Note

Far-ultraviolet absorption spectra of D-glucose phosphates in aqueous solution*

M. TRACHTMAN** AND M. HALMANN
Isotope Department, The Weizmann Institute of Science, Rehovot (Israel)

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The far-ultraviolet spectroscopy and photochemistry of various simple oxyacids of phosphorus have been reported[1-5], but at present there do not exist data concerning the far-u.v. absorption spectra of sugar phosphates. In connection with photochemical

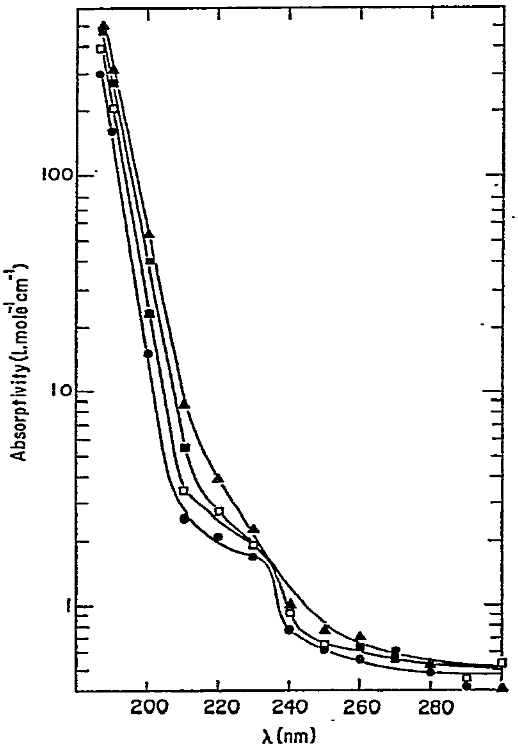

Fig. 1. Temperature dependence of the absorption spectrum of aqueous α-D-glucopyranosyl dipotassium phosphate at ●, 0°; □, 25°; ■, 56°; and ▲, 71°.

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**On leave from Philadelphia College of Textiles and Science, Philadelphia, Penn. 19144, U. S. A.

studies of the intermediates of carbohydrate metabolism, the absorption spectra of α-D-glucopyranosyl dipotassium phosphate and of D-glucose 6-(disodium phosphate) have now been measured.

The spectra of α-D-glucopyranosyl dipotassium phosphate and of D-glucose 6-(disodium phosphate) in aqueous solutions at temperatures from 0 to 71° are shown in Figs. 1 and 2. Changes in temperature appear to have no effect above 225 nm for the 6-phosphate, and little, if any, effect above 245 nm for the 1-phosphate. However, for both sugar phosphates, there is a strong temperature effect on the steep absorption edge below 210 nm. Increasing the temperature causes a shift of this edge to longer wavelengths. It is interesting to note the shoulder at 220 nm in the spectrum of the 1-phosphate and that this is most pronounced at 0°. There is no evidence of such a shoulder in the spectrum of the 6-phosphate, even at the lowest temperature.

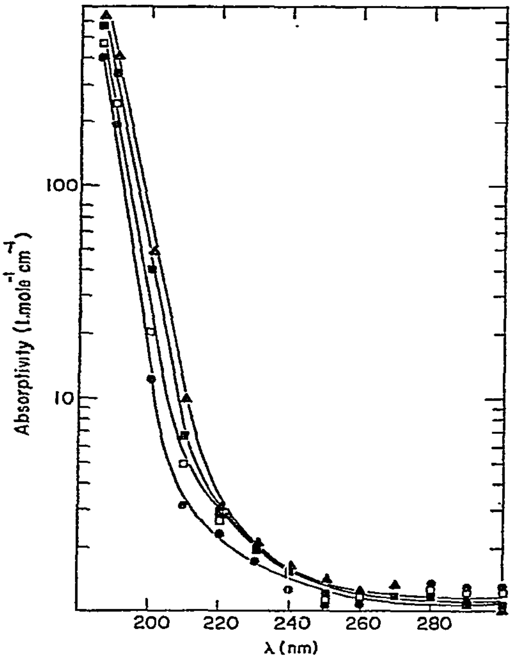

Fig. 2. Temperature dependence of the absorption spectrum of aqueous D-glucose 6-(disodium phosphate) at ●, 0°; □, 25°; ■, 56°; and ▲, 71°.

The solvent effect on the absorption was measured by comparing the spectra in water and in deuterium oxide solutions. As shown in Fig. 3a, the absorption edge for the 6-phosphate is markedly shifted towards shorter wavelengths in changing from water to the deuterated solvent. At an absorptivity $\varepsilon = 300$ mole^{-1}cm^{-1}, the blue-shift amounts to 500 cm^{-1}. The results for the 1-phosphate (Fig. 3b) indicate a much smaller solvent isotope effect. At $\varepsilon = 300$ mole^{-1}cm^{-1}, the blue-shift is only 300 cm^{-1}. At longer wavelengths, the blue-shift decreases further and vanishes at about 200 nm; at still longer wavelengths, there is a slight red-shift.

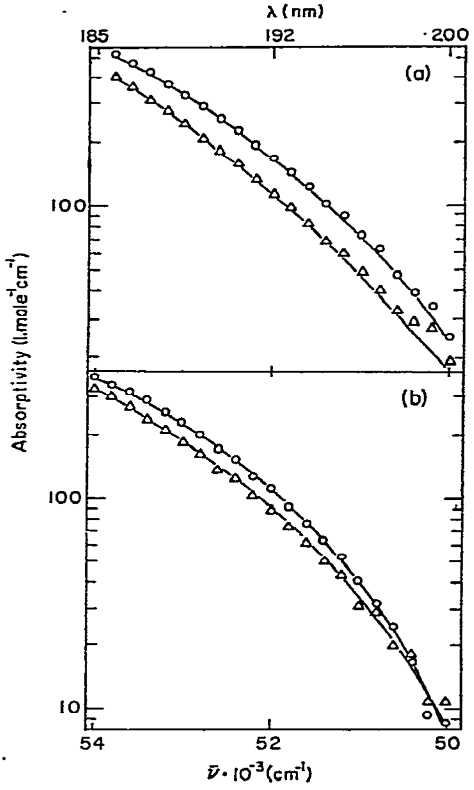

Fig. 3. Far-ultraviolet spectrum of D-glucose 6-(disodium phosphate) (a), and of α-D-glucopyranosyl dipotassium phosphate (b), in water (○) and in deuterium oxide (△) at room temperature.

Qualitatively, the temperature effect (red-shift with rising temperature) and solvent effect (blue-shift in D_2O *versus* H_2O) of the steeply rising absorption edge of the two sugar phosphates below 200 nm is very similar to that of the orthophosphate ions, of other phosphorus oxyanions (see Table I), and of halide ions[7]. For these ions, the strong, far-u.v. absorption band has been assigned as a "charge-transfer-to-solvent" (ctts) transition, the photochemical effect of which is formation of the hydrated electron[1c,5,7]. Quantitative application of the theory of ctts transitions, which was originally proposed for atomic and spherically symmetric ions[7,9], to such bulky and non-symmetric ions as sugar phosphates does not yet seem feasible.

EXPERIMENTAL

D-Glucose 6-(disodium phosphate) (Sigma) and α-D-glucopyranosyl dipotassium phosphate (Sigma and Calbiochem, two sources) were used without further purification. Aqueous solutions of the sugar phosphates were analyzed for their phosphorus

TABLE I

DEUTERIUM-ISOTOPE SOLVENT SHIFT OF THE FAR-U.V. ABSORPTION EDGE OF PHOSPHORUS OXYANIONS IN AQUEOUS SOLUTION

Phosphate	*Charge state*	ε $(mole^{-1}cm^{-1})$	$\Delta\nu$ (cm^{-1})	*Reference*
D-Glucopyranosyl	2−	300	300	This work
D-Glucose 6-	2−	300	500	This work
D-Glycerol 1-	2−	200	570	8
D-Glycerol 2-	2−	200	890	8
Hypophosphite	1−	6.5	320	2
Dihydrogen	1−	70	640	1*a*
Hydrogen	2−	200	760	1*a*
Dihydrogen hypo-	2−	500	400	2
Pyro-	4−	700	550	1*a*
Trimeta-	3−	50	700	1*a*

content by the Fiske–Subbarow method[6]; the assay agreed within ±3% with that calculated from the weight of the hydrates.

Triply distilled water was used for all aqueous solutions. Deuterium oxide (Carl Roth) was used without purification.

Absorption spectra were measured with a Zeiss PMQ II spectrophotometer. For measurements below 200 nm, the optical path was flushed with nitrogen. Suprasil quartz cells with optical paths of 0.01, 0.1, and 2.0 cm were used.

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