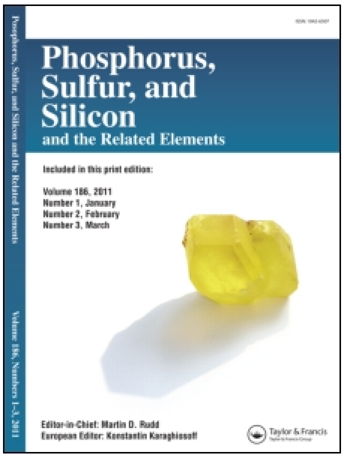

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE $_p$H DEPENDENCE OF UV SPECTRUM FOR THE P-P BONDING LINEAR OXOANION HEXAMER

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To cite this Article Nakashima, Toshio and Waki, Hirohiko(1984) 'THE $_p$H DEPENDENCE OF UV SPECTRUM FOR THE P-P BONDING LINEAR OXOANION HEXAMER', Phosphorus, Sulfur, and Silicon and the Related Elements, 19: 2, 195 — 198

To link to this Article: DOI: 10.1080/03086648408077579

URL: http://dx.doi.org/10.1080/03086648408077579

Phosphorus and Sulfur, 1984, Vol. 19, pp. 195–198
0308-664X/84/1902-0195/$18.50/0

THE pH DEPENDENCE OF UV SPECTRUM FOR THE P—P BONDING LINEAR OXOANION HEXAMER

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(*Received September 12, 1983*)

The absorption spectra of the linear P—P bonding hexamer have been measured at various pH and the presence of a new ring species with a hydroxyl ion bridge have been proposed in order to elucidate the spectral change with pH. This new compound has a large absorption peak at 298 nm and its formation constant has been determined to be log $K = 2.45 \pm 0.05$ ($I = 0.1$–0.2, 20 ± 1°C).

The P—P bonding linear oxoanions of phosphorus formed by the ring cleavage of dodecaoxohexaphosphate(III) have unique absorption spectra in the ultraviolet region depending on the phosphorus polymerization number,[1] whereas the ordinary oxygen bridged linear or cyclic polyphosphates do not have any appreciable absorption in this region. The linear P—P hexamer, which is the longest polymer among decomposition products from dodecaoxohexaphosphate(III), have characteristic absorption peaks at 248 and 272 nm at neutral pH. In the present work the spectral change of the P—P hexamer is studied in connection with its structural change.

RESULTS AND DISCUSSION

The pH dependence of the ultraviolet absorption spectrum on the linear P—P hexamer is shown in Figure 1. At pH 3 or less, the hydrolysis of the hexamer producing the P—P polymers of lower polymerization number takes place.[1] With proceeding from pH 3 to 10.5, the 248 nm peak gradually diminishes and the 268 nm peak shifts to 278 nm with an enhanced absorptivity. This spectral change may be due to the successive deprotonation toward a completely dissociated species $P_6HO_{13}^{7-}$ with increasing pH, since the change in spectral pattern is not so drastic over a wide pH range and the calculated first protonation constant (i.e. for the last dissociation step) seems reasonable for such a kind of species. The approximate protonation constant can be read to be log $K_1 = 8.9$ from the half difference point of the 278 nm absorbance, as shown in Figure 2, Curve (a). This value may reasonably be compared with log $K_1 \gtrsim 8$ for oxygen-bridged polyphosphates(V) of similar anionic

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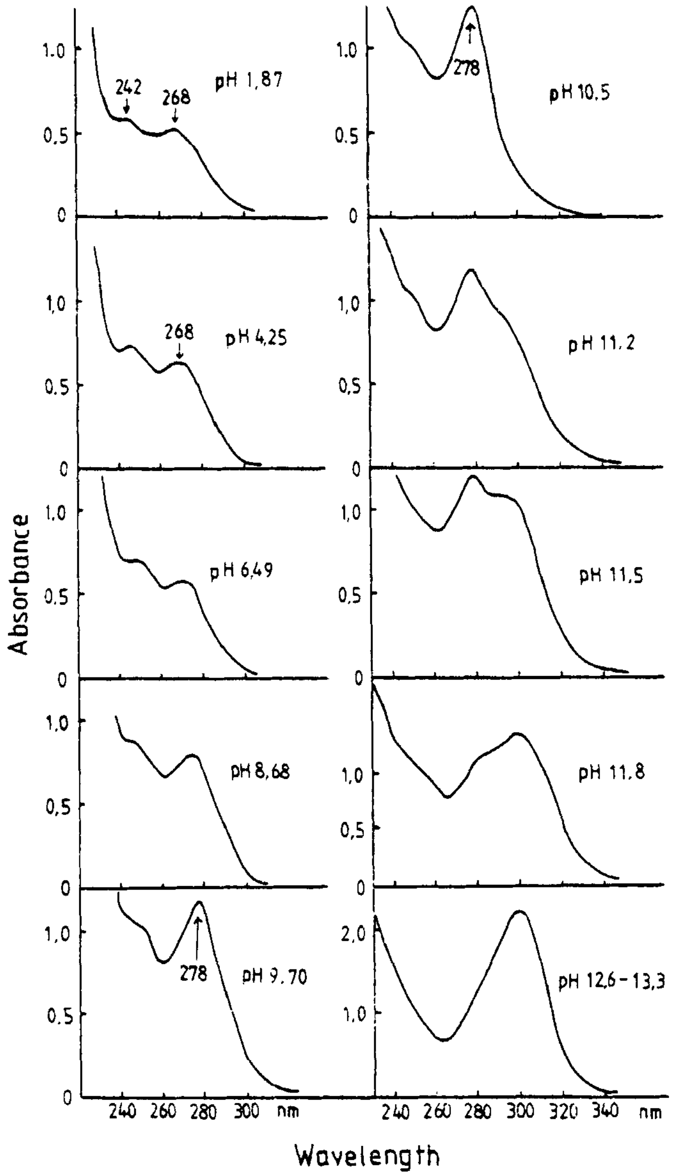
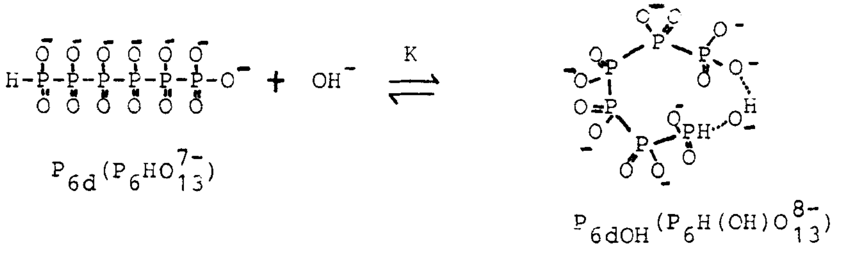


FIGURE 1 UV absorption spectra of the linear P—P bonding hexamer species in different pH. $[\Sigma P] = 1.2 \times 10^{-4}$ M, $I = 0.1$–0.2.

charge or similar length,[4] taking differences in charge density and bridging mode of molecular skeleton into consideration.

On the other hand, a drastic change in the spectral pattern at pH > 11 is more important and interesting. The 278 nm peak diminishes and a new peak appears at 298 nm instead, the latter reaching a constant absorbance at pH ≈ 13 ($\varepsilon_{max} = 1.83 \times 10^4$). The spectrum having such a long maximal wavelength as nearly 300 nm has not so far been known among pure P—P bonding oxoanions, with an only exception of parent ring hexamer which has a peak wavelength around 350 nm. The author concluded that the finally obtained species with the 298 nm peak in highly alkaline media may be a kind of ring compound in which two end phosphorus groups are bridged by a hydroxyl ion.



(1)

This idea is supported by the reasons as follows.

(1) The P—P bond of the species in problem has not been destroyed and the hexameric phosphorus skeleton is maintained, because its initial spectrum in acidic media was recovered when the solution pH was brought back to 6 from 13, that is, the formation reaction was reversible.

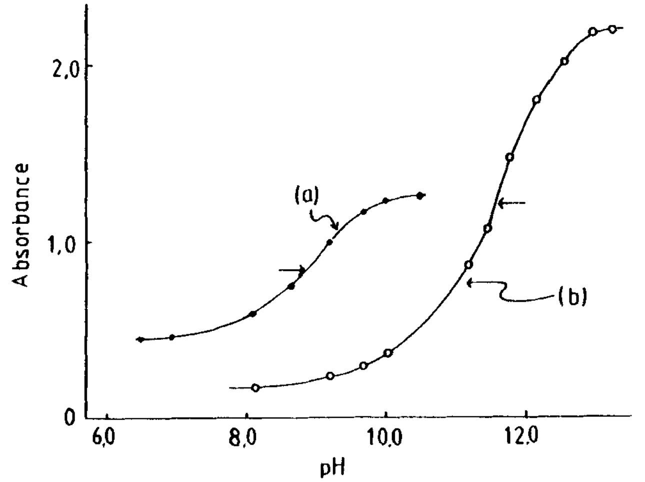


FIGURE 2 The pH dependence of peak absorbance for P—P bonding hexamer at wavelengths: (a) 278 nm, (b) 298 nm. → is the half difference point of absorbance.

(2) The shift of the absorption peak to a longer wavelength amounts to 20 nm, suggesting a remarkable alteration in molecular conformation, though the magnitude of wavelength shift can not be compared with parent ring hexamer[1,5] of a rigid structure consisting of only direct P—P bond ring.

(3) If the reaction is a simple deprotonation from a phosphorus group, the corresponding log K value becomes more than 11.5, which may be unreasonably high as a value for the protonation of polyphosphate oxoanions.

(4) The two end —H—P^{II}- and —P^{IV}—O- groups are convenient for forming a OH^- bridge between them in strong alkaline media, although they can not combine in acidic or neutral pH media.

The spectral change is monotonic (Figure 2, Curve (b)) and the formation constant $K = [P_{6dOH}^{8-}]/[P_{6d}^{7-}][OH^-]$ for Eq. (1) can be determined to be $\log K = 2.45 \pm 0.05$.

EXPERIMENTAL

Potassium sodium salt of dodecaoxohexaphosphate(III) (ring hexamer) was prepared by Blaser and Worms' procedure.[2] Conditions for hydrolytic decomposition of the ring hexamer, the anion-exchange separation method for decomposition products and the determination of each P—P oxoanion polymer were the same as described in the references.[1,3] The spectra were measured on the fractionated effluent from the anion-exchange chromatography using a Hitachi recording spectrophotometer EPS-3T with a 1 cm quartz cell at 20 ± 1°C. The pH of sample solution was adjusted with hydrochloric acid or potassium hydroxide solution before spectral measurements.

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