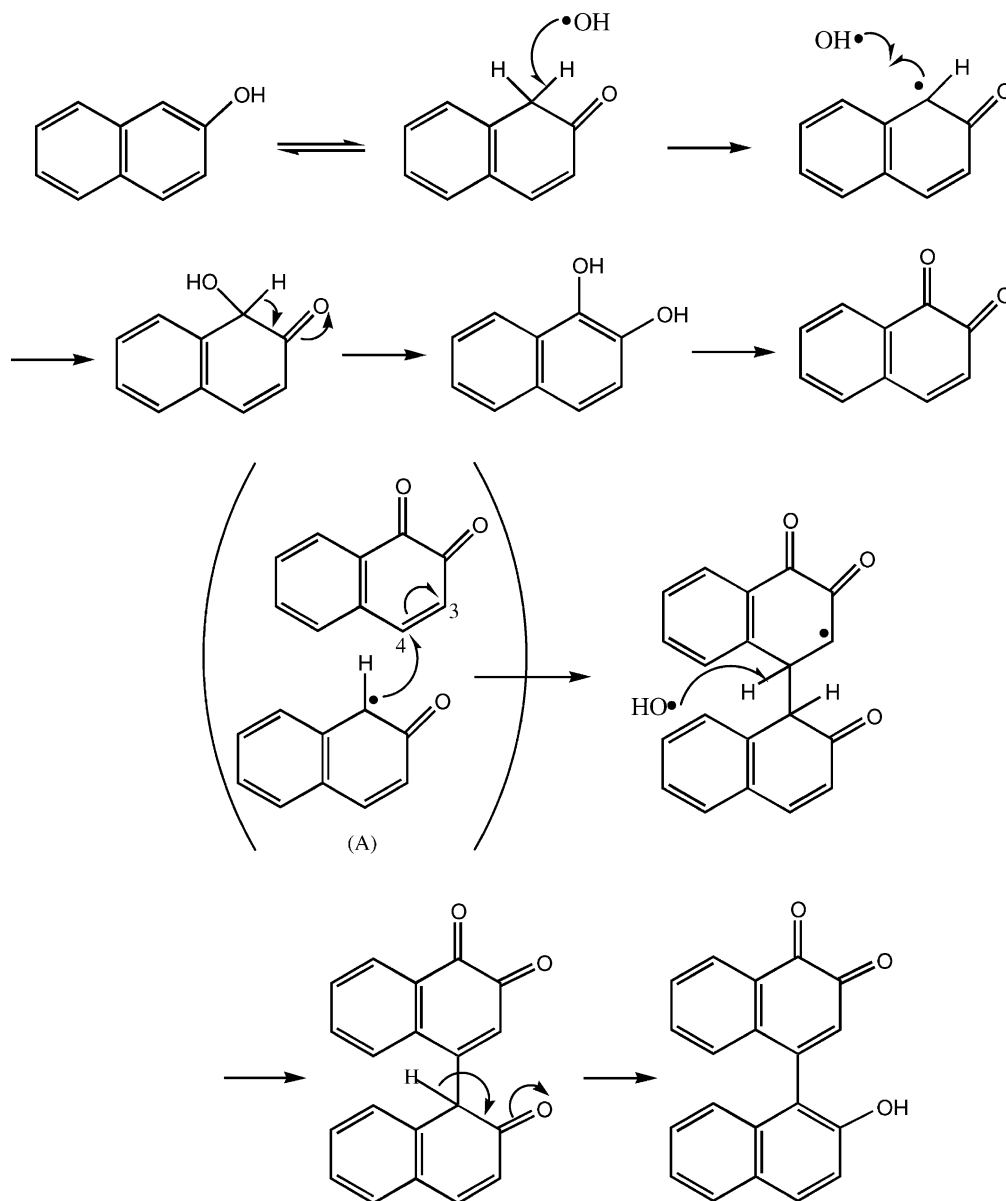


Scheme 3.

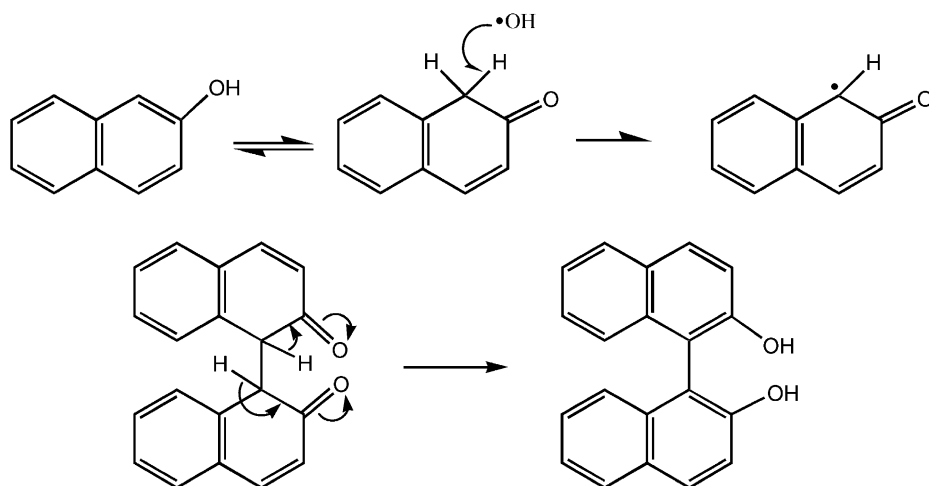
HPLC and characterised by nuclear magnetic resonance and infrared spectroscopy, mass spectrometry and melting point. In our laboratory an authentic sample of the predict compound was synthesised and characterised [30]. From the interpretation of the spectroscopic data of the two samples, the unknown

product was identified as 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone.

Oxidation of 2-naphthol with VOPC, results in much higher overall conversion. Furthermore, this reaction produces another product, 1,1'-bi(2-naphthol), which was identified by comparison with an authentic



Scheme 4.



Scheme 5.

sample (Aldrich). 1,1'-Bi(2-naphthol) can be also obtained by oxidative coupling of 2-hydroxynaphthalene in the presence of transition metal complexes [5,31].

The results, summarised in Table 2, show that 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone is formed exclusively, except in reactions catalysed by VOPC. In this last case, 1,1'-bi(2-naphthol) was also formed (Scheme 3). Reactions done without catalyst or with VOPC gave the lowest percentage of 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone. However, all the other phosphates acted as catalysts in respect to its production.

The probable mechanism for the 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone formation is shown in Scheme 4. As formally predicted, and given the contrasting differences of VOPC results relative to the phenol case, in these systems it is possible that the reactions follow a radical mechanism. The intermediate (A) can couple in the three or four positions of 1,2-naphthoquinone. In that case the products formed could be 3-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone or 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone, respectively. However, in our reaction conditions, it was verified the formation of 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone exclusively, as indicated in the proposed mechanism (Scheme 4). The formation of 1,1'-bi(2-naphthol) also proceeded through a radical mechanism similar to that illustrated in Scheme 5.

The 2-naphthol conversion differences may be explained by the direct reaction of metal phosphates with

hydrogen peroxide. If this reaction occurs, the substrate conversion depends on the rate of decomposition of the peroxides. This will be different for the various phosphates, given the diverse mechanisms of removing hydrogen peroxide from the reaction products.

4. Conclusions

The results presented in this contribution show that glacial acetic acid is an efficient solvent for the oxidation of phenol with H_2O_2 . In solvents such as acetonitrile, methanol or *tert*-butyl alcohol, no significant oxidation occurred. This solvent effect suggested that peroxyacetic acid was formed and presumably is the effective oxidant rather than H_2O_2 itself. This possibility was confirmed by examining the rate of formation of peroxyacetic acid, in the absence and presence of metal(IV) phosphates. The results clearly indicate that peroxyacetic acid is the major oxidant and that the phosphates have no catalytic effect on its formation. Although, the phosphates did not catalyse the formation of peroxyacetic acid, they did influence the nature of the oxidation products obtained from phenol.

In view of the formation of peroxyacetic acid, the reactions of phenol oxidation follow an acid catalysed "ionic" mechanism. Remarkably, for ZrPP and ZrWPA (acidic and basic), only muconic acids are observed with none hydroquinone or catechol formed. This suggests that formation of the latter compounds proceed

through a mechanism that involves the formation of a metal–catechol complex, which is quickly oxidised to muconic acid.

The oxidation of 2-naphthol in the presence of some tetravalent metal phosphates (α -ZrPA, SnPA, CePFC, TiPA, and ZrPP) to produce 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone, follows a radical mechanism. When using VOPC as catalyst, 4-(2-hydroxy-1-naphthyl)-1,2-naphthoquinone yield is not improved but 1,1'-bi(2-naphthol) was also formed, following a radical mechanism.

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