Cations of Phosphorus in Disulphuric Acid

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Summary The blue colour of phosphorus dissolved in $H_2S_2O_7$ is ascribed to P_8^{2+}, whereas P_4^{2+} solutions are colourless.

THE colours of solutions of Group VIB elements in disulphuric acid[1,2] have been attributed to homoatomic cations of the type Se_4^{2+}, Se_8^{2+}, Te_4^{2+}, S_4^{2+} *etc.*[3,4] Even arsenic[5] and antimony[6] form coloured solutions on oxidation with peroxydisulphuryl difluoride in fluorosulphuric acid, and with potassium persulphate and perchlorate in disulphuric acid.

Red phosphorus does not dissolve in disulphuric acid even in the presence of oxidising agents, and yellow phosphorus floats on disulphuric acid and catches fire, being converted into the oxide. However, if precautions are taken to add yellow phosphorus in small pieces, and an atmosphere of carbon dioxide is maintained, the phosphorus gradually dissolves to give a blue solution, and sulphur dioxide is evolved, indicating that the dissolution is a redox reaction. This solution gradually becomes colourless. But unlike the solutions of Se and S, addition of hydrazine does not regenerate the blue colour, indicating that this redox reaction is not reversible. Since disulphuric acid is an oxidising agent, the blue solution is at a lower oxidation state than the colourless solutions.

The absorption spectra of the blue and the colourless solutions of phosphorus in disulphuric acid clearly show the existence of two distinct species which are stable and obey Beer's law. The blue solution has a broad absorption band at 740 nm while the bands at 560 and 420 nm are weak. The colourless solution has an intense sharp band at 350 nm with a weak shoulder at 280 nm. The shape of the 350 nm absorption band is exactly similar to the spectrum reported for As_4^{2+} and Sb_4^{2+} *etc.*[5,6] and for S_4^{2+} which give colourless solutions Solutions of Se_4^{2+} and Te_4^{2+} also give similar spectra though at a higher wavelength. The blue and the colourless solutions of phosphorus are diamagnetic, indicating the absence of odd-electron species. Thus by analogy with the formulae of the various cations cited above, the colourless solutions of phosphorus may be attributed to P_4^{2+}.

Further information about the nature of these species has been obtained from cryoscopic and conductance studies of the solutions. Possible effects of further oxidation of the blue solutions were eliminated by extrapolation of results recorded over several hours to zero time. For the colourless species, sufficient time was allowed for the spectra of the solutions to be completely free of the 560 nm peak. The nature of these solutions has been elucidated by comparing the conductance and depression in freezing point of the solutions with those of sulphur[4] and it is found that the reactions may be represented as:

$$8P + 6H_2S_2O_7 \rightarrow \underset{\text{(Blue)}}{P_8^{2+}} + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

$$4P + 6H_2S_2O_7 \rightarrow \underset{\text{(Colourless)}}{P_4^{2+}} + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2$$

The amount of sulphuric acid formed in both these solutions has been determined by titration against sulphur trioxide. It is found that 0·6 and 1·25 moles of sulphuric acid are formed per gram-atom of phosphorus for the blue and the colourless solutions, respectively. It is therefore not unreasonable to believe that the species present are P_8^{2+} and P_4^{2+}. These cations are strongly electrophilic and are stable in highly acidic media. Attempts to prepare solid derivatives of the phosphorus cations have so far been unsuccessful.

(*Received, May* 3*rd*, 1971; *Com.* 693.)

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