Catalysis of gas and liquid phase ionic and radical rearrangements of α- and β-pinene by metal(IV) phosphate polymers

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Abstract

Gas-phase rearrangements of α- and β-pinene catalysed by metal(IV) phosphate polymers have been studied. The phosphates catalyse carbocation rearrangements in both substrates as expected, but catalysis of a modified radical rearrangement of α-pinene to yield α-pyronene has also been observed. Reduction in the acidity of the catalysts by exchange of protons with copper or ammonium ions, or by heating them to convert phosphates into pyrophosphates suppresses the carbocation reaction whilst having little effect on the rate of the radical reaction. Reasons for the alteration in the mode of the radical reaction, which normally yields ocimene and alloocimene, are discussed.

Keywords: Catalysis; Pinene; Zirconium phosphate; Rearrangement; Gas phase

1. Introduction

The structures of tetravalent metal phosphates have been well studied but their catalytic properties are less well known [1,2]. They are known to act as stable acid catalysts and their layered structures offer potential as surface catalysts at low and high temperatures. To investigate the latter property only, the possibility of catalysis of reactions in which protonation is *not* an essential step was investigated.

An ideal system for this study involves rearrangements of α-pinene (Scheme 1) and β-pinene (Scheme 2) both of which undergo thermal (radical) and acid catalysed rearrangement. These four reactions have been well inves-
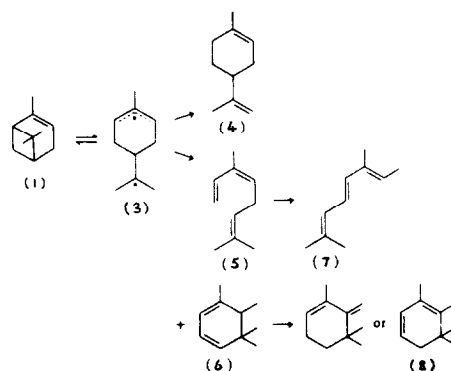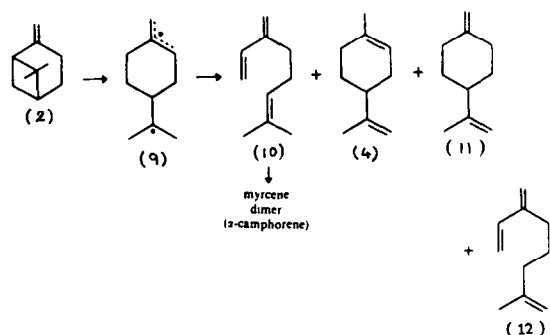

Scheme 1. Thermal isomerization of α-pinene.

tigated using catalysts [3] other than metal phosphates, and are of considerable industrial value. Thermal decomposition of α-pinene takes place at around 400°C and is believed to proceed through a biradical (3; Scheme 1). The primary rearrangement products are limonene (4) (also described confusingly as dipentene when it is

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Scheme 2. Thermal isomerization of β-pinene.
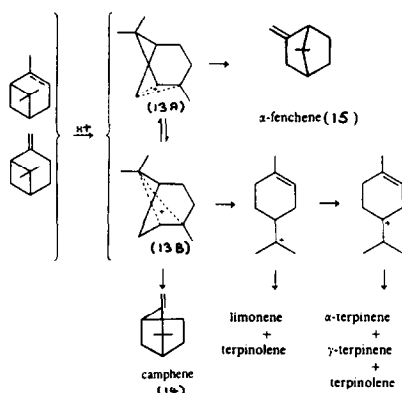
Scheme 3. Acid catalysed isomerization of α-pinene and β-pinene.

racemic), ocimene (5) and α-pyronene (6). Alloocimene (7), formed from ocimene, and β-pyronene (8), formed from α-pyronene, are observed. In the liquid phase, pyrolysis gives similar products [4].

Gas-phase pyrolysis of β-pinene (2) in a copper tube heated to 375°C (Scheme 2) has been described [5]. The reaction is again believed to involve a biradical (9) and yields β-myrcene (10) and limonene (4) (optically active in this case) as the main products, together with some 1(7),8-p-menthadiene (11) and α-myrcene (12; Scheme 2).

In the presence of acids, rearrangement is significantly different with both α-pinene and β-pinene reacting through the same carbocation (13a,b; Scheme 3), which can ring expand either by shift of the gem-dimethyl bridge to give camphene (14) or by shift of the methylene bridge to give α-fenchene (15). Alternatively, its ring can open to give a mixture of the p-menthadienes

(limonene, terpinolene and α-terpinene) as shown in Scheme 3.

These reactions have been found to take place on acidic clay surfaces where camphene and limonene are the main products [3].

2. Experimental

2.1. Amorphous zirconium phosphate (ZrPA)

This was prepared by a method described previously [6]: aqueous H_3PO_4 solution (54 ml; 54.2 g/l) was added rapidly to a well stirred aqueous solution of $ZrOCl \cdot 8H_2O$ (55.6 ml; 129 g/l). After stirring the resulting gelatinous suspension for 15 min at room temperature, it was washed several times with large volumes of distilled water; after each washing, the supernatant liquid was decanted when the suspension had settled out. Finally, the amorphous gel was centrifuged off and dried at 50°C. The dried product was converted completely into the protonic form by immersion in aqueous HNO_3 (1 M) for 24 hours. After centrifugation, the zirconium phosphate was washed several times with distilled water until the wash water reached pH 4–5 and was dried at 110°C. The sample was labelled as ZrPA.

2.2. Crystalline zirconium phosphate

This was prepared by a literature method [7]. Amorphous zirconium phosphate (2 g), obtained as described above, was refluxed for 126 h in orthophosphoric acid (100 ml, 11 M). The resulting crystalline ZrP(126.11) was washed with distilled water until the effluent attained pH 4–5 and was then dried at 110°C.

2.3. Amorphous tin phosphate (SnPA)

This was prepared by rapid addition with stirring of aqueous H_3PO_4 (108 ml; 54.2 g/l) to a solution of aqueous $SnCl_4 \cdot 5H_2O$ (74 ml; 104.2 g/l). After continued stirring for a further 30 min at room temperature, the gelatinous product was

worked up as described for amorphous zirconium phosphate and dried at 110°C.

2.4. Crystalline tin phosphate

This was prepared by a procedure from the literature [8], by refluxing the above amorphous tin phosphate gel in aqueous 8 M H_3PO_4 for 120 h. The gel, prepared by pouring aqueous Na_2HPO_4 (1.2 M) into an equal volume of vigorously stirred aqueous $SnCl_4 \cdot 5H_2O$, (0.6 M), was washed several times by decantation from distilled water and was then dispersed in aqueous 8 M H_3PO_4 to give a final concentration of 8 M of the tin phosphate. On heating the mixture, the solid gel first dissolved but continued refluxing resulted in the slow separation of a white, microcrystalline material. After refluxing the mixture for a total of 120 h, the white solid was washed several times in distilled water by decantation and was then stirred with 1 M HNO_3 for 24 h at room temperature to ensure complete conversion to the protonic form. The final product was again washed by decantation with distilled water to a pH 4–5, separated from the aqueous phase by centrifugation and dried at 110°C.

2.5. Amorphous titanium phosphate (TiPA)

This was prepared by the slow addition of aqueous HCl (2 M; 74.0 ml) containing 5.6 g of $TiCl_4$ to stirred aqueous H_3PO_4 (54.2 g/l; 108 ml). After continued stirring for 30 min at room temperature, the resulting precipitate was washed with water as for amorphous zirconium phosphate and then dried at 110°C.

2.6. Crystalline titanium phosphate

This was prepared by a procedure from the literature [9]. Aqueous 2 M HCl (2 M; 215 ml) containing $TiCl_4$ (12.5 g) was added slowly with stirring to aqueous H_3PO_4 (1.25 M; 400 ml). After 24 hours stirring, the precipitate was filtered off, washed well with distilled water to pH 3–3.5 and then dried at 110°C. The product was obtained

crystalline by refluxing this amorphous compound with aqueous 9 M H_3PO_4 for 120 h. On first heating to reflux, the solid dissolved but later separated again in a microcrystalline form. It was washed with distilled water to pH 4–5 and dried at 110°C.

2.7. Exchange of zirconium phosphate with copper ions

The source of copper ions was a stock solution of aqueous copper (11) sulphate (0.025 M). The solution was added to weighed samples of the zirconium phosphate so that the mixture contained 2.5 mmoles of copper salt to 1.0 mmole of the phosphate. The mixture was stirred at either 100°C or 25°C until exchange stopped (2 h at 25°C or 16 h at 100°C). The uptake of copper was monitored by u.v. spectroscopy at 700 nm. The final exchanged samples were washed several times with distilled water, and dried at 110°C. The uptake of copper observed was expressed as mmoles of copper per mmole of phosphate exchanger. The crystalline sample, ZvP (11:126) took up 12% at 25°C and 73% at 100°C. The amorphous sample took up 15% at 25°C, and 35% at 100°C.

2.8. Characterisation of catalysts

Thermogravimetric analysis measurements were carried out on a Dupont 9900 Thermal analysis apparatus. Thermogravimetric analysis curves for the zirconium phosphates are shown in Fig. 1. Tin phosphate samples lost about 15% of their weight up to 250°C and then remained steady until 600°C. Titanium phosphates showed a loss of 5% of their weight up to 450°C, above which temperature decrepitation made results unreliable. Surface areas were determined by a standard BET method with nitrogen as solvent. The following surface areas, measured in square metres per gram, were recorded:

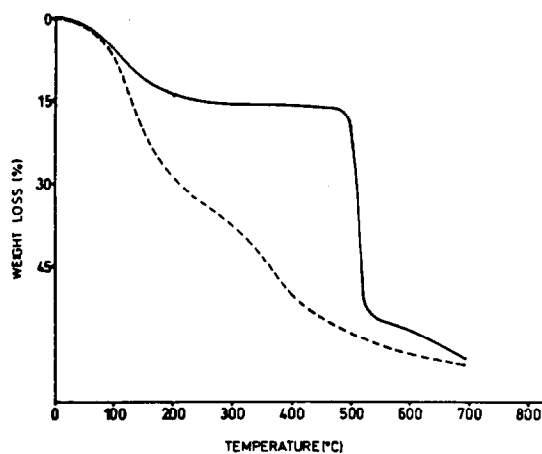|	
Zr PA	278
Zr P (11:126)	8.7
Ti PA	87

Fig. 1. TGA curves of amorphous and crystalline zirconium phosphate: ZrPA (50ZC) (- - -); ZrP (11:126) (—).

Acidity measurements of the acid strength distribution were carried out by titration with *m*-butylamine. Zirconium phosphate samples (0.2 g), immediately after drying at 110°C, were suspended in 2 ml of 60/80 petroleum ether (dried over KOH and distilled) and titrated with a solution of n-butylamine (0.25 M), using as indicators benzalacetophenone (pK_a −5.6), dicinnamylacetone (pK_a −3.0), *p*-dimethylaminobenzene (pK_a +3.3) and methyl red (pK_a +4.8).

	Base used (meq 1 g)			
	pK_a 4.8	pK_a 3.3	pK_a −3.0	pK_a −5.6
Zr P (11:126)	6.880	0.170	0	0
Zr PA	1.167	0.976	0.575	0.392
Zr PA (35% Cu)	0.710	0.607	0.461	0.360

2.9. Rearrangement reactions of α- and β-pinene

Gas-phase reactions were carried out in a glass tube reactor (250 × 23 mm) in which the catalyst was sprinkled over loosely packed glass wool. The tube was charged with catalyst (0.1 g), which had been dried to 110°C for 16 h immediately before use, by sprinkling and shaking so as to distribute it over the glass wool as uniformly as possible. α-Pinene (0.5 g) was placed in a 25 ml two-necked flask kept at 150°C and was vaporized into a stream of nitrogen gas. The flow of nitrogen was kept constant throughout the experiment, usually at 0.5 l min⁻¹ giving the reaction mixture a contact time of 15 seconds. After leaving the two-necked flask, the gas stream was pre-heated to 120°C before entering the heated reaction tube. The products were cooled first in a U-tube surrounded by ice water and finally condensed in a second U-tube cooled with liquid nitrogen. The effluent products were analysed using GC or GC/MS with an OV351 capillary column (25 m × 0.3 mm).

Reactions in the liquid phase were done in a flask fitted with a condenser and stirrer and heated in an oil bath. Typically, α-pinene (1 g) and dried zirconium phosphate (0.2 g) were reacted at the temperatures indicated in the Tables. Samples were removed at regular intervals for GC/MS analysis.

3. Results and discussion

In the present work, gas-phase rearrangements of α- and β-pinene were examined in a conventional apparatus in which a carrier gas, nitrogen, was bubbled through the gently heated substrate so that the entrained vapour passed through a heated glass tube carrying the catalyst distributed over a glass wool support. At a nitrogen flow rate of 0.5 l min⁻¹, the pinene was in the reaction zone (heated tube) for an average of about 15 seconds.

The materials examined as catalysts were the polymeric phosphates of zirconium, titanium or tin, used either in the amorphous form (ZrPA, TiPA and SnPA) or the crystalline (after crystallisation from refluxing aqueous phosphoric acid): these crystalline samples are designated by the phosphoric acid concentration (molarity, M) and reflux time (h) so that, for example, ZrP (11:126) specifies a sample of crystalline zirconium phosphate (ZrP) prepared by refluxing the amorphous phosphate (ZrPA) in 11 M phosphoric acid for 126 h.

Table 1
Isomerisation of α-pinene in the gas phase over metal(IV) phosphate polymers at 300°C

Catalyst[a]	α-Pinene converted (%)	Composition of products (%) of total									
		α-Fenchene	Camphene	α-Pyronene	β-Pyronene	α-Terpinene	Limonene	γ-Terpinene	p-Cymene	Terpinolene	Isoterpinolene
ZrPa	94	3	6	14	3	3	31	10	14	4	10
ZrP (11:126)	37	0	5	30	2	8	35	0	5	14	0
TiPA	87	2	5	21	4	2	29	8	11	3	12
TiP (9:120)	92	3	3	28	5	3	23	8	4	14	7
SnPA	52	0	6	33	2	6	37	4	0	13	0
SnP (8:120)	88	0	6	25	3	22	11	9	8	5	10
None[b]	2										

[a] Contact time 15 seconds.
[b] Only glass wool packing was placed in the reactor tube.

Table 2
Isomerisation of β-pinene in the gas phase over zirconium phosphate polymer at 250°C

Catalyst[a]	α-Pinene converted (%)	Composition of products (%) of total								
		α-Pinene	Camphene	β-Myrcene	α-Terpinene	Limonene	γ-Terpinene	p-Cymene	Terpinolene	Isoterpinolene
ZrPa	50	16	32	0	12	20	4	2	10	2
ZrP (11:126)	24	36	24	0	4	28	0	0	8	0
None (a)[b]	1									
None (b)[b]	23	0	4	73	0	23	0	0	0	0
None (c)[b]	75	0	4	73	0	23	0	0	0	0

[a] Contact time 15 seconds.
[b] Only glass wool packing was placed in the reactor tube at (a) 250°C, (b) 350°C and (c) 450°C.

Pyrolysis of α-pinene was studied first at 300°C, a temperature below that reported previously for thermal gas-phase pyrolysis; results are given in Table 1. As a check on catalytic activity, an experiment without the catalyst in the heated tube showed that reaction proceeded to only about 2% under such conditions. All six phosphates showed catalytic activity towards the rearrangement of α-pinene. In all cases at 300°C, camphene, a typical product of carbocation formation (Scheme 2) was found but some α-pyronene a typical product of the biradical reaction (Scheme 2) usually affected at 400°C was also isolated. Thus, there is clear evidence that all of the metal(IV) phosphate polymers catalyse both carbocation and biradical reactions. The carbocation products are qualitatively similar to those obtained during standard acid catalysis in solution, but the radical products reveal an absence of ocimene. Both α- and β-ocimene were found independently to be stable

under the reaction conditions used here so it must be concluded that ocimene could not have been formed initially and have then rearranged to something else. It appears that the phosphates modify the uncatalysed, higher temperature thermal radical reaction. α-Pyronene has not been reported as being produced by any carbocation reactions. However, a radical formed on a catalyst surface would be more likely to undergo cyclisation than one formed in the gas phase. It is not possible to estimate the relative amounts of the radical and carbocation reactions, since limonene may well be a product of either.

Reaction of β-pinene was studied under similar conditions to those used for α-pinene and the results are given in Table 2. The reaction was carried out at 250°C, lower than the temperature used in earlier work [5]. No significant pyrolysis of β-pinene was observed during its passage over glass wool in a glass reactor tube at 250°C but

Table 3
Isomerisation of α-pinene in the gas phase catalysed by zirconium phosphate exchanged with copper ions at 300°C

Catalyst[a]	Copper content Cu^{2+}; % moles	α-Pinene converted (%)	Composition of products (% of total)									
			α-Fenchene	Camphene	α-Pyronene	β-Pyronene	α-Terpinene	Limonene	γ-Terpinene	p-Cymene	Terpinolene	Isoterpinolene
CuZrP (11:12)	73	21	0	0	45	8	0	40	0	0	0	8
	12	24	0	0	36	4	0	36	0	4	0	20
	[b]	24	0	0	36	8	0	40	0	0	0	12
CuZrPA	35	90	1	4	23	2	2	24	8	7	2	10
	15	90	2	3	16	2	2	27	9	5	3	12

[a] Contact time 15 seconds.
[b] Exchanged with NH$_4^+$ rather than with Cu^{2+}.

Table 4
Isomerisation of α-pinene in the liquid phase at 165° with metal(IV) phosphate catalysts

Catalyst	Reaction time (hours)	α-Pinene converted (%)	Composition of products (% of total)							
			Camphene	α-Pyronene	β-Pyronene	α-Terpinene	Limonene	α-Terpinene	p-Cymene	Terpinolene
SnP (8:120)	1	95	18			9	26	9	19	20
SnP (8:120)	2	96	22			6	9	3	51	7
SnP (8:120)	3	98	22			5	5		63	4
ZrP (11:126)	2	12		25	13		50			
TiP (9:120)	2	14		42	16		42			

when the temperature of the glass reactor was raised to 350°C, both β-myrcene and limonene were formed. The small yield of camphene is unexpected and may result from some acidic impurities on the surface of the glass wool or the walls of the glass reactor.

For β-pinene, zirconium phosphate polymers exclusively catalyse the carbocation reaction and yielded some of the more stable α-pinene (a known product of proton catalysis in solution [10]), together with typical products of acid catalysed rearrangement.

Conditions were sought by which it might be possible to enhance the radical reaction at the expense of carbocation rearrangement. One approach was to exchange the protons in the phosphate polymers with copper ions. This exchange replaces acidic surface ('phosphate') protons by copper ions and should decrease the degree of ionic reaction. Our work [11] on ion exchange in metal(IV) phosphates has shown that it takes place first at weaker acidic sites and tends to leave the stronger sites intact.

This exchange of protons for copper ions reduced the extent of the carbocationic reaction (Table 3). Overall conversion of pinenes into products was also less and it seems that the effect of the copper(II) ions was simply removal of acidic sites from the catalyst surface. Even exchange with only 12 moles % copper had a significant effect (Table 3), suggesting that both strong and weak acid sites have a role to play in catalysis of the rearrangement since weak acid sites take up copper ions more readily than strong acid sites. Copper ion itself does not appear to

have any catalytic effect because exchange of the surface protons with ammonium ions produced similar product mixtures to those obtained using catalysts exchanged with copper ions.

By contrast with the above gas-phase work, in the liquid phase at 165°C and with longer reaction time (2 h), the isomerisation of α-pinene was entirely carbocation in nature with tin phosphate but was entirely radical with zirconium and titanium phosphate catalysts (Table 4). The marked contrast with gas-phase results is unexpected and unexplained, although it may be that, at the lower temperatures, entropy effects are better able to direct reaction along the most favoured pathways. Also, in the liquid phase, third body collisions can remove much of the excess of energy present in 'activated' molecules on the catalyst surface, again allowing true differentiation in reaction pathways.

An alternative approach for studying the effect of loss of acidity from polymeric metal phosphates is to study the loss of water from the material on heating. It has been reported that nickel phosphate, on heating to 700°C, loses practically all its phosphate (POH) groups even though it continues to exhibit appreciable activity in the dehydration of isopropanol [12]. Therefore, it was decided to examine the effect of pretreatment heat on the catalytic activity of zirconium phosphates.

Thermogravimetric analyses, summarised in Fig. 1 show that crystalline zirconium phosphate loses water between 100 and 120°C, and again at around 530°C. This is similar to the results reported earlier [6]. In contrast, the amorphous

Table 5
Isomerisation of α-pinene at 300°C in the gas phase over zirconium phosphate catalysts which had been heat treated at the temperatures shown

Catalyst[a]	Heat treatment (°C) for 16 h	α-Pinene converted (%)	Composition of products (% of total)											
			α-Fenchene	Camphene	α-Pyronene	β-Pyronene	α-Terpinene	Limonene	γ-Terpinene	p-Cymene	Terpinolene	Isoterpinolene
ZrP (11:120)	110	37	0	5	30	2	8	35	0	5	14	0
	320	45	0	7	33	7	9	27	0	4	13	0
	400	79	0	5	28	0	14	24	0	8	17	5
	500	64	0	5	34	2	14	22	0	6	13	5
ZrPA	110	94	3	6	14	3	3	31	10	14	4	10
	320	93	3	7	15	2	3	29	10	13	4	13
	400	94	4	7	13	3	3	30	10	14	3	13
	500	87	1	4	49	1	1	24	5	2	2	5

[a] Contact time 15 seconds.

sample loses water steadily as the sample is heated.

The effect of water loss on the catalytic properties of these phosphate materials is less clear. The amorphous zirconium phosphate sample, while losing water steadily, is relatively unaffected in catalytic activity towards the pinenes (Table 5). Thermal pretreatment of the phosphate to 500°C does produce a diminution in reaction at 300°C via the carbocation route.

Formation of pyronene through the radical route dominates, presumably due to intermolecular conversion of phosphate ≡P–OH groups into pyrophosphate during thermal pretreatment at 500°C which reduces the acidity of the catalyst. In contrast, the crystalline sample produced a gradual increase in catalytic activity with increasing temperature of heat pretreatment, without significant change in the relative amounts of reaction by the carbocation and radical routes.

Complete understanding of a mixed ionic/radical reaction system such as this is not possible with only the present experiments but general trends are clear. The metal(IV) phosphates described here catalyse carbocation rearrangement of pinenes and catalyse a modified radical rearrangements of pinenes. It is possible to suppress the carbocationic reaction by removal of surface protons through exchange with copper(II) or ammonium ions.

Our results clearly show that metal(IV) phosphates catalyse radical rearrangements of the pinenes in addition to catalysing acid-catalysed rearrangements. Catalysis of radical reactions is more significant in α-pinene than β-pinene. Catalysis of a radical reaction probably is initiated by absorption of the double bond of the substrate onto the surface of the catalyst, and it is in this step that the explanation of different catalytic effects on the two molecules lies. Sterically, the double bond of α-pinene can rest in contact with a surface while the bulk of the molecule is arranged away from

the surface, so that there is little hindrance to π-type binding. β-Pinene is much less favoured in this respect. The vinylic double bond projects normally from the surface of a roughly spherical molecule so that no orientation exists in which the double bond can lie on a flat surface with its reactive π-electrons in close contact with surface molecules. For β-pinene, all orientations present considerable steric hindrance to binding and adsorption would be expected to be less efficient than for the α-isomer. Thus the double bond of α-pinene is readily activated by the catalyst, while the double bond of β-pinene is less affected.

Acknowledgements

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