

The Canonical Structure and ^{31}P Nuclear Magnetic Resonance Properties of Inorganic Thiophosphate

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The broad ^{31}P n.m.r. signal of the dianion of inorganic thiophosphate is shown to be caused by slow proton transfer which is subject to general base catalysis; the trianion shows a narrow ^{31}P n.m.r. signal allowing the ^{18}O isotope shift to be measured and from which it is concluded that sulphur bears a single negative charge, the other two charges being shared by the three oxygen atoms.

A new method for the stereochemical analysis of chiral inorganic [^{16}O , ^{17}O , ^{18}O]thiophosphate has been developed,¹ but before undertaking stereochemical experiments, a study of its susceptibility to isotope exchange was undertaken. In the course of this study the unusually broad linewidth of the ^{31}P n.m.r. signal of inorganic thiophosphate was investigated.

It is known that inorganic thiophosphate loses sulphur in aqueous solution in a pH-dependent manner with a maximum at pH 4;² the loss of sulphur is also catalysed by metal ions with a predilection for sulphur, e.g. Zn^{2+} and Cd^{2+} .³ Inorganic [$^{18}\text{O}_3$]thiophosphate, prepared by hydrolysing thiophosphoryl chloride with sodium [^{18}O]hydroxide in [^{18}O]water by an adaptation of the method of Åkerfeldt,⁴ exhibited a ^{31}P n.m.r. signal which was too broad to allow the isotopically labelled species to be resolved. After conversion into its *S*-methyl ester by treatment with methyl iodide, the normal linewidth (<1 Hz) was observed, which allowed the isotope enrichment to be established.

Inorganic [$^{18}\text{O}_3$]thiophosphate (94 atom % ^{18}O per site) was used to explore the possibility of isotope exchange between pH 7 and 12.5 at room temperature over three days and the recovered material analysed by ^{31}P n.m.r. spectroscopy after conversion into its *S*-methyl ester. No exchange was observed. Similar experiments in the presence of ZnCl_2 (10 mM), and MgCl_2 (10 mM) did not lead to any detectable loss of isotope in the recovered material.

The unusually broad ^{31}P n.m.r. signal of inorganic thiophosphate, which prevents the resolution of the ^{18}O labelled species, has been noted before,⁵ although the cause is not known. Inorganic phosphate, for example, under the same conditions, has a narrow linewidth if care is taken to remove paramagnetic ions from solution. In a carefully prepared solution of the bis-pyridinium salt of inorganic thiophosphate in [$^2\text{H}_4$]methanol, the ^{31}P n.m.r. linewidth at half-height was

shown to be linearly dependent on the spectrometer frequency, $7 \pm 1\text{ Hz}$ at 101.4 MHz and $14 \pm 1\text{ MHz}$ at 202.46

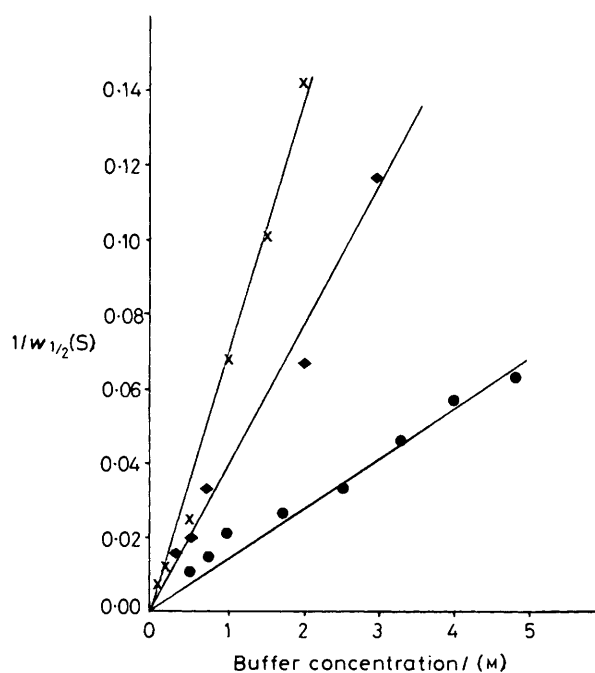


Figure 1. A plot of the reciprocal of the linewidth at half-height ($w_{1/2}$) of the ^{31}P n.m.r. signal of the dianion of inorganic thiophosphate at 202.46 MHz and 25 °C as a function of buffer concentration at pH 7.0 in imidazole HCl buffer (●), at pH 7.5 in HEPES-NaOH buffer (♦),† and at pH 8.2 in Tris-HCl buffer (×).

† Available from Aldrich.

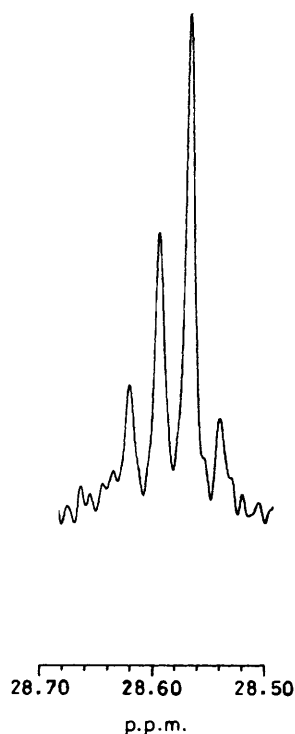
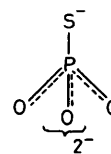


Figure 2. The ^{31}P n.m.r. spectrum at 202.46 MHz of ^{18}O -labelled inorganic thiophosphate in $\text{D}_2\text{O}/\text{NaOD}$ at pD 13.9. The four lines (from low to high field) are due to PO_3S^{3-} , $^{18}\text{OPO}_2\text{S}^{3-}$, $^{18}\text{O}_2\text{POS}^{3-}$, and $^{18}\text{O}_3\text{PS}^{3-}$. The spectral parameters were: sweep width 3250 Hz, pulse width $3\ \mu\text{s}$ (49°), acquisition time 5.05 s, Gaussian multiplication (line broadening -1 Hz, Gaussian broadening 0.05) in 32K and Fourier transform in 64K.

MHz, ruling out chemical shift anisotropy as a possible cause since this depends on the square of the spectrometer frequency.⁶

We had observed the linewidth of the dianion of inorganic thiophosphate to vary considerably in different samples at a given spectrometer frequency. A systematic study of the effect of buffer ion concentration and pH revealed that the reciprocal of the linewidth at half-height increases linearly as the buffer ion concentration increases, the slope of the line increasing as the pH is raised (Figure 1). This suggests that the cause of the line broadening is due to intermediate-to-slow



(1)

proton transfer in the dianion and is subject to general base catalysis. In accord with this conclusion narrow linewidths were observed for inorganic thiophosphate at pH values above the third ionisation constant ($\text{p}K$ 10.14)⁷ which allowed the ^{18}O -isotope shifts to be observed in a labelled (48 atom % ^{18}O per site) sample (Figure 2). The isotope shift per site (0.027 ± 0.002 p.p.m.) was identical within instrumental error with that of *S*-methyl ester (0.028 ± 0.002 p.p.m.) where the PO bond order is unambiguously $4/3$. Since the isotope shift is related to bond order,⁸ this suggests that the trianion of inorganic thiophosphate should be represented by the structure (1) in which a single charge is located on sulphur and two charges distributed between the three oxygen atoms. The proton associated with the dianion presumably resides predominantly on oxygen,⁹ the intermediate-to-slow exchange being caused by slow proton transfer to sulphur which is subject to general base catalysis.

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