

A New Synthesis of Thiophosphoric Acid

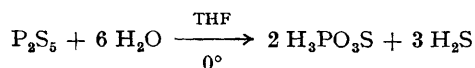
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INSPECTION of the chemical literature reveals that thiophosphoric acid ($\text{H}_3\text{PO}_3\text{S}$) is accessible only *via* circuitous routes comprising metathetical reactions of $\text{Ba}_3(\text{PS}_4)_2$,^{1,2} $\text{Ba}_3(\text{PO}_3\text{S}_2)_2$,^{1,2} or $\text{KH}_2\text{PO}_3\text{S}$,^{2,3} with strong acids† and allegedly *via* the hydrolysis of thiophosphoryl halides.²

The synthetically more direct approach *via* hydrolysis of phosphorus pentasulphide with water is reported⁴ to yield predominantly orthophosphoric acid (H_3PO_4) and hydrogen sulphide.

However, we have found that the relatively stable‡ monothio-acid, $\text{H}_3\text{PO}_3\text{S}$, is indeed an intermediate in the hydrolysis of P_2S_5 ; moreover, thiophosphoric acid can be readily synthesized *via* the low-temperature hydrolysis of P_2S_5 in the presence of oxygen-containing solvents, such as acetone or tetrahydrofuran (THF). The latter solvents appear to be *uniquely effective* in the rapid and selective conversion of P_2S_5 into thiophosphoric acid in excellent yields:



On the basis of extensive studies, this general procedure for the preparation of thiophosphoric acid appears to be optimal:

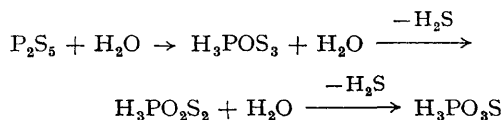
A quarter mole of reagent grade P_2S_5 (55.56 g.) is suspended in 250 ml. of tetrahydrofuran (THF) in a 1 litre, 4-neck round-bottom flask which is equipped with a mechanical stirrer, thermometer, and dropping funnel. After purging the reactor with nitrogen, the suspension is cooled to about 10° , and 45 g. (2.5 moles) of distilled water is added dropwise

during half an hour. The controlled hydrolysis at *ca.* 10° is accompanied by H_2S evolution and gradual dissolution of the P_2S_5 . The reaction mixture is stirred at 10° for about one hour. At this point the reaction mixture becomes a clear solution which is then allowed to warm to ambient temperature. Complete conversion into monothio-phosphoric acid is accomplished by removal of the solvent and hydrogen sulphide from the reaction mixture under high vacuum at room temperature. The viscous, occasionally turbid, residue is then diluted with 500 ml. of cold methanol. Rapid filtration of the methanolic thiophosphoric acid solution through Celite analytical filter-aid effectively removes any colloidal sulphur formed due to air oxidation of the thio-acid. The $\text{H}_3\text{PO}_3\text{S}$ titre is determined by the gravimetric analysis of the bis-ammonium thiophosphate salt obtained *via* treatment of a portion of the 0.5 molar thio-acid solution with excess of ammonium hydroxide (28—29%) at -20° . Consonant with the work of Klement and Koch,⁵ we find that the neutralization reaction with ammonium hydroxide affords quantitative yields of $(\text{NH}_4)_2\text{HPO}_3\text{S}$. Accordingly, the gravimetric method provides a convenient, accurate assay of the thiophosphoric acid titre. Thiophosphoric acid when stored at -20° in an amber bottle previously flushed with nitrogen is stable for several months. The above procedure consistently produced quantitative yields of thiophosphoric acid. Since colloidal sulphur forms *via* air oxidation of thiophosphoric acid,¹ all operations should be routinely conducted under a nitrogen atmosphere to minimize thio-acid decomposition.

† For example, Klement (ref. 1) found that treatment of $\text{Ba}_3(\text{PS}_4)_2 \cdot 12\text{H}_2\text{O}$ (freshly prepared from Na_3PS_4 and BaCl_2) with sulphuric acid at *ca.* 0° followed by rapid removal of barium sulphate and evacuation of hydrogen sulphide at 0° afforded a dilute solution of $\text{H}_3\text{PO}_3\text{S}_2$. Further hydrolysis of the dithiophosphoric acid at about 0° for approximately 12 hr. gave a *ca.* 5% solution of thiophosphoric acid.

‡ Klement reported (ref. 1) that a 5.6% aqueous solution of thiophosphoric acid maintained at -2° underwent only 10% decomposition after 18 weeks.

A plausible hydrolysis mechanism, compatible with Klement's earlier work¹ and our current ³¹P n.m.r. studies, involves the initial formation of intermediary tri- and di-thiophosphoric acids. The latter thio-acids, owing to their instability, undergo further reaction with water to yield ultimately the more stable monothiophosphoric acid:



The unique role that certain oxygen-containing solvents play in the ready conversion of P₂S₅ to thiophosphoric acid awaits elucidation, though we suggest that such solvents increase P₂S₅ solubility in the hydrolysis reaction and perhaps enhance thiophosphoric acid stability *via* solvation effects.

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¹ R. Klement, *Z. anorg. Chem.*, **1947**, **253**, 237.

² G. Hantke, *et al.*, "Gmelins Handbuch der Anorganischen Chemie," Verlag Chemie, GMBH, Weinheim, 1965, System No. 16, Part C, Phosphorus, p. 584.

³ F. Vial, Dissertation, Köln, 1954.

⁴ (a) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans Green, London, 1928, vol. VIII, p. 1056; (b) J. R. Van Wazer, "Phosphorus and Its Compounds," Interscience, New York, 1958, vol. I, p. 293; (c) T. Moeller, "Inorganic Chemistry," John Wiley, New York, 1958, p. 655; (d) D. M. Yost and H. Russell, jun., "Systematic Inorganic Chemistry of the Fifth and Sixth Group Non-metallic Elements," Prentice-Hall, New York, 1946, p. 188; (e) G. D. Parks, "Mellor's Modern Inorganic Chemistry," John Wiley, New York, 1961, p. 833; (f) W. D. Treadwell and C. Beeli, *Helv. Chim. Acta*, 1935, **18**, 1161; (g) J. C. Penert and J. H. Brown, *Chem. and Eng. News*, 1949, **27**, 2143.

⁵ R. Klement and O. Koch, *Chem. Ber.*, 1954, **87**, 333.