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Photolysis of Triphenyl Phosphate in Aqueous Methanol

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ABSTRACT

Upon UV irradiation in methanol, triphenyl phosphate (1a) gave biphenylyl phenyl phosphate (2a) as the main product, whereas the addition of water to the solution caused an increase of the yield of biphenyl (3a). These products were formed through a singlet excited state and an intramolecular excimer, respectively. *© 1996 John Wiley & Sons, Inc.*

INTRODUCTION

During preceding decades, water as a solvent has frequently been excluded from organic syntheses for several reasons. Among them were the insolubility of the reactants in water and the incompatibility of the intermediates with water. However, many biochemical processes occur in the presence of water, and the diversity of the reactions in vivo prompts chemists to reconsider the potential of water as a solvent [1]. It is known that photochemical intermolecular dimerizations are accelerated by the addition of water [2]. For example, dimerization of *trans*-stilbene can be achieved in water at a concentration as low as 10^{-6} M, while a 0.1 M concentration is necessary in benzene [3]. Coumarin dimerizes at a much lower concentration in water (10^{-3} M) than in organic solvents, and the quantum yield is improved by 100-fold [4]. Intramolecular photodimerization has not yet been observed.

Finnegan and Maston [5] have reported that, upon UV irradiation in methanol, tris(4-methoxyphenyl) phosphate (**1c**) gave 4,4′-dimethoxybiphenyl (**3c**) as the main product (quantum yield $\phi = 0.17$), but triphenyl phosphate (**1a**) hardly gave any biphenyl (**3a**). We have reinvestigated the photolysis of **1a** and found that biphenylyl phenyl phosphate (**2a**) is produced in a moderate yield ($\phi = 0.045$), whereas the yield of **3a** ($\phi = 0.002$) is very small (Scheme 1).

RESULTS AND DISCUSSION

Fluorescence Spectrum of 1

Two emission bands were observed in the fluorescence spectrum of **1a** in MeOH (Figure 1).

A shorter (290 nm) and a longer (330 nm) wavelength band were assigned to emission bands of a monomeric singlet excited state (monomer) and of an intramolecular excimer (excimer), respectively, by comparison with the spectrum of diethyl phenyl phosphate and by the fact that the spectrum was virtually invariant with change of the concentration. A plausible reaction scheme is shown in Scheme 2,

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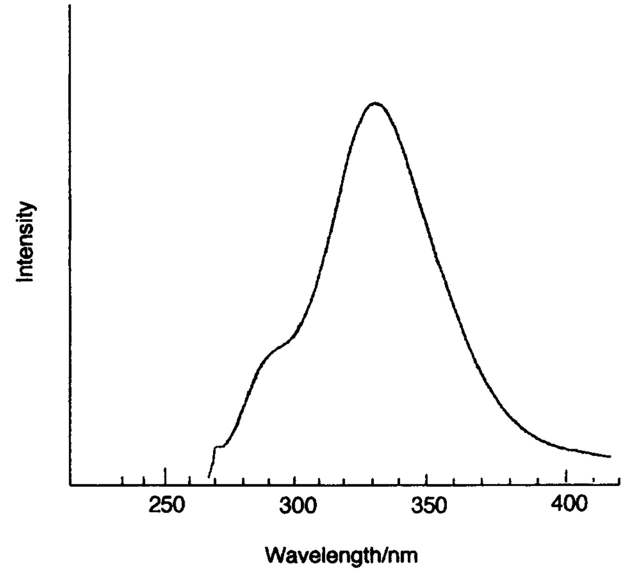
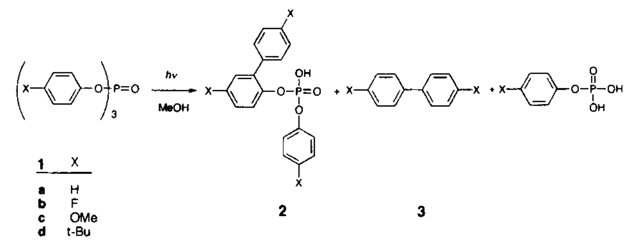
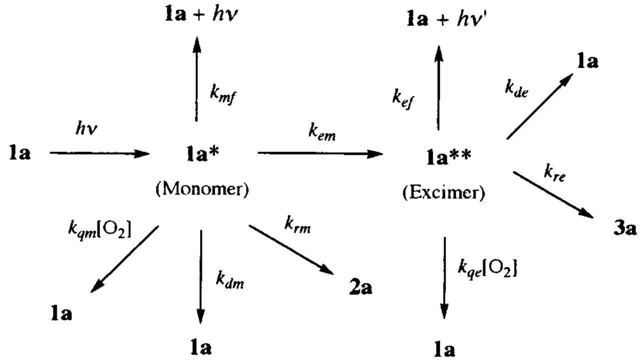


FIGURE 1 Fluorescence spectrum of **1a** in methanol (1.0 × 10^{-4} M, excitation by 260 nm light).



SCHEME 1



SCHEME 2

where it is presumed that the monomer and excimer are not in equilibrium. From the quenching of the fluorescence spectrum by oxygen (Stern-Volmer analysis), the values of $k_q\tau$s were determined by use of Equations 1 and 2.

For monomer,

$$\phi^0_m/\phi_m = 1 + k_{qm}\tau_m [O_2] \qquad (1)$$

For excimer,

$$(\phi^0_e/\phi_e) = (1 + k_{qm}\tau_m [O_2])(1 + k_{qe}\tau_e [O_2])$$

therefore,

$$(\phi^0_e/\phi_e)/(\phi^0_m/\phi_m) = 1 + k_{qe}\tau_e [O_2] \qquad (2)$$

where ϕs are quantum yields of fluorescence, τ_m and τ_e are fluorescence lifetimes, and k_{qm} and k_{qe} are oxygen quenching rate constants of the fluorescence of the monomer and the excimer, respectively. The values of $k_q\tau$s were obtained from the slope of the straight line obtained from a plot of ϕ^0/ϕ versus $[O_2]$. The values of $k_{qm}\tau_m$ and $k_{qe}\tau_e$ were 25 (correlation coefficient; $r = 0.997$) and 184 M^{-1} ($r = 0.996$), respectively. On the other hand, by the single photon-counting method, the lifetimes τ_m and τ_e of fluorescence were determined as 0.6 and 8.1 ns, respectively. Therefore, k_{qm} and k_{qe} were 4×10^{10} and 2×10^{10} $M^{-1}s^{-1}$, which were close to the diffusion rate constant of oxygen in methanol, and, consequently, the rates of the reactions may be determined by the rate of the diffusion of oxygen. When water was added to the solution (0.6 mole fraction), a slight increase of the intensity of the emission band (330 nm) was observed.

Photolysis of 1 *and Its Mechanism*

Upon UV irradiation of 1a in methanol (10^{-2} M) under an Ar atmosphere for 1 hour, biphenylyl phenyl phosphate (2a) and 3a were produced in quantum yields (ϕ) of 0.045 and 0.0020, respectively.

In order to clarify the mechanism of formation of 2a, a quenching experiment utilizing oxygen was carried out. From Scheme 2, Equations 3 and 4 can be derived in a manner similar to that shown previously.

For 2a,

$$\phi^0_2/\phi_2 = 1 + k_{q2}\tau_2 [O_2] \qquad (3)$$

For 3a,

$$(\phi^0_3/\phi_3)/(\phi^0_2/\phi_2) = 1 + k_{q3}\tau_3 [O_2] \qquad (4)$$

where ϕs are the quantum yields of formation of products and k_{q2} and k_{q3} are oxygen-quenching rate constants of excited species for the formation of 2a and 3a, respectively. From the plot of ϕ^0/ϕ versus $[O_2]$, the values of $k_{q2}\tau_2$ and $k_{q3}\tau_3$ were determined to be 27 ($r = 0.990$) and 186 M^{-1} ($r = 0.991$), respectively. These values were approximately equal to those of $k_{qm}\tau_m$ (25 M^{-1}) and $k_{qe}\tau_e$ (184 M^{-1}), respectively. Therefore, it was concluded that 2a and 3a are formed through a monomeric excited and a dimeric excited state (excimer), respectively [6].

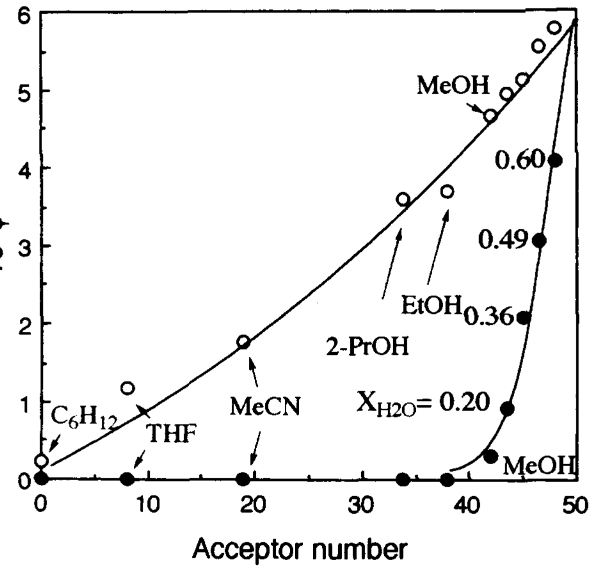


FIGURE 2 Correlation between the quantum yields of **2a** (○) and **3a** (●) and the acceptor number of the solvent (X_{H_2O} = molarity of water). Reaction conditions: the solutions of **1a** (10^{-2} M) were irradiated with a high-pressure Hg lamp for 10 minutes.

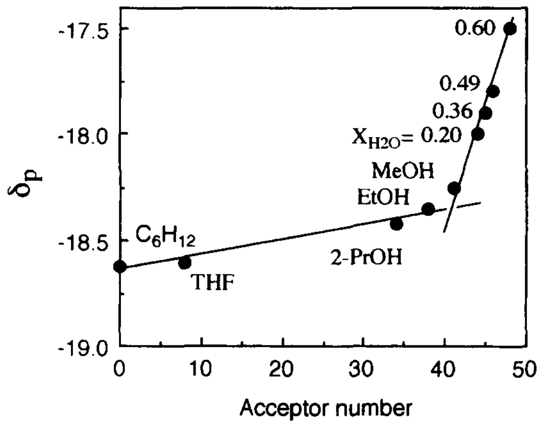


FIGURE 3 Correlation between ^{31}PNMR chemical shift (δ_p) of **1a** and the acceptor number of the solvent (X_{H_2O} = molarity of water). δ_ps were recorded under the following conditions: **1a** (10^{-2} M) in a 10 mm tube, 100 scans in the Fourier-transform mode of operation at a 20 second repetition rate, with proton decoupling, and at a definite temperature (30°C).

Solvent Effect of Photolysis of 1a

The correlation between the quantum yields of the products and the acceptor number of the solvent is shown in Figure 2. Acceptor numbers express the electrophilic properties of given solvents [7]. The yield of 2a increased in proportion to the acceptor number, but the yield of 3a did not change. The more electrophilic solvent coordinates more strongly to the phosphoryl oxygen, inducing a greater positive charge on the phosphorus atom. The effect might contribute to greater weakening of the β-O–Ph bond with facilitation of the heterolytic bond cleavage as in phenoxy phosphonium salts [8].

When water was added to the methanol solution, the yield of 3a increased markedly (Figure 2). This result suggests that another solvent factor may affect the reactivity of 1a. The correlation between the acceptor number of the solvent and the ^{31}P chemical shift (δ) of 1a in the solvents is shown in Figure 3. A linear correlation was observed in anhydrous solvents. When water was added to a methanol solution, the correlation curve greatly deviated from the line. Specifically, the ^{31}P chemical shift (δ_p) was significantly shifted to lower magnetic field.

The effects that cause the change in δ_p may be viewed in terms of (1) the effect on electronegativity of substituents relative to phosphorus, (2) the effect on bond angle, and (3) the effect on the occupation of the phosphorus $d\pi$ orbital [9,10]. The origin of the change in δ_p in this case can be interpreted by consideration effect (2). The hydrophobic interaction is the tendency of apolar groups to aggregate in aqueous solution to minimize unfavorable interactions with water. With increasing quantity of water, phenyl groups (apolar group) of the phosphate aggregate intramolecularly and narrow the bond angle of O–P–O, although the bond of P–O–Ph may also be bent. These effects may increase the interaction between the phenyl groups and accelerate the rate of the coupling reaction.

A similar behavior could be observed in the photolysis of tris(4-fluorophenyl) phosphate (**1b**); 4-fluorophenyl 2(4-fluorophenyl)-4-fluorophenyl phosphate (**2b**), and 4,4′-difluorobiphenyl (**3b**) were obtained in the quantum yields of 0.053 and 0.020 in methanol. With a 0.5 molar fraction of water in methanol, the quantum yield of **3b** increased to 0.080, while the yield of **2b** was hardly changed (0.052). In the cases of tris(4-methoxyphenyl) phosphate (**1c**) and tris(4-*t*-butylphenyl) phosphate (**1d**), such phenomena could not be observed, probably because the presence of a hydrophilic or a bulky group may inhibit the aggregation.

EXPERIMENTAL

Apparatus

Melting points were obtained with a Yanagimoto micro point apparatus. CHN microanalyses were carried out with a Perkin-Elmer Model 240 analyzer. UV-visible spectra were recorded with a Hitachi 150-20 spectrometer. Steady-state fluorescence spectra were recorded with a Hitachi 850-type fluorescence spectrometer. Lifetimes of fluorescence spectra were measured with a Horiba time-resolved fluorescence spectrometer. ^{1}H- and ^{13}C-NMR spectra were obtained in $CDCl_3$ with tetramethylsilane as an internal standard on a JEOL EX-270 spectrometer. ^{31}P-NMR spectra were obtained in $CDCl_3$ with 80% H_3PO_4 as an external standard on a JEOL FX 90Q spectrometer. The GLC analyses were carried out by use of a 2% Silicone OV-17 on Chrom. Gas chromatography-mass spectroscopy (GC-MS) spectra were recorded with a JMS-DX 300 instrument and high-resolution mass spectra were also obtained on a JMS-01SG-2 instrument. High-pressure liquid chromatography (HPLC) analyses were carried out by use of a Shimadzu LC-10AS instrument with a column of Shiseido CAPCELL PAK C18 AG 120. Photolyses were carried out with a 300 W high-pressure mercury lamp EHBW-300 (Eikosha Co., Ltd.) and a 60 W low-pressure mercury lamp.

Materials

Commercially available triphenyl phosphate (**1a**) was used; λ_{max}(MeOH) = 285 nm (ε = 1200). Tris(4-fluorophenyl) phosphate (**1b**) was prepared by the reaction of phosphorus oxychloride with 4-fluorophenol in the presence of triethylamine: mp 55–56°C, λ_{max}(MeOH) = 264.4 nm (ε = 3391), ^{1}H NMR (250 MHz, in $CDCl_3$); δ = 7.04 (6H, ddd, 8.9, 3.6, 2.0 Hz), 7.14 (6H, ddd, 8.9, 5.6, 1.3 Hz). Tris(4-methoxyphenyl) phosphate (**1c**) was prepared in a similar manner to that described previously, bp 180–200°C/0.2 mm Hg, λ_{max}(MeOH) = 277.2 nm, (ε = 5700), ^{1}H NMR (250 MHz, in $CDCl_3$); δ = 3.77 (9H, s), 6.97 (12H, m). Tris(4-*t*-butylphenyl) phosphate (**1d**) was prepared in the similar manner to that described previously, mp 94–96°C, λ_{max} (MeOH) = 263.6 nm (ε = 1360), ^{1}H NMR (250 MHz, in $CDCl_3$); δ = 1.30 (27H, s), 7.16 (6H, dd, J_{HH} = 8.9, 2.0 Hz), 7.34 (6H, dd, J_{HH} = 8.9, 2.0 Hz).

Photolysis of 1 *in MeOH*

Argon gas was bubbled into a 100 mL methanol solution of **1a** (10^{-2} M) contained in a quartz doughnut-type cell for 10 minutes, and the solution was irradiated with a 300 W high-pressure Hg lamp for 1 hour. After irradiation, the reaction mixture was methylated with diazomethane; compounds **2a** and **3a** were isolated by silica gel chromatography and identified by comparison with the spectral data of a commercially available biphenyl or by use of ^{13}C and ^{1}H NMR spectroscopy. Product **2a**: ^{13}C NMR (150 MHz, $CDCl_3$), δ = 53.6, 120.6, 123.4, 123.5, 126.7, 127.8, 128.8, 129.0, 129.4, 130.4, 132.3, 138.1, 138.1, 149.2, 151.9; ^{1}H NMR (250 MHz, $CDCl_3$), δ = 6.98 (2H, d, J = 2.0), 7.70 (1H, d = 7.0), 7.09 (2H, dd J = 9.4, 7.0), 7.21 (1H, dd J = 6.0, 8.0), 7.26 (5H, s), 7.40 (1H, d, J = 2.0), J = 2.0), 7.43 (1H, d, J = 2.0), 7.72 (1H, dd, J = 8.3, 6.0); FD-MS *m/z* 340(M^+). After hydrolysis of **2a** with 6N HCl solution, 2-phenylphenol was isolated, which was identified by comparison with the spectral data of an authentic sample. Product **3a** was identified as biphenyl.

Photolyses and product analyses on other compounds (**1b–d**) were carried out in the same manner.

Measurement of Quantum Yield

The quantum yields were measured as follows: A 3 mL solution of **1a** (1.0×10^{-2} M) saturated with argon gas in a quartz cell (10 × 10 mm) was irradiated using a low-pressure Hg lamp (60 W). Photolysis was carried out to within 10% conversion. Actinometry was carried out by use of a potassium trioxalatoferrate (III) solution [11]. The product yield was determined by HPLC.

Quenching of Fluorescence by Oxygen

Six 3 mL methanol solutions of **1a** (1.0×10^{-4} M) were charged into six separate quartz cells (10 × 10 mm). Argon; air; 40, 60, or 80% oxygen/nitrogen; or pure oxygen gas was bubbled into the solutions until saturation at 20°C during 10 minutes had occurred. Concentrations of oxygen in these solutions were evaluated from solubilities in methanol as 0.0, 1.51, 3.82, 5.72, 7.63, and 9.54×10^{-3} M, respectively. The emission spectra of these solutions were recorded on a fluorescence spectrometer.

Quenching of Quantum Yield of Product by Oxygen

Six 3 mL methanol solutions of **1a** (1.0×10^{-2} M) were charged into six separate quartz tubes (diameter 10 mm) and saturated with the respective prescribed concentrations of oxygen, and, after UV irradiation using a low-pressure Hg lamp (60 W), quantum yields were measured in manner similar to that described earlier.

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