Photochemical Phosphorylation

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IN a recent study of the hydrolysis of a series of phosphate monoesters[1] we observed a number of cases in which the reaction is accelerated by light. We have now established that the photochemical reaction involves cleavage of the phosphorus–oxygen bond of the ester, and leads to phosphorylation of the solvent.

Havinga, De Jongh, and Dorst[2] were the first to observe this photohydrolysis, using *m*-nitrophenyl dihydrogen phosphate. The most light-sensitive ester we have studied is 3,5-dinitrophenyl phosphate. In the absence of light the dianion has a half-life of many months in aqueous solution at 39°. On irradiation the half-life falls to 5 min. A solution $2 \cdot 8 \times 10^{-3}$M in cyclohexylammonium 3,5-dinitrophenyl hydrogen phosphate[1] at pH 9 was irradiated at room temperature through a Pyrex filter, using a Hanovia photochemical reactor with a 125w medium pressure mercury lamp. Release of inorganic phosphate was followed by the method of Allen.[3] Photolysis of the monoanion (at pH 4) was also rapid. The half-life for the dianion of mono-*m*-nitrophenyl phosphate under these conditions is 44 min.

On irradiation in methanol–water mixtures both orthophosphate and methyl phosphate were produced: no 3,5-dinitroanisole was detected (by u.v. or t.l.c.). The molar ratios of the two products were broadly similar to those obtained[1] on solvolysis of 2,4-dinitrophenyl phosphate in the same solvent mixtures (see Table). This ester is known to be solvolysed by P–O bond cleavage, in a reaction which is not affected by light.[1]

TABLE

% Monomethyl phosphate formed in methanol–water

Vol. % MeOH	30	50	70
From 3,5-dinitrophenyl phosphate			
monoanion	33	50	68
dianion	30	47	58
From 2,4-dinitrophenyl phosphate			
monoanion	32	39	52
dianion	45	63	80

The photochemical reaction is unlikely to be of synthetic importance, since it becomes extremely slow when dry solvents are used. 2,4-Dinitrophenyl phosphate similarly is remarkably stable to methanolysis in the dry solvent.

The behaviour of the photochemically-excited state of 3,5-dinitrophenyl phosphate is that expected[1] for the ester of a phenol of $\mathrm{p}K_a < 3$. Although the $\mathrm{p}K_a$'s of the excited states of 3,5-dinitrophenol are not known,* that of the triplet might be expected to be about 5—6, since for many singly-substituted phenols the triplet is 1—2 p*K* units more acidic than the ground state.[4] The excited singlet, on the other hand, is commonly some 6 p*K* units more acidic than the ground state. Our evidence suggests therefore that photochemical phosphorylation by 3,5-dinitrophenyl phosphate involves solvolysis of the excited singlet state.

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* 3,5-Dinitrophenol has $\mathrm{p}K_a$ 6·68 in the ground state.

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[3] R. J. L. Allen, *Biochem. J.*, 1940, **34**, 848.
[4] E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1965, **87**, 4234.