Matrix-isolation Studies on Alkali-metal Phosphates. Part 1. The Characterisation of Molecular $NaPO_3$

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This paper describes the results of a matrix-isolation i.r. study on the vaporisation of trisodium orthophosphate. When this material is heated *in vacuo* to *ca.* 1 600 K, and the products condensed in a low-temperature argon matrix, the i.r. spectrum obtained is shown to be due to a trapped species $NaPO_3$. With the aid of ^{18}O-enrichment, this molecule is shown to have a C_{2v} bidentate structure with characteristic i.r. bands at 1 341.7, 1 211.2, 1 004.0, 536.6, 474.0, and 287.0 cm^{-1}.

ALKALI-METAL phosphates constitute a major area of inorganic chemistry, and numerous books and review articles have been published describing their properties in the solid phase and in solution.[1] The last decade has also seen a growing interest in molten phosphates as potential solvents,[2] but it is only quite recently that alkali-metal phosphate molecules have been identified in the vapour phase. Here, high-temperature mass spectrometry in particular [3] has shown that the monomeric species MPO_3 (M = Li, Na, K, Rb, or Cs) are prominent species in the vapour above heated metaphosphates, but no structural data have yet been reported for these molecules.

We are currently studying a range of alkali-metal phosphate systems, using matrix isolation coupled with vibrational spectroscopy in an attempt to characterise these molecular species more completely, and this paper describes our experiments on trisodium orthophosphate, Na_3PO_4, isolated in argon.

In comparison with many other phosphates, we found that this material gives rise to a relatively simple matrix i.r. spectrum, and for this system we were also able to obtain the ^{18}O isotope data essential for a definitive characterisation of the trapped species.

EXPERIMENTAL

Anhydrous trisodium orthophosphate was obtained in quantitative yield from the hydrated salt $Na_3PO_4{\cdot}12H_2O$ (B.D.H.) by heating *in vacuo* to >250 °C.[4] Samples of ^{18}O-enriched phosphate were obtained by elemental oxidation of the metal phosphide in a reaction sequence initially explored using $^{16}O_2$. A stoicheiometric (3 : 1) mixture of sodium and freshly distilled white phosphorus was gently warmed in an atmosphere of argon until reaction was complete. After removing the argon, the resulting black-red phosphide (Na_3P) was reacted with an excess of oxygen gas of known isotopic abundance until there was no further take-up. During this stage it was necessary to apply gentle heat from time to time to ensure continuous reaction. The product of this oxidation was typically a colourless glassy solid containing small amounts of embedded dark material, which is almost certainly unreacted phosphide coated with an impervious layer of phosphate. However, although this oxidation only occasionally went to completion, all ^{16}O-phosphate samples prepared in this way ultimately yielded matrix i.r. spectra identical to those obtained from authentic samples of Na_3PO_4. This route was therefore used to prepare ^{18}O-material from $^{16}O_2$–$^{18}O_2$ gas mixtures.

In the subsequent matrix isolation studies, phosphate samples were degassed in cylindrical alumina holders maintained at 1 300—1 400 K by induction heating of a closely fitting external tantalum sleeve, and samples were subsequently vaporised at 1 550—1 650 K. The principal features of our matrix-isolation apparatus have been described elsewhere.[5]

High purity argon (B.O.C. 99.999%) was employed as a matrix gas and with an estimated matrix ratio of *ca.* 1 000 : 1 satisfactory i.r. spectra could be obtained after deposition times of *ca.* 1 h. During this period, the deposition surface (CsI window) was maintained at *ca.* 10 K, but in subsequent diffusion studies was allowed to rise as high as *ca.* 30 K. All i.r. spectra were recorded at *ca.* 10 K using a Perkin-Elmer 225 spectrometer (5 000—200 cm^{-1}).

RESULTS

Several experiments were carried out on Na_3PO_4 and on samples of oxidised phosphide, but only three of these need to be discussed in any detail. When Na_3PO_4 was heated to 1 550—1 650 K and the products condensed in an argon matrix, the i.r. spectrum of the deposit showed two intense, sharp bands at 1 341.7 and 1 211.2 cm^{-1}, and weaker features at 1 004.0, 536.6, 474.0, and 287.0 cm^{-1}. Minor variations in deposition conditions (*e.g.* matrix-gas flow rate, sample temperature) produced no detectable changes in the relative intensities of these bands, whilst controlled diffusion studies led to a decrease in intensity of all six bands, and the growth of weak broad polymer features. The six bands thus appear to be associated with a single molecular species. The same bands were present from phosphate samples prepared by oxidation, and a typical spectrum is shown in Figure 1(*a*).

The effect of ^{18}O-enrichment on this system is shown in Figure 1(*b*). Here, a phosphate sample containing † *ca.* 28 atom % ^{18}O has been isolated in an argon matrix, and it is evident that extensive isotope fine structure is present. In particular, the intense band at 1 341.7 cm^{-1} now appears as a basic doublet, each component of which consists of a closely spaced triplet, whilst the second intense band at 1 211.2 cm^{-1} appears as a well spaced triplet. Isotope fine structure was also resolved for the weaker 474.0 cm^{-1} band, but could not be satisfactorily obtained for the remaining bands, primarily because of their low relative intensities. Figure 2(*a*) shows the isotope patterns associated with the 1 341.7, 1 211.2, and 474.0 cm^{-1} fundamentals under high resolution, and a list of all the bands observed is given in the Table.

Spectral Interpretation.—The i.r. bands observed in these matrix isolation studies may all be assigned to vibrations of the C_{2v} species $NaPO_3$. This interpretation is suggested first by the qualitative similarity between the ^{16}O spectrum obtained here and the i.r. spectrum [6,7] of matrix-isolated KNO_3; and secondly by the isotope patterns observed on ^{18}O-enrichment. It has recently been shown [7]

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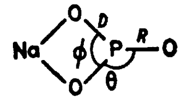
† Gas composition: $^{16}O_2$: $^{16}O^{18}O$: $^{18}O_2$ = *ca.* 11 : 1 : 4.

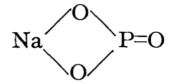
Vibrational frequencies (cm^{-1}) of isotopically labelled $NaPO_3$ species isolated in argon matrices at 10 K

Observed [a]	Calculated [b]	Assignment	
1 341.7	1 341.7	$Na^{16}O^{16}OP^{16}O$	(A_1)
1 338.0	1 337.6	$Na^{16}O^{18}OP^{16}O$	
1 333.2	1 332.8	$Na^{18}O^{18}OP^{16}O$	
1 312.2	1 311.9	$Na^{16}O^{16}OP^{18}O$	
1 307.5	1 306.8	$Na^{16}O^{18}OP^{18}O$	
1 302.0	1 300.5	$Na^{18}O^{18}OP^{18}O$	
1 211.2	1 211.2	$Na^{16}O^{16}OP^{16}O$	(B_2)
	1 211.2	$Na^{16}O^{16}OP^{18}O$	
1 193.3	1 193.4	$Na^{16}O^{18}OP^{16}O$	
	1 192.8	$Na^{16}O^{18}OP^{18}O$	
1 173.5	1 173.3	$Na^{18}O^{18}OP^{16}O$	
	1 173.3	$Na^{18}O^{18}OP^{18}O$	
1 004.0	1 004.0	$NaP^{16}O_3$	(A_1)
536.6	536.6	$NaP^{16}O_3$	(B_2)
474.0	474.0	$NaP^{16}O_3$	(B_1)
470.4	470.5	$NaP^{16}O_2{}^{18}O$	
466.8	467.1	$NaP^{16}O^{18}O_2$	
463.3	463.6	$NaP^{18}O_3$	
287.0		ν_{Na-O}(?)	

[a] Frequency accuracy ± 0.3 cm^{-1}. [b] The following parameters were used in these calculations;



with $D = 1.65$ Å, $R = 1.40$ Å, $\theta = \phi = 120°$, $F_R = 10.14$ mdyn $Å^{-1}$, $F_D = 8.42$ mdyn $Å^{-1}$, $F_{RD} = 0.35$ mdyn $Å^{-1}$, $F_{DD} = 0.183$ mdyn $Å^{-1}$, $F_\theta = 1.36$ mdyn Å rad^{-3}, $F_\phi = 1.23$ mdyn Å rad^{-2}, $F_{R\theta} = 0.63$ mdyn rad^{-1}, and $F_{D\theta} = 0.62$ mdyn rad^{-1}. 1 dyn = 10^{-5} N.

that ^{18}O-enrichment in salt molecules of general formula $M^+XO_3^-$ is expected to give rise to characteristic frequency and intensity patterns in the i.r. which not only establish the presence of a co-ordinated XO_3 group, but allow a clear-cut distinction to be made between mono- and bi-dentate C_{2v} binding. In particular, bidentate structures are readily identified by the doublet of triplets associated with the highest frequency X–O mode, and on this basis, the spectrum shown in Figure 1(*b*) points clearly to  $Na\langle{}^{O}_{O}\rangle P{=}O$ as the shape of $NaPO_3$. This structure has $\Gamma_{vib} = 4A_1 + 3B_2 + 2B_1$ (B_1 out-of-plane) and the contribution due to cation motion is $A_1 + B_1 + B_2$. These modes are expected to be significantly lower in frequency than the PO_3 vibrations which are distributed as $\Gamma_{stretch} = 2A_1 + B_2$ and $\Gamma_{bend} = A_1 + B_1 + B_2$. By analogy with KNO_3, the following specific (^{16}O) assignments may be made for the stretching modes: 1 341.7 cm^{-1} A_1 $\nu_{P=O}$, 1 211.2 cm^{-1} B_2 ν_{P-O}, and 1 004.0 cm^{-1} A_1 ν_{P-O}. These have a very similar pattern of intensities to the three corresponding N–O stretching modes in KNO_3 which occur at 1 460.5, 1 293.1, and 1 031.1 cm^{-1} in argon matrices.

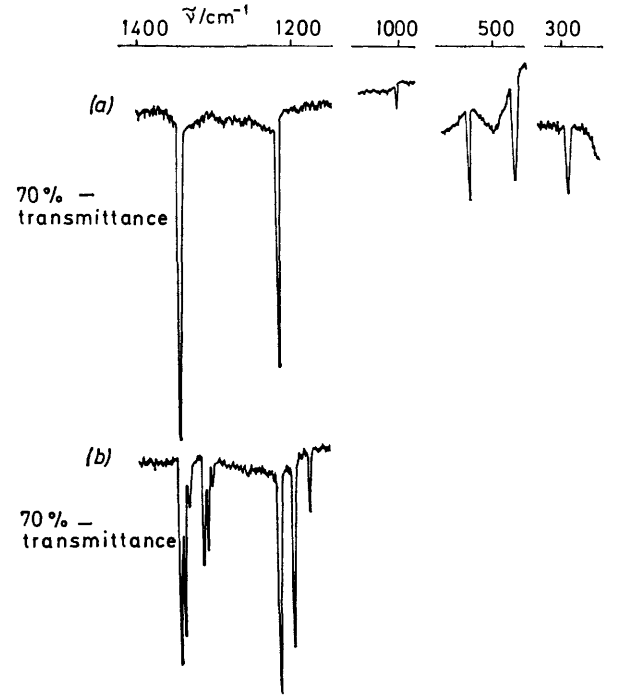


FIGURE 1 (*a*) I.r. spectrum (1 400—250 cm^{-1}) of $NaPO_3$ isolated in an argon matrix at 10 K under low resolution; (*b*) i.r. bands of a 28% ^{18}O-enriched sample in spectral region 1 150—1 400 cm^{-1}

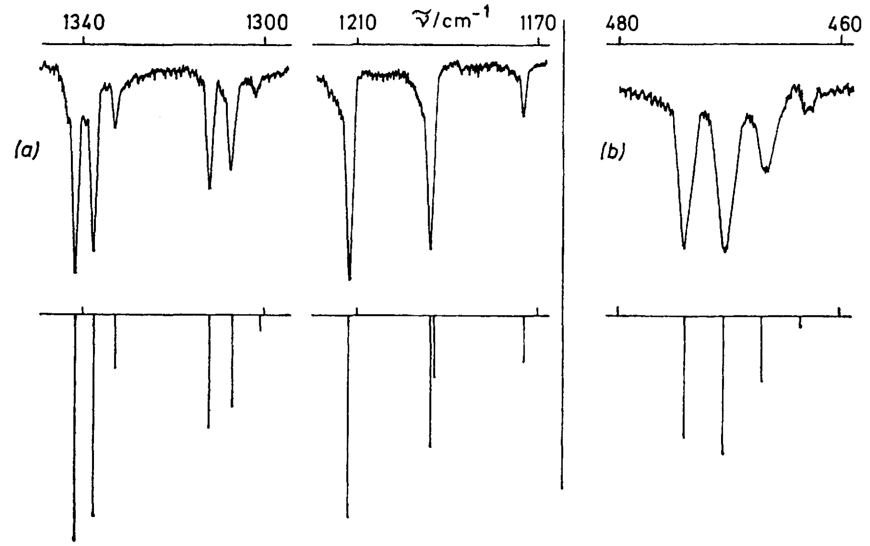


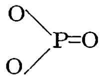
FIGURE 2 (*a*) I.r. bands of 28% ^{18}O-enriched $NaPO_3$ in the spectral region 1 150—1 400 cm^{-1} under high resolution; (*b*) high-resolution i.r. spectrum of ^{16}O–^{18}O isotope pattern in the spectral region 460—480 cm^{-1}

At somewhat lower frequencies, KNO_3 shows two relatively weak features at 827.3 and 721.1 cm^{-1}, which have been assigned [7] as the B_1 out-of-plane and B_2 in-plane NO_3 bending modes, respectively. For $NaPO_3$, corresponding features are observed at 536.6 and 474.0 cm^{-1}, and these are similarly assigned as deformations of the PO_3 group. However, as discussed below, the isotope fine structure on the 474.0 cm^{-1} band indicates a reversal of assignment for $NaPO_3$ with ν_{B_2} lying above ν_{B_1}. One additional absorption was observed in these studies at 287.0 cm^{-1} and this is attributed to a cation stretching mode ν_{Na-O}. A corresponding band in KNO_3 has not yet been reported, but if our assignment here is correct, the analogous ν_{K-O} frequency could lie below the range of the spectrometers used in these studies.[6,7] Confirmation of these frequencies as fundamentals of matrix-isolated $NaPO_3$ rests on the quantitative interpretation of the ^{18}O isotope patterns.

The simplest assignment to be considered is that for the out-of-plane (B_1) mode of the PO_3 group. This is a non-degenerate mode involving the in-phase motion of three oxygen atoms, and for a *free* $[PO_3]^-$ ion with idealised D_{3h} symmetry, 28% ^{18}O-enrichment would yield a 17 : 20 : 8 : 1 quartet pattern in the related A_2'' vibration. These four bands arise from the four distinct species $P^{16}O_n{}^{18}O_{3-n}$ ($n = 0$—3) and the frequencies (ν) are obtainable from the relation (1)*, where K_Δ/l^2 is an out-of-plane bending

$$4\pi^2\nu^2 = \frac{K_\Delta}{l^2}\left(\frac{9}{m_P}+\frac{1}{m_{O'}}+\frac{1}{m_{O''}}+\frac{1}{m_{O'''}}\right) \tag{1}$$

constant, $m_{O'}$, $m_{O''}$, and $m_{O'''}$ are the masses of the three oxygen atoms, and m_P is the mass of phosphorus. On coordination, this equation will no longer hold exactly, but it may nevertheless be used to predict the general appearance of the isotope pattern since the corresponding B_1 mode is almost certainly well removed from the perturbing influence of out-of-plane cation motion. The line diagram accompanying Figure 2(*b*) shows the isotope frequency and intensity pattern calculated for this mode in $NaPO_3$ using the above equation, and assuming 28% ^{18}O-enrichment. The agreement with the fine structure observed on the 474.0 cm^{-1} band is excellent.

The quantitative analysis of the remaining modes follows a procedure very similar to that previously described [7] for matrix-isolated KNO_3. Coupling between the  in-plane vibrations and cation motion is neglected, and agreement is sought between the eleven distinct bands assigned to the isotopically substituted species $NaP^{16}O_n{}^{18}O_{3-n}$ ($n = 0$—3) and frequencies calculated from an appropriate model. The Table compares our observed frequencies with those calculated on the basis of the C_{2v} bidentate structure illustrated, whilst the line diagram accompanying Figure 2(*a*) shows the intensity and frequency fit for the isotope patterns on the two intense stretching modes assuming a statistically random distribution of ^{18}O atoms. The overall agreement is very satisfactory.

DISCUSSION AND CONCLUSIONS

These i.r. matrix studies therefore indicate that molecular $NaPO_3$ is an important species in the vaporisation of Na_3PO_4, and that this species has a bidentate C_{2v} structure in low-temperature argon matrices. The same molecule has been identified by mass spectrometry [3] in vaporisation studies on 'sodium metaphosphate' and it could be regarded as the first example of a compound containing the monomeric $[PO_3]^-$ ion. However, the identification of $NaPO_3$ as a product of Na_3PO_4 vaporisation prompts an obvious question concerning stoicheiometry, and in particular, whether the residual 2Na + O remains behind (possibly as sodium aluminate) or is present in the vapour whilst remaining undetected by matrix i.r. In general, our experiments on this system involved sample degassing at *ca.* 1 400 K prior to deposition and during this process it was commonly observed that a dark film would slowly form on the cold off-axis walls of the vaporisation chamber. This was initially thought to arise from impurities in the tantalum susceptor used for our r.f. heating, but subsequent tests showed that this film reacted vigorously with water to yield a strongly alkaline solution containing sodium ions. Clearly, when Na_3PO_4 is heated under these conditions, a significant amount of sodium is lost as elemental vapour. This observation is perhaps not too surprising in view of a recent report [8] that solid Na_2SO_4 vaporises to give Na, O_2, and SO_2, in addition to molecular Na_2SO_4, but it suggests that alkali-metal orthophosphates are unlikely to exist in the vapour phase.

Finally, it is interesting to note that although our synthetic route to ^{18}O-enriched phosphate typically starts from a statistically non-random distribution of oxygen atoms (principally $^{16}O_2 + {}^{18}O_2$, with very little $^{16}O^{18}O$), the resulting i.r. spectra indicate that complete isotope scrambling has taken place. At the present time it is not possible to decide whether the principal scrambling mechanism is in the phosphide oxidation or in equilibria set up in the phosphate melt.

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* Equation derived using standard Wilson GF matrix approach.

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