

**1001. The Photochemistry of Phosphorus Compounds. Part III.¹ *
 Photolysis of Ethyl Dihydrogen Phosphate in Aqueous Solution**

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Ethyl dihydrogen phosphate in aqueous solution under irradiation with ultraviolet light yields acetaldehyde, hydrogen, and phosphate in equimolar amounts. With ultraviolet light above 2000 Å, the quantum yield in the absence of air is 0.02 at about pH 4—5. The yield increases to 0.04 in acid and basic media. No hydrogen peroxide, acetic acid, or acetyl phosphate could be detected. Photolysis in D₂O yields H₂, HD, and D₂ in the ratio (30 ± 10) : 100 : (30 ± 10). Thus, in most of the hydrogen molecules, one hydrogen atom is due to the alkyl group, and one hydrogen atom is derived from the solvent. Photolysis in ¹⁸O-enriched water in the presence or absence of oxygen, and in the pH range 1.4—11.5, occurs with 95 ± 2% alkyl-oxygen fission. Photolysis in normal water, in the presence of CD₃OH as scavenger for H atoms, yields HD. The primary photochemical process seems to be ejection of an H atom from the CH₂ group of an excited ethyl phosphate molecule.

THE relative rates of photolysis of a number of alkyl dihydrogen phosphates in water ² and in aqueous hydrogen peroxide ³ have been measured, but the organic products have not been identified, and no mechanistic conclusions have been reported.

RESULTS

Ethyl dihydrogen phosphate in aqueous solution had a weak absorption maximum at 2650 Å ($\epsilon_{\text{max.}} = 1 \text{ l. mole}^{-1} \text{ cm.}^{-1}$) (see Figure 1) which was not affected by changes in the pH of the solution. Below 2300 Å, a strongly increasing absorption edge was found, which was shifted to longer wavelengths by increase in the pH. In order to study the direct photolytic effect of light on the alkyl phosphate, and to avoid the indirect effects of photolysis of water, all irradiations were carried out with mercury lamps in which light below 2000 Å was filtered out by a layer of aqueous sodium chloride.

Reaction Products.—The photolysis of ethyl dihydrogen phosphate in water yielded acetaldehyde, hydrogen, phosphoric acid, methane, and carbon monoxide (see Table 1). The yield of phosphoric acid and of hydrogen are equimolar within experimental error. Acetaldehyde is known to decompose photolytically to methane and carbon monoxide; ⁴ it is therefore possible to account for the slightly smaller yield of acetaldehyde compared with that of phosphoric acid and hydrogen by the photolysis of the acetaldehyde. In fact, the yields of methane and carbon monoxide are equal to the decreased yield of acetyldehyde.

* In Part II ¹ the equation at the top of p. 1447 should read:

$$\beta = \{zR_1[1 - 1/(2z) + 1/(2zD_0) - 1/D_a]\} / \{R_x[1/2 + 1/(2D_0) - 1/D_a]\}.$$

¹ Part II, M. Halmann and I. Platzner, *J.*, 1965, 1440.

² E. Bamann, K. Gubitz, and H. Trapmann, *Arch. Pharm.*, 1961, **4**, 240.

³ J. A. V. Butler and B. E. Conway, *Proc. Roy. Soc.*, 1953, *B*, **141**, 562.

⁴ S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, 1960, p. 384.

TABLE 1
Yield of products after photolysis of evacuated aqueous ethyl dihydrogen phosphate at 30°

Initial concn. of EtO·PO(OH) ₂	pH	Relative yields of products				
		CH ₃ ·CHO	H ₃ PO ₄	H ₂	CH ₄	CO
3·7 × 10 ⁻²	1·5	95	100	99 *		Traces
3·7 × 10 ⁻²	1·5		100	108 †		
6·6 × 10 ⁻²	1·5	96	100			
3·7 × 10 ⁻²	3·1	96	100	102 †		
3·7 × 10 ⁻²	6·4	94	100	101 *		Traces
3·7 × 10 ⁻²	6·4	97	100	102 †		
3·7 × 10 ⁻²	8·8	94	100	106 †		
3·7 × 10 ⁻²	10·5	97	100	100 *		
3·7 × 10 ⁻²	10·5	95	100	103 †		Traces

* Determination of H₂ yield by gas chromatography. † Determination of total non-condensable gases (H₂ + CH₄ + CO) by gas-volumetric methods.

FIGURE 1. Ultraviolet absorption spectrum of ethyl dihydrogen phosphate in aqueous solution

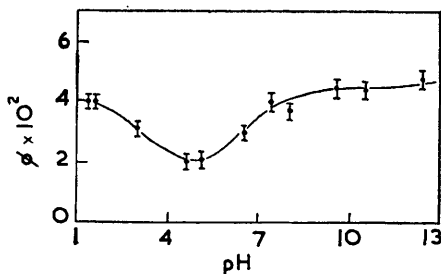
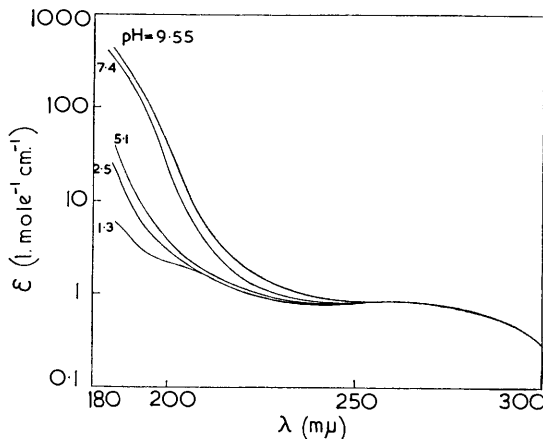


FIGURE 2. Quantum yield of photolysis of aqueous ethyl phosphate at 30° as a function of pH

Quantum Yield as a Function of pH.—By use of a chloroacetic acid actinometer, the quantum yield for photolysis of ethyl phosphate was determined as a function of pH. As seen in Table 2

TABLE 2

Quantum yield, ϕ , as a function of pH in the photolysis of aqueous ethyl phosphate (initial concentration about 0.2M) at 30°, using a high-pressure (H) or a low-pressure (L) mercury lamp

pH	1.3	1.6	3.0	4.6	5.1	6.5	7.4	8.0	9.55	10.5	12.4
Hg lamp ...	L	H	H	H	L	H	L	H	L	H	L
10 ² ϕ	4	4	3.1	2.0	2.1	3	4	3.7	4.5	4.4	4.8

and in Figure 2, the quantum yield has a minimum at pH 4—5. This effect, appearing as a minimum in the rate of release of phosphate by photolysis of various alkyl phosphates, has been previously reported.²

Deuterium Tracer Experiments.—In order to find out the origin of the hydrogen produced during photolysis of aqueous ethyl dihydrogen phosphate, barium ethyl phosphate was dissolved in deuterium oxide containing KD_2PO_4 , thus producing a solution of ethyl phosphate at pH 6. The hydrogen gas resulting from ultraviolet irradiation was analysed by mass spectrometry, yielding for $\text{H}_2 : \text{HD} : \text{D}_2$ the relative abundances 13 : 100 : 18. The same relative abundances of hydrogen isotopes were obtained at different acidities from pH 1 to 12 by using D_2O -washed cation-exchangers. The ratio obtained was $\text{H}_2 : \text{HD} : \text{D}_2 = (30 \pm 10) : 100 : (30 \pm 10)$. Thus, one hydrogen atom of the H_2 molecules produced by photolysis comes from the alkyl group, and one hydrogen atom from the solvent.

Oxygen Tracer Experiments.—In order to find out the point of bond-fission during the photolysis, ethyl dihydrogen phosphate dissolved in ^{18}O -enriched water was irradiated, and the phosphate produced was analysed for its ^{18}O content. Results are in Table 3, and show that 95% of the photolysis reaction of ethyl phosphate takes place with alkyl-oxygen fission.

TABLE 3
Photolysis of ethyl dihydrogen phosphate in ^{18}O -enriched water in the presence and absence of oxygen

pH	Gas atm.	A. ^{18}O atom % excess in H_2O	B. ^{18}O atom % excess in PO_4^{2-}	B/A	P-O fission (%)
1.4	N_2	7.30	0.104	0.0142	5.7
3.1	N_2	7.58	0.057	0.0077	3.1
6.4	N_2	8.65	0.081	0.0095	3.8
8.8	N_2	8.72	0.104	0.0119	4.8
11.0	N_2	8.41	0.092	0.0109	4.4
					Average 4.4
1.1	O_2	9.78	0.109	0.0112	4.5
6.7	O_2	7.95	0.154	0.0193	7.7
11.5	O_2	6.58	0.060	0.0092	3.7
					Average 5.3

Methanol Scavenger Experiments.—Methanol is known to be a very effective scavenger for hydrogen atoms. In order to find out the possible role of hydrogen atoms as intermediates in the photolysis of ethyl phosphate, two types of experiment were carried out, both in the absence of air.

(a) *Irradiation in normal water containing varying concentrations of CD_3OH .* In this case H atoms have the choice of reacting with CD_3OH to produce HD, or with some species from the solvent or with the ethyl phosphate to produce H_2 . Results are in Table 4 and Figure 3.

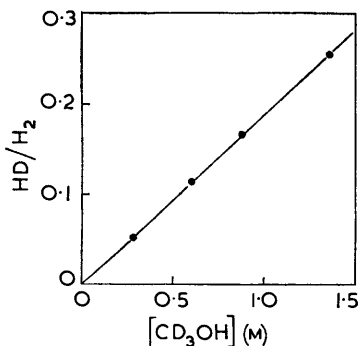


FIGURE 3. Isotope ratio HD/H_2 produced during photolysis of aqueous ethyl dihydrogen phosphate at 30° at pH 1.3 as a function of CD_3OH concentration

TABLE 4
Photolysis of ethyl dihydrogen phosphate (initially 0.25M) at 30° at pH 1.3 in normal water containing CD_3OH

CD_3OH (M)	0.28	0.60	0.87	1.36
HD/H_2	0.053	0.114	0.167	0.256

(b) *Irradiation in deuterium oxide solvent containing varying concentrations of CH_3OH .* In this case H atoms released from the CH_2 group of ethyl phosphate have the choice of reacting

with CH₃OH (or with another ethyl phosphate molecule) to produce H₂, or with some species from the solvent to produce HD. Results are in Table 5.

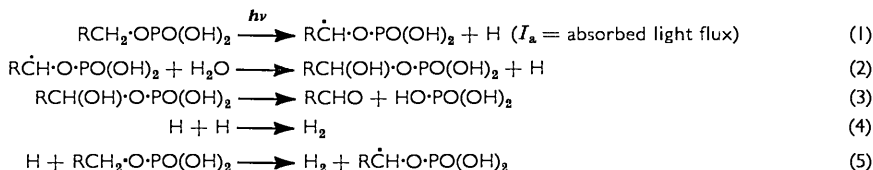
TABLE 5
Photolysis of ethyl dihydrogen phosphate (initially 0.25M) at 30° at pH 1.3 in D₂O containing CH₃OH

CH ₃ OH (M)	0	0	0.28	0.45	0.87	1.31
H ₂ /HD	0.138	0.37	0.38	0.27	0.46	0.38
D ₂ /total hydrogen	0.38	0.43	0.08	0.058	0.024	0.011

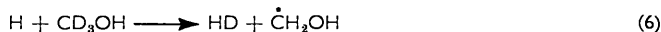
Nitrous Oxide Scavenger Experiments.—Nitrous oxide is known as an efficient scavenger for hydrated electrons.⁵ In order to check the possibility of intermediate formation of hydrated electrons, aqueous solutions of ethyl phosphate at pH 1.3 and 9 were irradiated in the presence of 0.02M-nitrous oxide. No nitrogen was found in either case, which ruled out this possibility.

DISCUSSION

The absorption spectrum of ethyl dihydrogen phosphate (Figure 1) consists of a weak pH-independent band (λ_{max} 265 m μ), and a steep absorption edge below 200 m μ , the shape of which is pH-dependent. By analogy with the interpretation of the weak ultraviolet absorption bands of many inorganic oxyanions,^{1,6,7} the band of ethyl phosphate at 265 m μ can be tentatively assigned to a ($\pi^* \leftarrow n$) transition. Since the photolysis experiments were carried out with ultraviolet light in which the indirect effects of photolysis of water were avoided by filtering out light below 200 m μ , only the direct photochemical effects of the electronic excitation of the alkyl phosphate molecule or ion have to be considered. Also, the photolysis of ethyl phosphate must involve only the weak low-energy band, and not the absorption edge below 200 m μ (which may be due to a "charge-transfer to solvent" type of transition as with the inorganic phosphorus oxyanions¹). Any mechanism of the photolysis of aqueous ethyl phosphate must account for the following observations reported in the Results section: (a) formation of acetaldehyde, hydrogen, and phosphate; (b) the low quantum yield (about 0.04) which has a shallow minimum at about pH 4.5; (c) the predominant C-O bond fission, which is pH-independent; (d) the formation of HD in the presence of even low concentrations of CD₃OH; (e) the formation of HD and D₂ in the presence of CH₃OH in D₂O solvent. The reactions (1)–(5) seem to account for these results (R = methyl).



In the presence of deuteromethanol, H atoms will be deuteroscavenged preferentially by



Rates of formation of H₂ and of HD will therefore be given by

$$\begin{aligned} d[\text{H}_2]/dt &= k_4[\text{H}]^2 + k_5[\text{H}][\text{RCH}_2\cdot\text{O}\cdot\text{PO(OH)}_2] \\ d[\text{HD}]/dt &= k_6[\text{H}][\text{CD}_3\text{OH}] \end{aligned}$$

therefore,

$$[\text{HD}]/[\text{H}_2] = k_6[\text{CD}_3\text{OH}]/\{k_4[\text{H}] + k_5[\text{RCH}_2\cdot\text{O}\cdot\text{PO(OH)}_2]\}$$

⁵ F. S. Dainton and S. A. Sills, *Nature*, 1960, **186**, 879; E. J. Hart, *Science*, 1964, **146**, 19.

⁶ H. McConnell, *J. Chem. Phys.*, 1952, **20**, 700; S. P. McGlynn and M. Kasha, *ibid.*, 1956, **24**, 481.

⁷ M. Halmann and I. Platzner, *Proc. Chem. Soc.*, 1964, 261.

Thus, the isotope ratio $[\text{HD}]/[\text{H}_2]$ in the hydrogen evolved should be proportional to the concentration of $[\text{CD}_3\text{OH}]$, which is in agreement with the results in Figure 3. Also, at zero $[\text{CD}_3\text{OH}]$, the yield of $[\text{HD}]$ is obviously zero, and therefore the ratio $[\text{HD}]/[\text{H}_2]$ should also become zero. This too is in agreement with the extrapolation of the plot in Figure 3. The maximum stationary concentration, $[\text{H}]$, at an absorbed light flux $I_a = 3.5 \times 10^{-8}$ (einstein $\text{l}^{-1} \text{sec}^{-1}$), and a quantum yield $\phi = 0.04$, must be

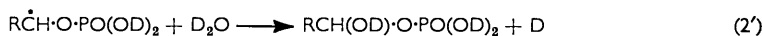
$$[\text{H}]_{\text{max.}} = I_a \phi = 3.5 \times 10^{-8} \times 0.04 = 1.4 \times 10^{-9} \text{M}$$

The slope of the plot of $[\text{HD}]/[\text{H}_2]$ against $[\text{CD}_3\text{OH}]$ is 0.19. Therefore,

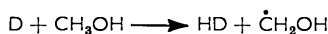
$$k_6 / \{k_4[\text{H}] + k_5[\text{RCH}_2\text{O}\cdot\text{PO}(\text{OH})_2]\} = 0.19$$

Inserting the values $k_6 = 8 \times 10^4 \text{M}^{-1} \text{sec}^{-1}$, $k_4 = 10^{10} \text{M}^{-1} \text{sec}^{-1}$, $[\text{H}]_{\text{max.}} = 1.4 \times 10^{-9} \text{M}$, and $[\text{RCH}_2\text{O}\cdot\text{PO}(\text{OH})_2] = 0.25 \text{M}$, we get $k_5 = 1.7 \times 10^6 \text{M}^{-1} \text{sec}^{-1}$.

Since the photochemical yield is very low, it must be concluded that only some of the excited molecules undergo chemical reaction, while the major part becomes deactivated, e.g., by collision with solvent molecules. Reaction step (2) seems required because it accounts for the formation of D atoms and therefore D_2 molecules by step (4'') in the photolysis of ethyl phosphate in D_2O solvent (see Table 5).



In the presence of increasing concentrations of CH_3OH the relative yield of D_2 drops sharply (see last row of Table 5) by competition with the reaction:



The fate of the $\dot{\text{C}}\text{H}_2\text{OH}$ radicals is presumably as in the analogous photolysis of aqueous sodium hydrogen sulphate in the presence of methanol.⁹

EXPERIMENTAL

Light Sources.—A Hanau immersion type (model Q-81) high-pressure mercury lamp was used for irradiation procedures (a) and (b). A Thermal Syndicate (T/M5/544A) low-pressure mercury lamp was used for procedure (c) and for the actinometry irradiations.

Irradiation Procedures.—(a) *Evacuated samples.* Ampoules (i.d. 10.0 mm.) with break-seals, containing degassed (1 hr. at 10^{-4} mm.) solutions (3 ml.) of ethyl phosphate, were placed around the inner wall of a beaker, about 1 cm. from the mercury lamp dipping in the centre of the beaker which contained 0.1M-sodium chloride. The filtered solution was maintained at $30^\circ \pm 0.5^\circ$ by passing cooling water through a glass coil. The beaker was attached to a motor which caused the beaker and ampoules to rotate slowly around the lamp and provided for uniform irradiation.

(b) *Samples under nitrogen or oxygen.* The mercury lamp was placed inside a double-walled tube. The light thus passed through a 5-mm. layer of 0.5M-sodium chloride¹⁰ (which also served as coolant and was circulated through a bath at $30^\circ \pm 0.5^\circ$), a 1-mm. quartz wall, and a 1-cm. layer of ethyl phosphate solution (150 ml.) through which a gas could be bubbled. The whole apparatus was placed in a 30° thermostat. Volatile products were carried with the outgoing gas stream, and were collected in spiral tubes cooled with liquid nitrogen.

(c) *In the presence of CH_3OH or CD_3OH .* The solutions for these irradiations were prepared in a two-legged flask connected through a stopcock to a vacuum system. One leg contained a

⁸ M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1965, **16**, 227.

⁹ J. Barrett, M. F. Fox, and A. L. Mansell, *Nature*, 1963, **200**, 257.

¹⁰ W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold, New York, 1941, pp. 82—85.

tube with aqueous 0.25M-ethyl dihydrogen phosphate, while the other leg was fitted into a quartz absorption cell (5-cm. length). Methanol (B.D.H. spectroscopic grade), or CD₃OH (Fluka; 99.5% deuterium in the methyl group), in the required amount was distilled into the degassed, liquid-air frozen ethyl dihydrogen phosphate. This was then thawed and transferred by rotation into the absorption cell. After irradiation, the evolved hydrogen was collected through Dry Ice and liquid-air traps, using a Toepler pump. Its deuterium content was determined by mass spectrometry.

Actinometry.—The light flux I_0 in the reaction cell was determined with a fresh solution of 0.1M-chloroacetic acid, which is known to undergo photolysis to form Cl⁻ with a quantum yield of 0.33.¹¹ The chloride ion was determined by titration with mercuric nitrate.¹² Both during the actinometry, and during irradiation of ethylphosphate, a 1-cm. thick layer of 0.5M-aqueous sodium chloride solution was placed between the light source and the reactant solution, which was in a 5-cm. long quartz cell. Since the absorption of light in such a cell by 0.25M-ethyl phosphate is not complete, calculations of quantum yield had to include corrections for the unabsorbed light at 253.7 m μ , which were taken from measurements of the absorption spectrum of the solution.

Analytical Methods.—Phosphate was determined by a modified Fiske-Subbarow method using stannous chloride as reducing agent. Hydrogen gas was determined by thermal conductivity following gas-chromatographic separation on a Molecular Sieve 5A column operated at 80°, with argon carrier gas at 30 ml. min.⁻¹ flow rate.¹³ Acetaldehyde was determined colorimetrically by its reaction with 4-hydroxybiphenyl.¹⁴ ¹⁸O-Analysis in orthophosphate, following 20 hours' irradiation of ethyl dihydrogen phosphate in ¹⁸O-enriched water, was carried out by precipitation of barium phosphate at pH 9, dissolution in dilute hydrochloric acid, and reprecipitation with ammonia. Oxygen isotope determination was made by conversion into carbon dioxide using the HgCl₂-Hg(CN)₂ method.¹⁵

Deuterium Tracer Experiment.—Barium ethyl phosphate (prepared from the monohydrate by drying at 10⁻⁴ mm. for 18 hr.) was shaken with deuterium oxide. The resulting saturated solution (8 ml.) was treated with potassium dihydrogen phosphate (0.10 g.) (prepared by twice crystallising KH₂PO₄ in D₂O), resulting in a solution of pH 6. Aliquots (3 ml.) were placed in a quartz tube fitted with a small Teflon covered magnetic bar. The tube was closed with a stopcock, and was carefully degassed. Irradiation (3 hr.) was carried out as with the evacuated break-seal tubes, while the solution was stirred magnetically. After irradiation, the resulting gas was analysed mass spectrometrically for the peaks at $m/e = 2, 3,$ and 4 . The solvent heavy water before the reaction was analysed by heating a sample with zinc for 4 hr. at 400° in a break-seal tube. The resulting hydrogen gas contained H₂ : HD : D₂ = 1.23 : 15.4 : 100 or 92 atom % deuterium.

Materials.—Laboratory distilled water was redistilled once from alkaline permanganate and once from phosphoric acid, and had a resistivity of 2 M ω cm.⁻¹. Barium ethyl phosphate monohydrate was prepared by repeated recrystallisation at 100° from a solution containing a mixture of ethyl dihydrogen phosphate and diethyl hydrogen phosphate¹⁶ (Eastman) (Found: Ba, 47.3; P, 11.15. Calc. for C₂H₇BaO₅P: Ba, 49.1; P, 11.11%). Ethyl dihydrogen phosphate was prepared from the barium salt using Dowex 50-X cation-exchanger (Fluka AG, washed with distilled water until the effluent was of similar u.v. absorptivity to distilled water). ¹⁸O-Enriched water was obtained from the separation plant of this Institute.

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¹¹ Daniels *et al.*, "Experimental Physical Chemistry," McGraw-Hill, New York, 1956, p. 246.

¹² I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Interscience, New York, 1947, vol. 2, p. 334.

¹³ E. Bayer, "Gas Chromatography," Elsevier, Amsterdam, 1961, pp. 130, 131.

¹⁴ F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd edn., Van Nostrand, New York, 1957, vol. III, pp. 261—263.

¹⁵ M. Anbar and S. Guttman, *Internat. J. Appl. Radiation Isotopes*, 1959, 233.

¹⁶ O. Bailly, *Compt. rend.*, 1920, 170, 1061.