

Rates of formation of peroxyacetic acid from hydrogen peroxide and acetic acid in the presence of metal(IV) phosphates

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Received 8 October 2001; received in revised form 6 November 2001; accepted 16 February 2002

Abstract

Amorphous zirconium, tin, titanium, vanadyl, cerium and scandium/zirconium phosphates have been evaluated in relation to their effects on the catalysed formation of peroxyacetic acid (PAA) from hydrogen peroxide and acetic acid. The rate of formation of PAA remained almost the same whether the phosphates were present or absent, for most of the phosphates. However, by exchanging the acidic hydroxyl centres in ZrPA with scandium(III), it was found that the resulting solid, ScZrPA, strongly accelerated the formation of PAA, even more so than the scandium(III) ions in homogeneous solution. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tetravalent metal phosphates; Scandium; Peroxyacetic acid; Hydrogen peroxide

1. Introduction

The synthesis and application of porous materials has shown extraordinary growth over the past 25 years. The success of these materials as shape-selective catalysts, adsorbents, molecular sieves, sensor materials and ion-exchangers have contributed significantly to advances in basic and applied research. An ultimate important goal in the syntheses of these compounds is control of size, shape and hydrophilic or hydrophobic character of micropores and greater thermal stability so as to control a variety of industrial processes [1–7].

Oxidation of phenol is one important reaction industrially, since it can produce hydroquinone and catechol, both of which are important starting materials for production of fine chemicals used in agrochemicals, pharmaceuticals, flavours and aromatic essences. However, most of the methods available for production of hydroquinone and catechol are not selective to one or the other or they give low yields with large amounts of tarry by-products. Metal(IV) phosphates provide one group of meso- and microporous materials, which have shown promise for selectivity in formation of oxidised products from phenol [8]. It was not clear from this last work whether or not the phosphates affected the course of oxidation directly or indirectly through catalysed formation of peroxyacetic acid (PAA).

Metal(IV) phosphates are interesting as potential catalysts because of their lamellar structures and their Brønsted and Lewis acidic sites, which may be used

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for ion exchange with a range of metal cations. Most of the catalytic activity so far reported in the literature for metal(IV) phosphate has been attributed to their acidic nature [9–13], but the selective oxidation reactions [8] provide an example of a different use for them. The present work reports an investigation into the effects of various phosphates on the rate of formation of PAA from acetic acid and hydrogen peroxide, which is itself a major industrial process.

2. Experimental

2.1. Characterisation of catalysts and reaction products

For metal(IV) phosphates already described in the literature, sufficient X-ray spectroscopic and other data were obtained to confirm their identities. High-pressure liquid chromatography (HPLC) analysis was performed using a Hypersil ODS column (25 cm \times 5 μ m). Infrared spectra were recorded on a Fourier-transform spectrometer, liquid compounds as films and solids as KBr disks. A diode array spectrometer was used to record ultraviolet/visible (UV/VIS) spectra. Mass spectra were obtained using electron ionisation at 70 eV. Melting points, ^1H -nuclear magnetic resonance (NMR) and solid state ^{31}P MAS NMR spectra were measured to characterise the materials. For the latter spectra, chemical shifts are quoted in parts per million relative to phosphoric acid, for which the chemical shift is made equal to zero.

2.2. Synthesis of metal(IV) phosphates

Amorphous α -zirconium phosphate (ZrPA) [14], tin phosphate (SnPA) [15], titanium phosphate (TiPA) [16], together with crystalline vanadyl phosphate (VOPC) [17], fibrous crystalline cerium phosphate (CePFC) [18] and pellicular zirconium phosphate (ZrPP) [19] were prepared as previously described in the literature. Amorphous scandium ion-exchanged zirconium phosphate (ScZrPA) and amorphous zirconium tungstate phosphate (ZrWPA) (basic form) were prepared as described below.

2.2.1. Amorphous ScZrPA [20]

Scandium(III) triflate (0.5 g, 2.25 mmol) was added to a sample of zirconium phosphate (ZrPA, 0.32 g,

1.44 mmol) in water (10 ml). The resulting suspension was stirred at room temperature for 3 days after which the solid was filtered off under vacuum (water pump), washed with water (3 \times 10 ml) and allowed to dry at room temperature for 18 h to give 0.22 g of product. Elemental analysis: found, ZrO_2 12.9; P_2O_5 10.5; Sc 23.9 (Zr:P:Sc ratio = 2:1:5; 5.3 mmol Sc^{3+} per gram of solid).

2.2.2. Amorphous ZrWPA (basic form) [21]

A solution of zirconyl chloride (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 $^\circ\text{C}$ 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%; 28.5 m^2/g .

2.3. Oxidation of phenol with H_2O_2 in the presence and absence of metal(IV) phosphates

Because of the many potential variables in these systems, the oxidation of phenol was examined by use of the Simplex method [22]. This method uses sequential optimisation of the variables influencing the outcome of a system, such as a chemical reaction. It requires the repeated observation of the system response, selection of new values for the variables in accordance with the Simplex rules, followed by a new observation, in an iterative process repeated until the optimum response is obtained. In our case, the yields of the reaction products as well as the substrate conversion were the criteria used for the application of the Simplex method.

We have performed a series of reactions with α -ZrPA, to determine the optimum reaction conditions. By changing these conditions, we have found that the variables with greater impact on the reaction were the temperature, the reaction time, the concentration of H_2O_2 and the amount of H_2O_2 oxidant. The Simplex method was then applied to obtain the following optimum conditions for best yields of

hydroquinone and catechol: temperature (60 °C), time (6 h), concentration of H₂O₂ (35%, w/w) and amount of H₂O₂ oxidant (2 mol to each mole of phenol). These define the standard conditions, used in all subsequent oxidations with other metal phosphates [8].

2.4. Determination of hydrogen peroxide and PAA in mixtures [23]

The total available oxygen content (H₂O₂ and CH₃CO₃H) was determined by addition of NaI to an aliquot of a solution of the oxidant, followed by titration (A) of the released I₂ with sodium thiosulphate. The H₂O₂ content was determined on another aliquot of the oxidant by titration (B) against ceric sulphate (0.1 M), using ferroin as indicator. The difference (A – B) gave PAA content.

2.5. Rates of reaction of hydrogen peroxide with acetic acid

2.5.1. In the absence of any added catalyst [20]

Hydrogen peroxide (65%, w/w, 0.2 g, 4 mmol) was added dropwise to acetic acid (4.2 g, 70 mmol) and the resulting solution was stirred gently at room temperature for 6 h. Aliquots were taken at regular intervals to determine the concentrations of PAA and hydrogen peroxide. This reaction is weakly self-catalysed.

2.5.2. With added scandium(III) triflate as homogeneous catalyst [20]

Hydrogen peroxide (65%, w/w, 0.26 g, 5 mmol) was added dropwise to a solution of scandium(III) triflate (0.98 g, 2 mmol of Sc³⁺) in acetic acid (4.2 g, 70 mmol). The solution was stirred at room temperature for 6 h. The amounts of PAA and hydrogen peroxide were determined at intervals.

2.5.3. With added amorphous ScZrPA as catalyst [20]

Hydrogen peroxide (65%, w/w, 0.26 g, 5 mmol) was added dropwise to a mixture of ScZrPA (0.02 g; 1.8 × 10⁻⁴ mmol of Sc³⁺) in acetic acid (4.2 g, 70 mmol) and the whole solution was stirred gently at room temperature for 6 h. Aliquots of the liquid were removed at intervals to determine the contents of PAA and hydrogen peroxide.

2.6. Determination of hydrogen peroxide absorbed by amorphous zirconium phosphate [21]

2.6.1. Content of hydrogen peroxide after brief washing

A sample of ZrPA was added to a stirred aqueous solution of hydrogen peroxide (70%, w/w) at room temperature. At suitable intervals, aliquots of solid plus liquid were removed from the mixture, filtered through a sintered glass funnel and then washed briefly for 10 s with distilled water (2 ml) under suction. The still wet solid was added to the titration solution, where it was stirred for 5 min and then titrated with ceric sulphate solution (0.1 M). This gives the content of hydrogen peroxide, except that which had been removed from the surface by the quick wash.

2.6.2. Content of hydrogen peroxide after thorough washing

Aqueous hydrogen peroxide (70%, w/w) was stirred at room temperature with a sample of amorphous zirconium phosphate. At suitable intervals, aliquots of solid plus liquid were removed from the reaction mixture, filtered with suction and then washed very well (for about 1 min) with distilled water (7 ml) to remove hydrogen peroxide residual on the surface or held just inside the pores. The resulting wet solid was added to the titration solution, where it was stirred for 5 min and then titrated against ceric sulphate solution (0.1 M) to determine the content of hydrogen peroxide.

3. Results and discussion

The object of earlier work [8] was to study the catalytic activity of several metal(IV) phosphates, for oxidation of phenol with hydrogen peroxide. As the work proceeded, it became apparent that, in solvents such as acetonitrile, methanol or *tert*-butyl alcohol, no significant oxidation of phenol occurred but that, in glacial acetic acid, oxidation gave various products (Table 1). This solvent effect suggested that PAA was likely to be the effective oxidant, rather than H₂O₂ itself. However, the marked variations in selectivity towards different oxidation products (Table 1) indicated that the phosphates must be having a shape effect on either the reaction of oxidant (either H₂O₂ or PAA) with phenol or on the rate of formation of PAA or both effects

Table 1

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

	Phosphates							No catalyst (%)
	α -ZrPA ^b (%)	SnPA ^c (%)	CePFC ^d (%)	TiPA ^e (%)	VOPC ^f (%)	ZrPP ^g (%)	ZrWPA ^h basic (%)	
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	–
Yield of <i>cis,trans</i> -muconic acid based on phenol conversion	–	–	–	–	–	–	13.8	–
Phenol conversion (w/w)	20.9	17.1	16.8	29.2	–	24.6	28.9	20.7

^a Reaction conditions were all similar and are described in Section 2. In all cases, acetic acid was used as solvent. Remaining products are non-identified tars. HPLC was used to monitor the reactions. Quantifications were performed by comparison with calibration curves obtained with known amounts of hydroquinone, catechol, *cis,cis*-muconic acid and *cis,trans*-muconic acid.

^b Amorphous zirconium phosphate.

^c Amorphous tin phosphate.

^d Fibrous crystalline cerium phosphate.

^e Amorphous titanium phosphate.

^f Crystalline vanadyl phosphate.

^g Pellicular zirconium phosphate.

^h Amorphous zirconium tungstate phosphate.

combined. The heterogeneous lamellar nature of the phosphates suggested that shape selectivity could be involved with or without catalysed formation of PAA.

Sulphuric and of methylsulphonic acids, are used routinely to catalyse the formation of PAA from hydrogen peroxide (1). Without added strong acid, reaction (1) is very slow.



Since metal(IV) phosphates have various effective acid strengths [25], it was decided to explore the possibility that the phosphates could be influencing the oxidation through an ability to catalyse the rate of formation of PAA. In typical experiments, a mixture of aqueous hydrogen peroxide and glacial acetic acid was maintained at 60 °C over a period of about 6 h. Aliquots of the liquid were removed at regular intervals and the contents of H₂O₂ and CH₃CO₃H were determined by titration. Typical results are shown in Fig. 1. It can be seen immediately that, ZrPA, SnPA and CePFC had no significant effect on the rate of formation of PAA, despite their known acidities. In the case of vanadyl phosphate, there was actually no formation of PAA and the hydrogen peroxide was decomposed. With titanium phosphate, the initially formed PAA was itself

decomposed by the phosphate so that the total oxidant level rose initially but then fell over time.

When the effect of ZrPA was examined over a further period of 6–24 h, no more PAA was formed and the total oxidant level remained constant (an equilibrium state). Thus, ZrPA neither significantly altered the rate of formation of PAA (no catalytic effect) nor did it have any effect on the position of equilibrium (no thermochemical effect) in reaction (1) through, e.g., trapping and removing PAA from the reaction products [21].

To discover what other role the porous structure of ZrPA might have on reaction (1), the phosphate was stirred with aqueous 70% H₂O₂ alone. Over a period of 6 h, samples of ZrPA were removed. These samples were either washed very quickly with cold water, to remove most H₂O₂ from the outside of the phosphate particles or were washed well with water, so as to leave only any H₂O₂ remaining tightly bound inside the lamellar structure. The results showed clearly that, after brief washing, about 6% H₂O₂ remained adsorbed into the ZrPA and, after extended washing, there still remained about 1% [21]. These results suggest that H₂O₂ must penetrate right inside the phosphate structure and possibly be held there by hydrogen

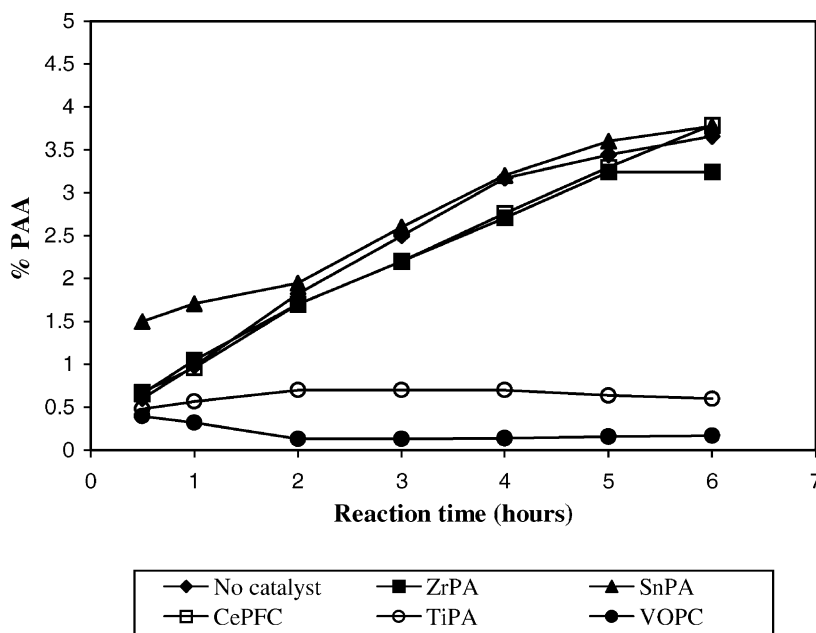


Fig. 1. Formation of PAA from glacial acetic acid and aqueous hydrogen peroxide (35%, w/w) in the absence and presence of metal(IV) phosphates. The percentages of PAA are quoted as millilitres of substrate per 100 ml of solution. The reactions were carried out at 60 °C.

bonding. This indicated that any effect of the phosphates on oxidation of phenol with H_2O_2 , could occur by affecting selectivity towards product formation in their pores and not by catalysed formation of PAA.

Although previous results show that PAA must be the major phenol oxidant, the effect of the phosphates was not catalytic in formation of the PAA. Since the phosphates did control the type of oxidation product (hydroquinone, catechol, *cis,cis*-muconic acid and *cis,trans*-muconic acid), it is concluded that they exert shape selectivity [8].

The uncatalysed conversion of acetic acid into PAA with hydrogen peroxide (1) is very slow but can be accelerated with added acid. Good conversions in reasonable reaction time are only possible through the use of very strong acids [24]. Although the metal(IV) phosphates described above contained moderately strong acid centres [8,18,19,25] as determined by titration [26], there were no centres having $\text{p}K_a$ between +3.3 and -3.3. Neither the Lewis nor Brønsted acid centres in these metal(IV) phosphates were sufficiently strong as to catalyse PAA formation, more than acetic acid does itself. Use of Sc(III) and La(III) salts as good Lewis acid catalysts in aqueous

environments has been reported in the direct acetylation of alcohols [27]. Also, a Nafion-supported scandium catalyst for allylation of carbonyl compounds has been described [28]. Hydrogen peroxide can be considered to be an 'alcohol' and, therefore, it was decided to investigate whether or not scandium compounds would have any effect on the rate of reaction (1). The possibility of homogeneous and heterogeneous catalysis was examined.

When acetic acid was mixed with aqueous hydrogen peroxide at room temperature, in the presence of soluble scandium(III) triflate, formation of PAA was found to be six times faster than when no scandium was present (Fig. 2). Optimum times, temperatures and catalyst concentration for this homogeneous reaction were not investigated. Instead, because a reusable heterogeneous catalyst was preferable to conserve scandium, a sample of ZrPA was stirred with scandium triflate solution to exchange H^+ for Sc^{3+} . The resulting ScZrPA was used, under the same conditions as for the homogeneous scandium triflate and a greater acceleration in the production of PAA was observed (Fig. 3). If the accelerations are compared on a molar basis for Sc^{3+} content, the heterogeneous catalyst

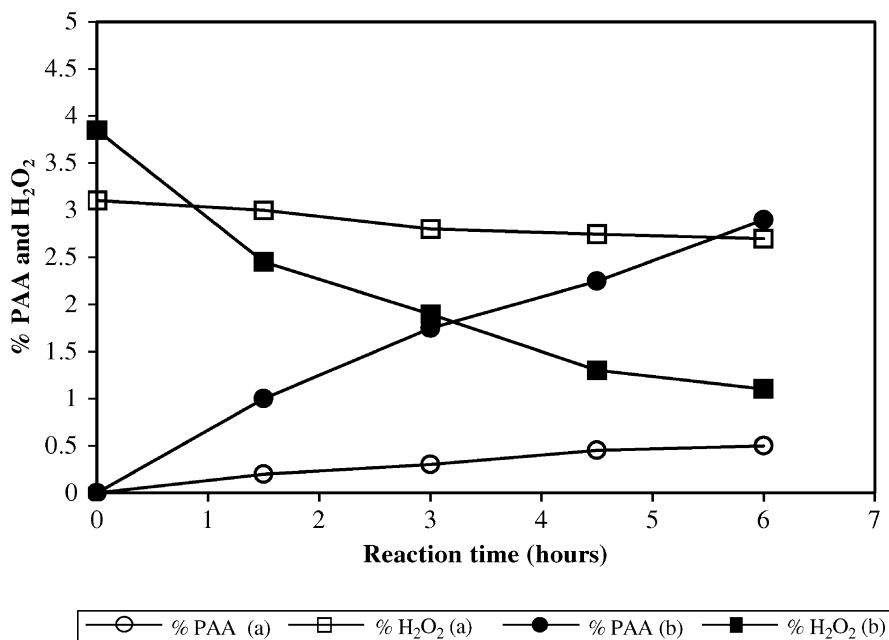


Fig. 2. Formation of PAA and consumption of hydrogen peroxide with: (a) no catalyst and (b) scandium(III) triflate. The percentages of hydrogen peroxide and PAA are quoted as millilitre of substrate per 100 ml of solution. The reactions were carried out at 20 °C.

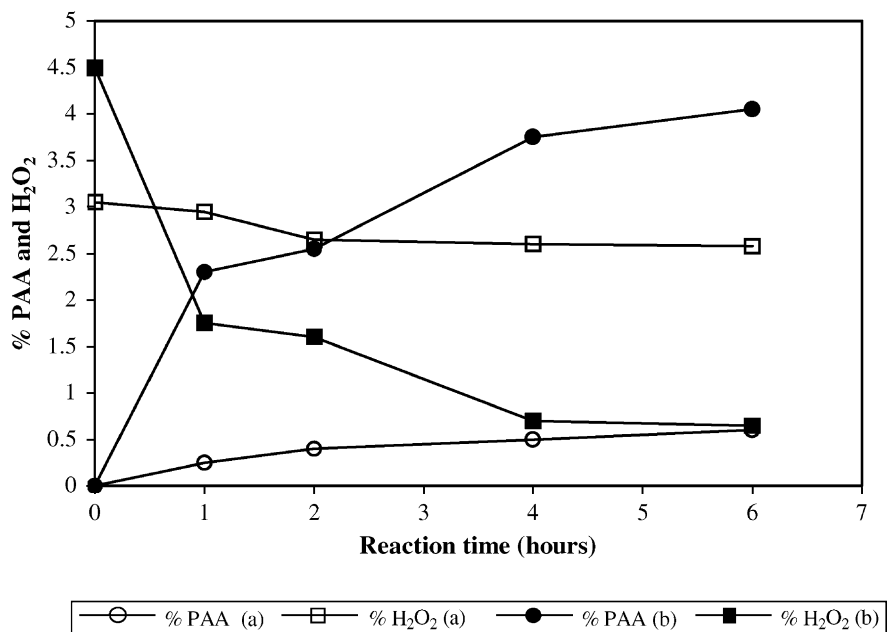


Fig. 3. Formation of PAA and consumption of hydrogen peroxide with: (a) no catalyst and (b) amorphous ScZrPA as catalyst. The percentages of hydrogen peroxide and PAA are quoted as millilitres of substrate per 100 ml of solution. The reactions were carried out at 20 °C.

was about 20 times more effective than the homogeneous one and some 80 times more effective than the self-catalysed reaction (1).

To clarify the possibility of a homogeneous contribution (Sc release in the media) in the case of the reaction with ScZrPA, we should mention that the latter catalyst was reused for catalysis four times without loss of activity. Additionally, the liquid filtrate from a typical catalysed reaction did not catalyse the formation of PAA unless a fresh amount of the Sc-exchanged phosphate was added. This, together with the greatly enhanced activity of the exchanged material over the homogeneous Sc catalyst, shows clearly that the activity cannot be due to “homogeneous” scandium in solution.

4. Conclusions

In the presence of some metal(IV) phosphates, the action of H_2O_2 in glacial acetic acid is to produce four major products, viz., hydroquinone, catechol, *cis,cis*-muconic acid and *cis,trans*-muconic acid. Selectivities and conversions are markedly different depending on the phosphate used, but the overall yields of oxidation products are not greater than those observed for the oxidation of phenol in acetic acid, in the absence of the phosphates. These results indicate that the phosphates have a significant effect on the course of oxidation for the individual oxidation products but do not affect the overall amount of oxidation occurring. The results suggest shape-selectivity towards individual oxidation products.

There was also the possibility that these simple phosphates could influence the oxidation through catalysing the formation of PAA (the true oxidant) inside micro- or mesopores. This effect is unlikely because the rate of formation of PAA from hydrogen peroxide and acetic acid remained almost the same whether the phosphates were present or absent. The lack of catalytic activity towards formation of PAA was unexpected, since the phosphates have well-defined Lewis and Brønsted centres of acidity and the reaction of acetic acid with H_2O_2 is strongly catalysed by acid. By exchanging the acidic hydroxyl centres in ZrPA with scandium(III), it was found that the resulting solid ScZrPA strongly accelerated the formation of PAA, even more so than scandium(III)

ions in homogeneous solution. Since ZrPA by itself has no effect on the rate of formation of PAA, it cannot be the Brønsted centres that led to the observed acceleration and, instead, it must be Sc-enhanced Lewis acidity that is responsible, viz., ScZrPA is a strong Lewis acid promoter, even under aqueous conditions.

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