We regard these results as indicative of the formation of a series of closely related polymers in moderately concentrated peroxytitanic acid solutions. In the dilute concentration range where Beer's law is obeyed the solutions contain only the peroxytitanic acid monomer, but at higher concentrations equilibrium mixtures of polymeric species occur, accounting for the gradual transition in the absorption characteristics of the solutions. This view is supported by the observation that increasing peroxytitanic acid concentrations do not produce increased molar absorptivities in any part of the visible or near ultraviolet spectrum, but rather a general decrease in absorption, which is indicative of a stabilization of the electronic system of titanium as polymerization progresses.

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Preparation and Properties of Anhydrous Trisodium and Tripotassium Monothiophosphates

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As part of a study of monothiophosphate salts as primary standard reducing reagents for iodometry, pure anhydrous trisodium monothiophosphate and tripotassium monothiophosphate were prepared and characterized. When anhydrous, the sodium salt is very stable at room temperature and may be heated at 100° without decomposition. It does not absorb moisture from the air at relative humidities below 31%. Hydrated trisodium monothiophosphate, $Na_3PO_3S \cdot 12H_2O$, the only one reported previously in the literature, decomposes slowly at room temperature as indicated by the odor of hydrogen sulfide above the solid salt, and decomposes rapidly at 60°.

The potassium salt prepared by this method was contaminated by potassium chloride, but probably could be obtained pure after a sufficient number of recrystallizations. Tripotassium monothiophosphate, which apparently has no water of hydration, was previously reported to be obtainable only in solution.[1]

Experimental

The reaction of sodium or potassium hydroxide solution with thiophosphoryl chloride[2]

$$PSCl_3 + 6NaOH = Na_3PO_3S + 3NaCl + 3H_2O$$

is an unequivocal method for obtaining the respective monothiophosphate salt without the di-, tri-, or tetrathiophosphate being formed at the same time. The only nonvolatile by-product is the alkali metal chloride.

Preparation of Thiophosphoryl Chloride.—The method of Knotz[3] was found to be the most convenient method for preparation on a laboratory scale. Phosphorus trichloride (54.6 ml.) and powdered sulfur (20.1 g.), with anhydrous aluminum chloride (approximately 2 g.) added as catalyst, reacted under reflux. The reaction is often vigorous, although slight heating may be necessary to get it started. The reaction products are distilled and the fraction boiling between 120 and 125° is collected.

Preparation of Anhydrous Trisodium Monothiophosphate.—Sodium hydroxide (40.0 g.) in 300 ml. of aqueous solution is heated with thiophosphoryl chloride (17.5 ml.) under reflux at 110–115° for 15 minutes or more, until the thiophosphoryl chloride layer has disappeared. The solid trisodium monothiophosphate and sodium chloride salts separate out on cooling in an ice-bath. These are filtered off and dissolved in a minimum quantity of warm (40–45°) water. For each 100 ml. of salt solution, approximately 185 ml. of anhydrous methanol is added to precipitate the trisodium monothiophosphate hydrated salt. This recrystallization procedure is repeated, and the hydrated salt dehydrated by suspending with constant stirring for one hour in 200 ml. of anhydrous methanol. The white anhydrous trisodium monothiophosphate crystals are filtered with suction at room temperature, heated at 100° for one hour, and stored in a tightly stoppered bottle.

The anhydrous trisodium salt decomposes without melting at 120–125° to release a volatile compound which discolors lead acetate paper. Solubilities in grams per liter of saturated solution at various temperatures are: 4°, 21.2; 18°, 79.2; 28°, 132.7; 38°, 241.5. Solutions of the sodium salt decompose slowly, but are apparently stable when stabilized with added sodium carbonate.

Anal. Calcd. for Na_3PO_3S: S, 17.83; P, 17.27. Found: S, 17.90, 17.78, 17.90, 17.68, 18.06; P, 17.09, 17.38, 17.25.

Sulfur was determined by oxidation to the sulfate and weighed as barium sulfate. Phosphorus was oxidized to the phosphate and weighed as magnesium ammonium phosphate. Titration with standard iodine solution in the *p*H range 0.5–0.8, using a potentiometric end-point with polarized platinum electrodes, gave consistent results between 99.9 and 100.0% of calculated purity, assuming the reaction[4]

$$2PO_3S^{=} + 2H^{+} + I_2^{-} \longrightarrow (HO_3PSSPO_3H)^{=} + 2I^{-}$$

Preparation of Tripotassium Monothiophosphate.—The preparation of the tripotassium monothiophosphate is similar to that of the sodium salt, except that 56.1 g. of potassium hydroxide in concentrated aqueous solution is treated with 17.5 ml. of thiophosphoryl chloride. Purification is attained slowly by repeated recrystallizations with methanol, but it is very difficult to remove potassium chloride completely, probably because of the slight solubility of potassium chloride in methanol–water solution. The gravimetric determination of sulfur as barium sulfate, and phosphorus as magnesium ammonium phosphate, agreed well with the degree of purity indicated by the iodimetric method using the potentiometric endpoint described above.

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