Photochemistry of Phosphorus Compounds. Part IX.[1] Photolysis of Trimethyl Phosphate in Aqueous Solution

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The products of irradiation (254 nm) of aqueous trimethyl phosphate, in the presence of argon or of oxygen, have been analysed. In accord with the very low absorption of aqueous trimethyl phosphate at 254 nm, almost no reaction takes place in an argon atmosphere. Mass spectrometry indicates that some dimer $(MeO)_2P(O)OCH_2CH_2OP(O)(OMe)_2$ is formed, probably *via* the reactive intermediate $(MeO)_2P(O)OCH_2\cdot$.

The photolysis proceeds much faster in an oxygen atmosphere to give, as initial products, dimethyl hydrogen phosphate, formaldehyde, and possibly formic acid. Prolonged irradiation leads to (i) stepwise further degradation of dimethyl hydrogen phosphate to methyl dihydrogen phosphate and subsequently to orthophosphoric acid; and (ii) formation of carbon monoxide and carbon dioxide as major reaction products, coinciding with the build-up of steady state concentrations of formaldehyde and formic acid. Carbon dioxide is probably formed by secondary photolysis of formic acid, whereas photolysis of formaldehyde might give carbon monoxide.

The quantum yields for the formation of dimethyl phosphate were determined, both in oxygen ($\Phi = 0{\cdot}11$) and in argon ($\Phi \leqslant 0{\cdot}01$) atmospheres.

PHOTOCHEMICAL decomposition (254 nm) in aqueous solution of some monoesters of phosphoric acid has been the subject of detailed investigations, including the identification of carbon-containing products.[1-3] Similar studies have not been made for diesters or triesters of

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[1] Part VIII, M. Halmann, M. Trachtman, and C. Triantaphylides, Abstracts, VIIth International Conference of Photochemistry, Jerusalem, August—September 1973, p. 15.

[2] M. Halmann, in 'Topics in Phosphorus Chemistry,' eds. M. Grayson and E. J. Griffith, Interscience, New York, 1967, vol. 4, p. 49.

[3] J. Greenwald and M. Halmann, *J.C.S. Perkin II*, 1972, 1095.

phosphoric acid, although these compounds are known to release orthophosphoric acid on irradiation with u.v. light.[4–6] The related mechanism of γ-ray decomposition of trimethyl phosphate,[7] and of other triesters, has been studied in more detail.

In this paper, we report the products of irradiation of trimethyl phosphate in aqueous solution, in the presence of oxygen or of argon. The present investigation may be regarded as a model study for the photolytic decomposition of organophosphorus insecticides.[8]

EXPERIMENTAL

Materials.—Trimethyl phosphate (B.D.H.) was distilled before use (b.p. 141° at 155 mmHg). ^{14}C-Labelled trimethyl phosphate (specific activity 4·0 μCi g^{-1}) was kindly donated by the Chemical Laboratory TNO, Rijswijk (Z.H.), The Netherlands. Chloroacetic acid (B.D.H., AnalaR) was used without further purification. Alkaline Phosphatase (orthophosphoric monoester phosphohydrolase, E.C. 3.1.3.1) from *E. coli* (Sigma Chemical Company, type III-S) had an activity of 144 units ml^{-1}. Water used for the photolysis was distilled twice.

U.v. Spectra.—The spectra were recorded with a Zeiss PMQ II spectrophotometer.

Irradiation Procedures for Samples under Oxygen or Argon.[3]—A high-pressure mercury immersion lamp (Hanau Q-81) was placed inside a double-walled quartz tube. In this way, the light first passed through a 5 mm layer of distilled water in order to filter out the 185 nm component of the lamp.[*] The water also served as a coolant by means of continuous circulation through a thermostat at 30 ± 0·5°. Next, the light passed through a 1 mm quartz wall, and finally through a 1 cm layer of the aqueous solution of trimethyl phosphate (total volume 110—200 ml).

A gas could be passed into the irradiated solution through a tube fitted with a sintered glass disk. Oxygen was bubbled through a wash-bottle filled with aqueous barium hydroxide, in order to remove traces of carbon dioxide. Argon was bubbled through a solution of sodium dithionite (15%, w/v) and of indigo carmine (1·5%, w/v) in 10% aqueous potassium hydroxide, in order to remove traces of oxygen and of carbon dioxide.[10]

Volatile reaction products were carried with the outgoing gas stream, and were analysed as described below. Samples were removed from the irradiated solution with a syringe *via* a rubber septum.

Irradiation of ^{14}C-Labelled Trimethyl Phosphate.—The aqueous solution of ^{14}C-labelled trimethyl phosphate was placed in a quartz tube surrounded by a quartz jacket, through which distilled water was circulated at 30·0 ± 0·5°. A small inlet tube permitted the passage of a gas (oxygen or argon) through the irradiated solution. The apparatus was irradiated externally with a low-pressure PCQX-1 mercury lamp (Ultraviolet Products, Inc.).

Quantum Yields for the Formation of Dimethyl Hydrogen Phosphate.—The experimental set-up [3] consisted of a low-pressure mercury lamp (Thermal Syndicate, model T/M5/544), with its flat end against the window of a cylindrical quartz cell. The latter cell, with an optical path of 5 cm, was filled with water in order to filter out the 185 nm component of the lamp. Subsequently, the light passed through a similar 5 cm long quartz vessel, containing the reaction mixture. The system was cooled with a stream of air in order to maintain a reaction temperature of 30°.

For the measurement of the luminous flux in the reaction vessel, the light-induced hydrolysis of 0·1M-aqueous chloroacetic acid was followed by means of titration of chloride anions with mercuric nitrate. The average of two measurements gave a luminous flux of $3{\cdot}15 \times 10^{-4}$ einstein l^{-1} min^{-1}, using a quantum yield of 0·33 at 30° and $\varepsilon = 1{\cdot}22$ for the molar absorptivity of chloroacetic acid in aqueous solution at 254 nm.[11]

The initial quantum yields for the formation of dimethyl hydrogen phosphate from trimethyl phosphate were determined while a slow stream of oxygen or argon was passing through the solution from a thin glass capillary. A 0·1M-aqueous solution of trimethyl phosphate was used for experiments in an oxygen atmosphere. The much slower reaction in an argon atmosphere was performed with a 0·5M-solution. The irradiation time was chosen so as to keep the extent of formation of dimethyl hydrogen phosphate to $\leqslant 1\%$, including the dark hydrolysis of trimethyl phosphate. A value $\varepsilon = 0{\cdot}015$ was used for the molar absorptivity of aqueous trimethyl phosphate at 254 nm.

Analysis of Photolysis Products.—*Orthophosphoric acid.* The molybdenum blue method of Fiske and Subbarow [12] was used for the determination of orthophosphoric acid.

Methyl dihydrogen phosphate. This product was determined as orthophosphate by means of the aforementioned method of Fiske and Subbarow, after hydrolysis with Alkaline Phosphatase.[13] In order to achieve complete hydrolysis, a 1 ml sample of the reaction mixture (containing $\leqslant 3$ μmol of methyl dihydrogen phosphate per ml) was mixed with Tris buffer (pH 9·1) (1 ml). The solution was then incubated with 20 μl of the Alkaline Phosphatase solution for 60 min at 37°. After cooling and dilution to 10 ml, an appropriate sample was taken for the colorimetric determination of orthophosphate. A blank value for the enzyme preparation should be subtracted. The amount of methyl dihydrogen phosphate in the sample was found by substraction of the amount of orthophosphoric acid, which was already present prior to enzymic hydrolysis.

Dimethyl hydrogen phosphate. The total acidity of the reaction mixture was determined by titration of a sample with 0·01N-aqueous sodium hydroxide against phenol-

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[*] The absence of a 185 nm component was shown by the fact that irradiation for 16 h of 5M-aqueous ethanol gave no observable amount of molecular hydrogen.[9]

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[11] F. J. Johnston and J. F. Hinton, *J. Phys. Chem.*, 1963, **67**, 2812.

[12] L. F. Leloir and C. E. Cardini, in 'Methods in Enzymology,' eds. S. P. Colowick and H. O. Kaplan, Academic Press, New York, 1957, vol. 3, p. 843.

[13] L. A. Heppel, D. R. Harkness, and R. J. Hilmoe, *J. Biol. Chem.*, 1962, **237**, 841.

phthalein. Under these conditions, orthophosphoric acid and methyl dihydrogen phosphate are titrated as dibasic acids. The amount of dimethyl hydrogen phosphate was found after substraction of the volumes of titrant used by orthophosphoric acid, methyl dihydrogen phosphate, and formic acid (see below).

Formaldehyde. This product was determined colorimetrically at 570 nm, after reaction with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid) in concentrated sulphuric acid.[14]

Formic acid. The acid was determined according to Grant's method.[15] This involves reduction of the formic acid with magnesium in acid medium to formaldehyde, which is subsequently determined by means of the forementioned colorimetric method. Blank values for formaldehyde, which was already present prior to the reduction, were substracted.

Methanol. Treatment of aqueous methanol with potassium permanganate in acid medium oxidized the product partly to formaldehyde, which was subsequently determined with chromotropic acid.[16,*] Blank values for formaldehyde, which was already present before oxidation, were substracted.

Carbon dioxide.—The gas which had passed through the irradiated solution, was led through a tube packed with glass wool (to hold back droplets) and was then bubbled through two wash-bottles containing saturated aqueous solutions of barium hydroxide. Immediately after the photolysis, the irradiated solution was acidified with sulphuric acid (20%) and heated at 80° by means of the circulating water. The system was then purged with a strong gas stream in order to collect the carbon dioxide completely. The amount of carbon dioxide was determined by titration of the barium hydroxide with 0·1N-aqueous hydrochloric acid, using phenolphthalein as indicator.

Carbon monoxide.—The presence of carbon monoxide was detected by passage of the gas stream through a wash-bottle filled with equal volumes of palladium chloride–phosphomolybdenic acid reagent[17] and acetone, heated at 60°. The yellow colour of the reagent changed to dark blue-green.

For a quantitative determination, the carbon monoxide was converted into carbon dioxide by means of oxidation with iodine pentoxide.[18] The gas which had passed through the irradiated solution was led through wash-bottles containing saturated aqueous solutions of barium hydroxide to remove carbon dioxide, and was subsequently led through: (i) a wash-bottle filled with concentrated sulphuric acid; (ii) a tube filled with glass wool to hold back small droplets; (iii) a U-tube filled with alternate layers of granulated iodine pentaoxide (Merck, Germany) and of glass wool. The U-tube was heated at 150—160°. Before use, the iodine pentoxide was heated in a stream of nitrogen at 240° for 8 h; (iv) a trap cooled with dry ice–alcohol in order to hold back iodine; and (v) two wash-bottles filled with saturated aqueous solutions of barium hydroxide in order to absorb carbon dioxide. Carbon dioxide was determined by titration (see above).

Peroxide(*s*). These were determined according to the procedure of Hochanadel.[19] The peroxide oxidizes an equivalent amount of iodide, which is determined colorimetrically as tri-iodide anion at 350 nm.

Paper (*radio*)*chromatography*. The chromatography was done in the descending mode with Whatman no. 1 chromatography paper. Samples from the irradiated solutions were applied directly to the paper for analysis of phosphorus-containing products. Orthophosphoric acid, methyl dihydrogen phosphate, and dimethyl hydrogen phosphate were detected by the ammonium molybdate–perchloric acid spray, followed by drying at 80° for a few minutes and exposure to sunlight.[20] The latter two phosphates, and trimethyl phosphate, were also detected by means of radiochromatography after photolysis of ^{14}C-labelled trimethyl phosphate. The superficially dried paper was cut into strips (1 × 3 cm). These were counted for ^{14}C in a Packard Tricarb liquid scintillation spectrometer.[†]

In order to detect formaldehyde, a 20 ml sample of the irradiated solution was treated with a 0·25% (w/v) solution (4 ml) of 2,4-dinitrophenylhydrazine (DNPH) in 30% (v/v) perchloric acid. After being left overnight at room temperature, the reaction mixture was extracted with carbon tetrachloride (4 × 5 ml). The combined organic layers were then washed with 10% aqueous sodium carbonate, water, 30% aqueous perchloric acid, and again with water. After drying (Na_2SO_4), the solvent was evaporated and the residue was redissolved in a small volume of carbon tetrachloride. The resulting deep yellow solutions were used for chromatography.[21] The spot was detected with u.v. light, and was made permanently visible by spraying with 10% aqueous sodium hydroxide.

R_F Values and solvent systems for the chromatograms are collected in Table 1.

TABLE 1

Paper chromatography of photolysis products (254 nm) of aqueous trimethyl phosphate in an oxygen or argon atmosphere

	R_F Values					
	Oxygen			Argon		
Solvent [a]	I	II	III	I	II	III
Compound						
Orthophosphoric acid	0·03	0·05				
Methyl dihydrogen phosphate	0·18	0·17				
Dimethyl hydrogen phosphate	0·64	0·59		0·66	0·58	
Trimethyl phosphate	0·82			0·83		
Formaldehyde-DNPH [b]			0·32			0·32

[a] Solvents: I = methanol–propan-2-ol–25% ammonia–water (9 : 6 : 3 : 2); II = propan-2-ol–25% ammonia–water (7 : 1 : 2); III = light petroleum (b.p. 80—100°)–methanol (2 : 1), upper layer. [b] 2,4-Dinitrophenylhydrazone derivative.

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[*] The procedure which is given in ref. 16 is obviously not complete. After addition of concentrated sulphuric acid, the reaction mixture should be heated for 30 min at 100°, in order to get a rapid and complete development of the colour.

[†] Trimethyl phosphate evaporated rapidly from the paper and could therefore only be detected qualitatively.

[14] C. E. Bricker and H. R. Johnson, *Ind. and Eng. Chem.*, 1945, **17**, 400.

[15] W. M. Grant, *Analyt. Chem.*, 1948, **20**, 267.

[16] F. D. Snell and C. T. Snell, 'Colorimetric Methods of Analysis,' 3rd edn., Van Nostrand, New York, 1957, vol. 3, p. 45.

[17] Ref. 16, vol. 2, p. 838.

[18] Ref. 16, vol. 2, p. 829.

[19] C. J. Hochanadel, *J. Phys. Chem.*, 1952, **56**, 587.

[20] I. M. Hais and K. Macek, 'Paper Chromatography,' Publishing House of the Czechoslovak Academy of Sciences, Prague, 1963, p. 819.

[21] G. Scholes, W. Taylor, and J. Weiss, *J. Chem. Soc.*, 1957, 235.

RESULTS

(A) *U.v. Spectroscopy.*—Trimethyl phosphate in aqueous solution has only a weak absorptivity in the region 300—230 nm. The absorptivity rises more sharply below 230 nm (Figure 1). There is no evidence for an absorption maximum at 219·8 nm, as reported by Bennoson and Williams.[22] The observed maximum is probably due to an impurity in their sample.

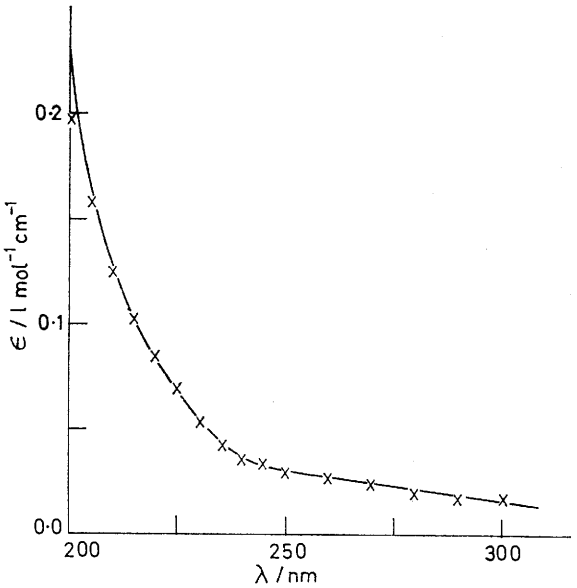

FIGURE 1 Absorption spectrum of 1·0M-aqueous trimethyl phosphate

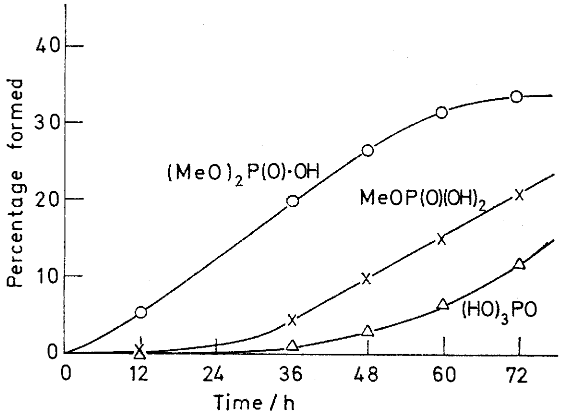

FIGURE 2 Photolytic dealkylation of 0·10M-aqueous trimethyl phosphate in an oxygen atmosphere at 30° (254 nm)

(B) *Photolysis in an Oxygen Atmosphere.*—(a) *Methyl phosphates and orthophosphoric acid.* Irradiation at 254 nm of 0·10M-aqueous trimethyl phosphate in an oxygen atmosphere caused immediate production of acid. Paper (radio)chromatography of the photolysis mixture showed that dimethyl hydrogen phosphate, methyl dihydrogen phosphate, and orthophosphoric acid are formed. Apparently, progressive dealkylation of trimethyl phosphate takes place.

Quantitative determination of these components in the photolysis mixture was carried out by combining the results of acidimetric titration and spectrophotometric determination of orthophosphoric acid, followed by specific hydrolysis of methyl dihydrogen phosphate to orthophosphate with Alkaline Phosphatase (see Experimental section). In this way, the course of the dealkylation reaction could be followed as a function of time (Figure 2).

The curve for dimethyl hydrogen phosphate levels off after 72 h of irradiation. On further irradiation, the concentration of dimethyl hydrogen phosphate begins to decrease when less than 25% of the trimethyl phosphate is still intact.

Blank experiments have shown that the 'dark hydrolysis' of trimethyl phosphate under the photolysis conditions is insignificant with respect to the amount of acid produced by photolysis.

(b) *Formaldehyde, formic acid, carbon dioxide, and carbon monoxide.* Quantitative experiments on the fate of the methyl groups which are released from trimethyl phosphate are summarized in Table 2. When irradiation is allowed to proceed for 24 h, carbon dioxide and carbon monoxide are formed as major carbon-products together with smaller quantities of formic acid and formaldehyde. Within experimental error, the total yields of the four products are 100%. Since these yields are based on the calculated extent to which methyl groups have been released from dimethyl hydrogen phosphate, methyl dihydrogen phosphate, and orthophosphoric acid, it may be concluded that all *major* carbon products have been analysed quantitatively.

TABLE 2

Yields of products after three separate photolyses of 0·10M-aqueous trimethyl phosphate at 254 nm in an oxygen atmosphere (30°)

Photolysis time (h)	4	24	24
Dimethyl hydrogen phosphate [a]	1·4	13·1	11·3
Methyl dihydrogen phosphate [a]	<0·1	3·2	2·3
Orthophosphoric acid [a]	0·0	0·9	0·7
Carbon dioxide [b]	*c*	52·2	52·3
Carbon monoxide [b]	*c*	32·2	33·3
Formic acid [b]	50·0	13·5	10·1
Formaldehyde [b]	7·1	2·0	3·9
Methanol [b]	*c*	Traces	*c*
Peroxide(s) [a]	*c*	$5·8 \times 10^{-2}$	$4·4 \times 10^{-2}$

[a] Concentrations in mmol l^{-1}. [b] Percentages based on the *calculated* amount of carbon products that have been released from dimethyl hydrogen phosphate, methyl dihydrogen phosphate, and orthophosphoric acid. [c] Not determined.

A partial analysis after only 4 h irradiation revealed that dimethyl hydrogen phosphate and formic acid are the major reaction products when less than 1·5% of trimethyl phosphate has been photolysed. In that case, the relative amount of formaldehyde is also larger than after 24 h irradiation (Table 2).

During the photolysis, steady state concentrations of formic acid and formaldehyde are gradually formed. As shown in Figure 3, the concentration of formic acid is almost constant after 24 h, whereas the formaldehyde concentration increases still slightly afterwards.

(C) *Photolysis in an Argon Atmosphere.*—Photolysis of aqueous trimethyl phosphate in an argon atmosphere is much slower than in an oxygen atmosphere, as far as acid

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[22] M. Bennoson and D. J. Williams, *J. Phys. Chem.*, 1972, **76**, 3673.

production is concerned. The summary of results in Table 3 shows that irradiation of 0·50M-aqueous trimethyl phosphate for 48 h yields only 3·0 mmol l^{-1} of dimethyl hydrogen phosphate (0·6%). In contrast, *ca.* 15% of trimethyl phosphate is dealkylated after irradiation of a 0·1M-aqueous solution for 24 h in an oxygen atmosphere (*cf.* Table 2).

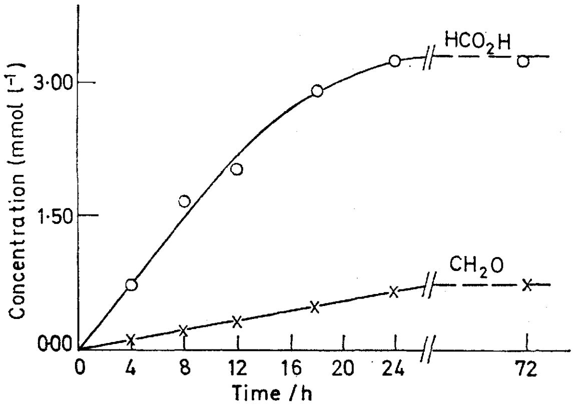

FIGURE 3 Concentrations of formic acid and formaldehyde during the photolysis (254 nm) of 0·10M-aqueous trimethyl phosphate in an oxygen atmosphere at 30°

TABLE 3

Yields of products after photolysis of 0·50M-aqueous trimethyl phosphate at 254 nm for 48 h in an argon atmosphere (30°)

Product	Concentration (mmol l^{-1})
Dimethyl hydrogen phosphate	3·0 [a]
Methyl dihydrogen phosphate	<0·1
Orthophosphoric acid	0·0
$[(MeO)_2P(O)\cdot OCH_2]_2$	Traces
Methanol	3·1 [a]
Formic acid	0·1
Formaldehyde	0·1
Carbon dioxide	*b*
Carbon monoxide	*b*
Peroxide(s)	Traces

[a] At least 60% of this product is due to ' dark hydrolysis,' as found from blank experiments. [b] Not detected.

As shown in Table 3, dimethyl hydrogen phosphate and methanol are the major reaction products after 48 h irradiation. However, at least 60% of these two products are due to ' dark hydrolysis ' of trimethyl phosphate. Small, but easily detectable, amounts of formaldehyde and formic acid are also formed.

$$(MeO)_2P(O)\cdot OCH_2CH_2O\cdot P(O)(OMe)_2$$
(1)

Indications for the formation of the dimer (1) (m.w. 278) were obtained from the mass spectrum of the evaporated reaction mixture. The spectrum shows a minor peak at *m/e* 279, and a major peak at 249. These two peaks are assigned to the molecular ion (+H) of (1) and to loss of formaldehyde from this ion, respectively.[23,*] Further analyses are necessary in order to confirm unequivocally the presence of the dimer in the reaction mixture.

(D) *Quantum Yields for the Formation of Dimethyl Hydrogen Phosphate.*—The quantum yields for formation of dimethyl hydrogen phosphate were determined at 30°. Since the reaction product is further photolysed, low conversion ratios ($\leqslant 1\%$) were used. Results are summarized in Table 4.

TABLE 4

Quantum yields for the formation of dimethyl hydrogen phosphate from trimethyl phosphate in aqueous solution (254 nm)

Atmosphere	Oxygen	Argon
Trimethyl phosphate (M)	0·1	0·5
Quantum yield ($10^2\Phi$) [a]	11·5 ± 0·5	1·0 ± 0·5

[a] Average value of two experiments.

In the presence of oxygen, the quantum yield for the formation of dimethyl hydrogen phosphate is slightly larger than for the formation of orthophosphoric acid from ethyl dihydrogen phosphate [25] and from glycerol phosphates.[3] Even the very low quantum yield in an argon atmosphere should be regarded as a maximum value, owing to the eventual presence of traces of oxygen.

DISCUSSION

Photolysis in an Argon Atmosphere.—In accordance with the weak u.v. absorption of aqueous trimethyl phosphate at 254 nm (Figure 1), photolysis at this wavelength in an argon atmosphere is very slow. The probable formation of the dimer (1) suggests that the radical (2) is an intermediate during the reaction.

$$(MeO)_2P(O)\cdot OCH_2\cdot \qquad CH_3\dot{C}H\cdot OP(O)(OH)_2$$
(2) (3)

This would be analogous to the photolysis of ethyl dihydrogen phosphate at 254 nm, for which the intermediate (3) has been proposed.[25] The e.s.r. signal of (2) was observed after u.v. irradiation (254 nm) of neat frozen trimethyl phosphate.[26] γ-Radiolysis of aqueous trimethyl phosphate also leads to the formation of (2).[7,27]

No evidence is yet available on the mechanism of formation of the intermediate (2), which may be by simple loss of a hydrogen atom, or as the result of some bimolecular process. Mechanisms obtained by e.s.r. techniques in neat frozen trimethyl phosphate [26] may not be relevant to our conditions of dilute aqueous solutions.

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[*] Apparently, hydrogen capture takes place under the experimental conditions in the ionization chamber of the mass spectrometer. The spectrum of trimethyl phosphate (m.w. 140) shows a large peak at *m/e* 141 under identical conditions.[24]

[23] D. A. Bafus, E. J. Gallegos, and R. W. Kiser, *J. Phys. Chem.*, 1966, **70**, 2614.

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[26] M. Sato, T. Katsu, Y. Fujita, and T. Kwan, *Bull. Chem. Soc. Japan*, 1973, **46**, 2875.

[27] A. Begum, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1334; E. A. C. Lucken, *ibid.*, 1966, 1354; A. R. Metcalfe and W. A. Waters, *J. Chem. Soc.* (*B*), 1967, 340.

The formation of methanol and of dimethyl hydrogen phosphate is largely, and possibly completely, due to 'dark hydrolysis' (Table 3). The small amounts of formic acid and formaldehyde could be due to traces of oxygen in the argon gas stream (see below). However, Halmann and Platzner also found acetaldehyde after irradiation of aqueous ethyl dihydrogen phosphate *in vacuo*.[25,26]

Photolysis in an Oxygen Atmosphere.—Saturation of the aqueous solution of trimethyl phosphate with oxygen leads to a substantial increase in the rate of photolysis. The cause of this rate enhancement is not clear. Since we found that the u.v. absorption of aqueous trimethyl phosphate in the region 300—200 nm is not influenced by the presence of oxygen, the relatively rapid photolysis is probably not due to the formation of a charge-transfer complex between trimethyl phosphate and oxygen.[28,29] Furthermore, hydrogen peroxide is not formed under our experimental conditions in the absence of trimethyl phosphate. Hence, the photolysis of hydrogen peroxide cannot explain the rate enhancement.[5]

The initial products of the photolysis, *i.e.* dimethyl hydrogen phosphate, formaldehyde, and formic acid (Table 2) are possibly formed *via* reaction of oxygen with the intermediate (2).

$$\underset{(2)}{(MeO)_2P(O)\cdot OCH_2\cdot} \xrightarrow{O_2} \underset{(4)}{(MeO)_2P(O)\cdot OCH_2O\cdot O\cdot}$$

Hydrogen abstraction reactions of (4) could give hydroperoxides, *e.g.* (5), which are only present in trace quantities during irradiation under argon (*cf.* Tables 2 and 3). Irradiative cleavage of the intermediate (5) may increase the quantum yield in the presence of oxygen by way of a chain reaction, *e.g.*:

$$\underset{(5)}{(MeO)_2P(O)\cdot OCH_2O\cdot OH} \xrightarrow{h\nu} (MeO)_2P(O)\cdot OCH_2O\cdot + \cdot OH \longrightarrow \text{chain reaction}$$

Such a reaction would resemble the situation found in the photochemical oxidation of alkyl ethers.[30]

The formation of formaldehyde and formic acid could result from hydrolysis of the rearranged intermediates (6) and (7), respectively.[2]

$$\underset{(6)}{(MeO)_2P(O)\cdot OCH_2OH} \qquad \underset{(7)}{(MeO)_2P(O)\cdot OCHO}$$

Photo-oxidation of formaldehyde is an alternative pathway for the formation of formic acid.[31,32] Since the 'dark hydrolysis' producing methanol from trimethyl phosphate is very slow, the photo-oxidation of such methanol cannot be a pathway for formation of formaldehyde and formic acid in an oxygen atmosphere.

The gradual build-up of steady-state concentrations of formic acid and of formaldehyde (Figure 3) strongly suggests that these two products are further photolysed. In this connection, the formation of carbon monoxide after prolonged irradiation of trimethyl phosphate can be the result of secondary photolysis of formaldehyde.[32] Similarly, carbon dioxide is formed by secondary photolysis of formic acid.[33] It should be noted that the presence of oxygen seems to prevent the photochemical formation (254 nm) of carbon monoxide from aqueous formic acid.[33]

Finally, the data in Figure 2 indicate clearly that the ultimate formation of orthophosphoric acid from trimethyl phosphate is the result of a stepwise process.[5]

$$(MeO)_3PO \xrightarrow{h\nu-O_2} (MeO)_2P(O)\cdot OH \xrightarrow{h\nu-O_2} (MeO)P(O)(OH)_2 \xrightarrow{h\nu-O_2} P(O)(OH)_3$$

The formation of methyl dihydrogen phosphate is retarded with respect to dimethyl hydrogen phosphate, whereas the production of orthophosphoric acid lags behind methyl dihydrogen phosphate.

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