JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY • Volume 42, Number 2, March/April 1998

Application of Triaryl Phosphate to Photosensitive Materials (III): Structure and Reactivity of Methyl-Substituted Triaryl Phosphate

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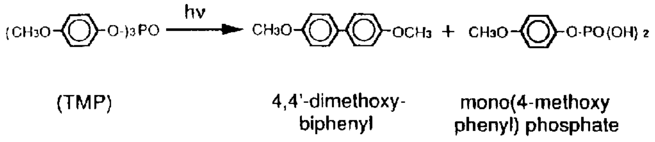
Six methyl-substituted triaryl phosphates (TAPs) were synthesized for application as acid generators for thermodeveloping type photosensitive materials [$(\text{Aryl-O})_3\text{PO}$; Aryl group, 2-tolyl (ToTP), 3-tolyl (TmTP), 4-tolyl (TpTP), 2,6-xylenyl (TooXP), 2,4-xylenyl (TopXP), and 3,4-xylenyl (TmpXP)]. The TAPs yielded a bisaryl compound and a phosphoric acid monoaryl ester equivalently after photoirradiation with 254-nm radiation. Among these compounds, TmpXP was the most reactive yielding 3,3',4,4'-tetramethylbiphenyl (78%) after only 4-h irradiation. During the photoirradiation of TAP, strong emissions were detected. Each spectrum had two emission maxima. The shorter wavelength maximum was assigned to monomer fluorescence and the longer one to excimer fluorescence. Emission quenching was carried out by using oxygen. The photosensitivities of thin films of poly(4-trimethylsiloxystyrene) (PSSt) and TAP were studied. Among the films, the PSST-TmpXP thin film was the most sensitive (35 mJ cm^{-2}).

Journal of Imaging Science and Technology 42: 163–168 (1998)

Introduction

Recently, thermodeveloping photosensitive materials attracted our interest from the viewpoint of catalyst formation and high sensitizability.[1–4] These materials are composed of a photoacid generator and either an acid degradable polymer (positive type) or an acid crosslinkable polymer (negative type). We reported the photoreaction of tri(4-methoxyphenyl) phosphate (TMP) to yield 4,4'-dimethoxybiphenyl and phosphoric acid mono(4-methoxyphenyl) ester (Eq. 1).[5,6] Because the latter product is a strong and nonvolatile acid, triaryl phosphate (TAPs) can be applied as a photoacid generator. A thin film of poly(4-trimethylsiloxystyrene) (PSSt) and TMP could be developed[5] after an irradiation of about 90 mJ cm^{-2}. The reaction proceeded by way of an intramolecular singlet excimer. Although an electron-donating substituent at the 4-position of the benzene ring increases the sensitivity, tri(3,4,5-trimethoxyphenyl) phosphate is, itself, of very low sensitivity.[6] This may be caused by difficulty forming the intramolecular excimer because of repulsion of the methoxy groups. Six kinds of mono- and dimethyl substituted TAPs were synthesized for application to photosensitive materials with PSSt to study the relation between structure and sensitivity for design of highly reactive materials [$(\text{Aryl-O})_3\text{PO}$ (TAP): Aryl = 2-tolyl (ToTP), 3-tolyl (TmTP), 4-tolyl (TpTP), 2,4-xylenyl (TopP), 3,4-xylenyl (TmpXP), and 2,6-xylenyl (TooXP)] .



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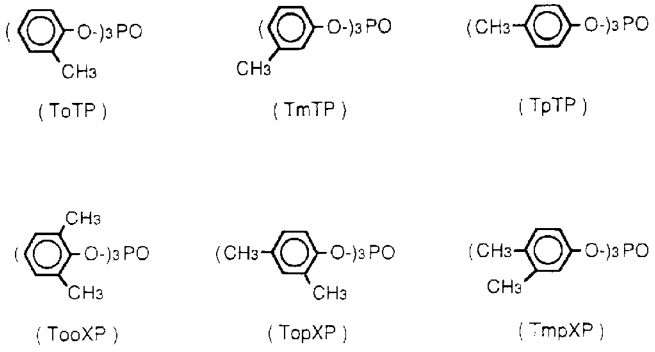

Scheme 1. Structure of studied TAPs.

Experimental

Materials. Six TAPs were synthesized by the reactions of methyl-substituted phenol with phosphoric trichloride, as described previously.[5,6] The TAPs were purified by double distillation or by double recrystallization from 1,2-dichloroethane solution. The TAPs were identified by elementary analysis and IR, NMR, and mass spectroscopies. Some physical data are listed in Table I.

PSSt was obtained by treating poly(4-hydroxystyrene) (Maruzen Petrochemical Co. Ltd., Mn = 5 × 10^5) with 1,1,1,3,3,3-hexamethyldisilazane.[7] A highly substituted polymer was obtained by repeating the reaction. The conversion was determined to be 77 mol% by NMR spectroscopy. Spectroscopic grade methanol was used without

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Original manuscript received March 25, 1997.

TABLE I. Yield and Physical Properties of TAP

TAP	Yield/ % *	Mp or BpK pas	Elementary†		Mass M+/z	IR / $cm^{-1,‡}$		UV§	
			C / %	H / %		$\nu_{P=O}$	$\nu_{P\text{-}O}$	λ_{max}/nm	ε_{max} / M^{-1} cm^{-1}
ToTP	88.0	195–198/0.3	68.32	5.88	368	1216	1157	263.0	1.14×10^3
			68.47	5.75				269.2	9.7×10^2
TmTP	34.8	175–177/0.3	68.49	5.73	368	1226	—	263.6	1.16×10^3
			68.47	5.75				270.4	1.01×10^3
TpTP	44.9	77.5–78.0	68.41	5.73	368	1234	1177	266.2	1.59×10^3
			68.47	5.75				272.6	1.41×10^3
TmpXP	36.2	255–260/0.2	70.33	6.57	410	1234	1186	267.0	1.59×10^3
			70.23	6.63				273.8	1.45×10^3
TooXP	13.5	141.6–142.5	70.28	6.58	368	1264	1143	260.4	1.71×10^3
			70.23	6.63				266.6	1.64×10^3
TopXP	22.3	64.4–65.0	70.26	6.66	368	1246	1179	268.2	1.65×10^3
			70.23	6.63				274.4	1.51×10^3

* Yield for trichlorophosphate

† found values (upper) and calculated values (lower)

‡ measured in KBr disk

§ measured in methanol

TABLE II. Biphenyl Yield and Its Spectra Data*

TAP	Bisaryl product	Yield/%	Mp or Bp/ °C $kpas^{-1}$	M^+/z	NMR† δ CH_3/ppm
ToTP	2,2'–dimethylbiphenyl	5.7	Liq.	182	2.16 (s,6H)
TmTP	3,3'–dimethylbiphenyl	31.7	Liq.	182	2.23 (s,6H)
TpTP	4,4'–dimethylbiphenyl	40.7	124.5-125.0	182	2.31 (s,6H)
TmpXP	3,3',4,4'–tetramethylbiphenyl	78.5	—	210	2.22 (s,12H)
TooXP	2,2',6,6'–tetramethylbiphenyl	13.5	145–148/13	210	2.24 (s,12H)
TopXP	2,2',4,4'–tetramethylbiphenyl	59.5	41.2-41.6	210	2.14 (s,6H) 2.23 (s,6H)

* Biphenyl yields were obtained in the reaction of TAPs in methanol after 4 h photoirradiation with 254 nm light.

† In $CDCl_3$ with TMS.

further purification. Commercial grade solvents were used without further purification for the sensitivity tests.

Photoreaction. Photoreactions of other TAPs were carried out for 4-h in methanol with 254-nm light. Each reaction yielded only one biphenyl product, which was identified by elementary analysis and NMR, IR, and mass spectroscopy, listed in Table II. The detailed procedure is illustrated as follows:

TpTP (325.0 mg) was irradiated in methanol (300 mL) with a N_2 purge for 4-h with a 20-W low-pressure Hg lamp. Filters were not used because TAPs do not absorb light with a wavelength longer than 300-nm. After evaporation of the solvent, the products were dissolved in ether and washed several times with a 2% sodium hydroxide aqueous solution. After the solution was dried over anhydrous sodium sulfate, the ether was evaporated. The remaining products were distilled under reduced pressure using a microtube oven. Only 55.4 mg of one product was obtained (yield: 40.7%). The distilled product was identified as 4,4'-dimethylbiphenyl by elementary analysis and IR and NMR spectroscopies. Yield and physical data of the biphenyl product are listed in Table II.

TpTP (137.8 mg) was irradiated once more in methanol (300 mL) with a N_2 purge for 4-h. After evaporation of the solvent, the products were dissolved in ether. The products were reacted with diazomethane in ether.[8] The products were identified to be 4,4'-dimethylbiphenyl, dimethyl 4-tolyl phosphate (ca. 40%), and a trace amount of 4-methylanisol by using gas chromatography and authentic samples. Dimethyl 4-toluyl phosphate, one of the authentic samples, was obtained in the reaction of trimethyl phosphate and 4-methylphenol (Yield: ca. 55%).

Emission Spectrum. Emission spectra of TAPs were measured in nitrogen-saturated methanol by 254-nm-light excitation using a Hitachi fluorescence photometer F4500 type ($d_{254nm} = 0.61 \pm 0.01$). The quantum yield of the emission was determined[9] by means of integrated emission intensities ($\int I_F \, d\nu$) using ϕ_F (= 0.066) of phenol as a standard compound, reported previously.[5] Fluorescence quenching was carried out using N_2–O_2 mixed gas. After saturation of the gas, the fluorescence spectra were measured in methanol.

Determination of Quantum Yield. Quantum yield determination was carried out using a 20-W low-pressure Hg lamp and a Schott glass filter UG-5. The cycloreversion reaction of r-1,t-2,t-3,c-4-tetraphenylcyclobutane to yield[10] trans-stilbene (ϕ = 0.67 in 1-chlorobutane) was used as the actinometer. The reactions were run to 10% conversion. The yield of biphenyl was determined using gas chromatography with a silicon grease column (OV-1). The acid was titrated with a 0.01 N aqueous sodium hydroxide solution using a phenolphthalein solution as an indicator.

Sensitivity Test. Commercial presensitized plates for printing (FPS type, Fuji) were used as some of the grained aluminum plates immediately after exposure and development. A dioxane solution of PSSt and TAP (TAP/PSSt = 1/20) was spin-coated onto a 1.00×10^{-2} m^2 square aluminum plate or a quartz plate. After drying under vacuum, plates coated with 3.0 (±0.3) g m^{-2} of the film were used. The plates, prebaked at 373 K for 5 min., were irradiated using the 20-W low-pressure Hg lamp. Filter solutions were not used. The light intensity was monitored with a Spectronics joule meter, type DRC-1000X with a radiom-

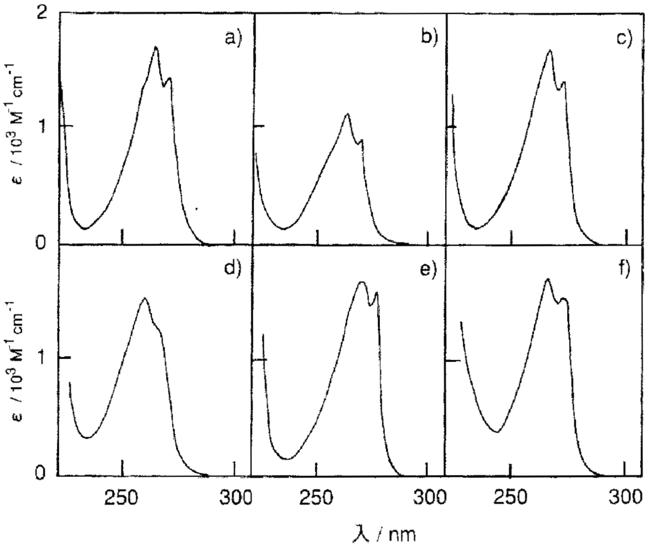

Figure 1. Absorption spectra of ToTP (a), TmTP (b), TpTP (c), TooXP (d), TopXP (e) and TmpXP (f) in methanol.

eter sensor DIX-254. After the irradiation, the plate was heated at 373 K for 10 min. The heat-treated plates were dipped into a 3.0% tetrabutylammonium hydroxide aqueous solution for 5 min to develop them.

Results and Discussion

Photoreaction of TAP. Because the biphenyl yield in methanol was the highest among the solvents used in the reaction of tri(4-methoxyphenyl) phosphate, methanol was used as the solvent in this study. Figure 1 shows absorption spectra of TAPs in methanol. These compounds have two absorption maxima around 270-nm (B band of aromatic compound) and around 215-nm (E2 band). Because the absorption tail ends around 300-nm, the photoreaction of TAPs was carried out by 254-nm irradiation in methanol.

Photolysis of TpTP yielded 4,4'-dimethylbiphenyl as a main product ($\phi_{biphenyl} = 0.10$). Dimethyl 2-toluyl phosphate was also obtained after the reaction of the irradiated products with diazomethane. The quantum yield of the acid formation was determined to be 0.12. Thus, the photoreaction of TpTP must yield 4,4'-dimethylbiphenyl and phosphoric acid 4-toluyl mono ester stoichiometrically, as shown in Eq. 2.

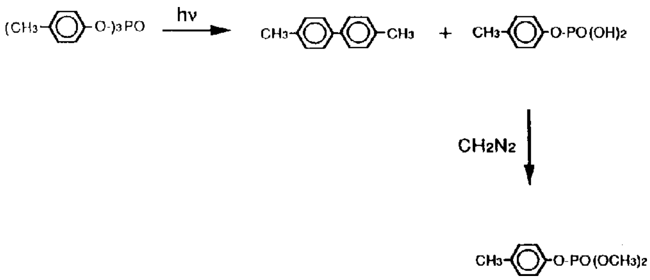

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TABLE III. Yield of Biphenyl, $Ø_{biph^*}$, $Ø_{acid}$[†] and Sensitivities of PSSt Films

TAP	Biphenyl Yield / %	$Ø_{biph}$[†]	Øacid[‡]	*E* / mJ cm^{-2}
ToTP	5.7	—	0.04	—
TmTP	31.7	—	0.08	500
TpTP	40.7	0.10	0.12	400
TooXP	13.5	—	—	—
TopXP	59.5	0.3	0.27	90
TmpXP	78.5	0.6_5	0.73	35

* Photoirradiations of TAPs were carried out in methanol with 254-nm light.
† Determined by aid of gas chromatography and a silicon wax column.
‡ Determined titremetrically.

The reaction of other TAPs yielded the biphenyl compound corresponding to the aryl group of TAPs. Table II listed the biphenyl product and its yield after 4 h irradiation with 254-nm light in methanol under N_2 bubbling. The biphenyl yield increased as ToTP (Yield: 5.7 %) < TooXP (13.5 %) < TmTP (31.7 %) < TpTP (40.7 %) < TopXP (59.5 %) < TmpXP (78.5 %). The $\phi_{biphenyl}$ values of TopXP and TmpXP were determined to be ca. 0.3 and ca. 0.6_5, respectively. The reaction must involve[6] the intramolecular excimer according to the same mechanism as the reaction of tri(4-methoxyphenyl) phosphate (TMP). It seems that steric repulsion between methyl groups at the 2-position decreases formation of intramolecular excimer. Because TmpXP yielded the biphenyl compound most effectively at about 80%, the inductivity of methyl substituents must promote formation of intramolecular excimer.

Acid Formation. TAPs produced phosphoric acid monoaryl ester upon photoirradiation at 254 nm. The yield of acid was determined titremetrically with 0.01 M aqueous sodium hydroxide solution. The quantum yields (ϕ_{acid}) are listed in Table III. The ϕ_{acid} value increased as; ToTP (0.04) < TmTP (0.08) ~ TooXP (0.08) < TpTP (0.10) < ToopMP (0.10) < TopXP (0.27) < TmpXP (0.73). The order of the ϕ_{acid} value agreed consistently with the order of the biphenyl yield. The maximum ϕ_{acid} value of TmpXP is 0.73, which agrees roughly with the $\phi_{biphenyl}$ value of TmpXP (0.65).

Emission Spectra. During the photoirradiation of TAPs, a strong emission was detected. The fluorescence spectra of TAPs measured under N_2 purge with 254-nm irradiation, are as shown in Fig. 2 ($d_{254nm} = 0.61$). Every spectrum, except that of TooXP, has two emission bands around 290 nm and around 325 nm, shown in Fig. 2. The longer wavelength emission band of TooXP seemed to be too weak compared with that of the other compounds. In the spectra of TpTP and TmpXP,* the shorter wavelength emission band is detectable as a shoulder of the longer wavelength emission. The spectra were independent of the chromophore concentration. Thus, these compounds exhibit two kinds of emission bands. The emission maximum at shorter wavelength is assigned to monomer fluorescence and that at longer wavelength to the excimer fluorescence, shown in Eq. 3.

$$\text{TAP} \xrightarrow{h\nu} \underset{(\lambda = ca.290nm)}{\text{monomer fluorescence}} + \underset{(\lambda = ca.325nm)}{\text{excimer fluorescence}} \tag{3}$$

The quantum yields of the fluorescence ($\phi_{Fexcimer}$ and $\phi_{Fmonomer}$) are determined[9] roughly by means of integrated fluorescence intensity ($\int I_F \, d\nu$) and the ϕ_F value of phenol (0.066), when shapes of the spectra of the monomer and the excimer fluorescences are approximately the same as

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* The emission spectrum of TmpXP exhibits two emission bands (λ = 312 and 321-nm) and two shoulder bands (ca. 290 and 340 nm). The 312-nm band seemed to be a vibration band of the excimer fluorescence like the shoulder band around 340-nm.

Table IV. Results of Fluorescence Maximum and Its Quantum Yield.*

TAP	Monomer fluorescence				Excimer Fluorescence			
	λ_{max}/nm	$ø_{Fmono}/10^{-2†}$	QR/10^2 $M^{-1‡}$	τ_s/ns§	λ_{max}/nm	$ø_{Fex} \times 10^{-2†}$	QR‡/$10^2 M^{-1}$	τex¶/ns
ToTP	283.5	8	1.41	12	320	4	1.90	?
TmTP\	291	3	1.55	13	330	9	2.84	8
TpTP	292	2	1.1	9	321	8	2.74	10
TooXP	289	3	1.11	9	319	1	2.80	10
TopXP	289	5	1.13	9	328	5	2.07	8
TmpXP	290	—	1.17	10	321	9	ca. 3	ca. 6

* Measured in methanol with 254 nm light (d_{254}nm = 0.61 ± 0.01).

† Determined roughly by means of integrated fluorescence intensity.

‡ Quenching rate (QR) measured at 290 nm by using O_2 gas.

§ QR at 350–370 nm.

¶ Estimated roughly by means of the QR value and a quenching rate constants.

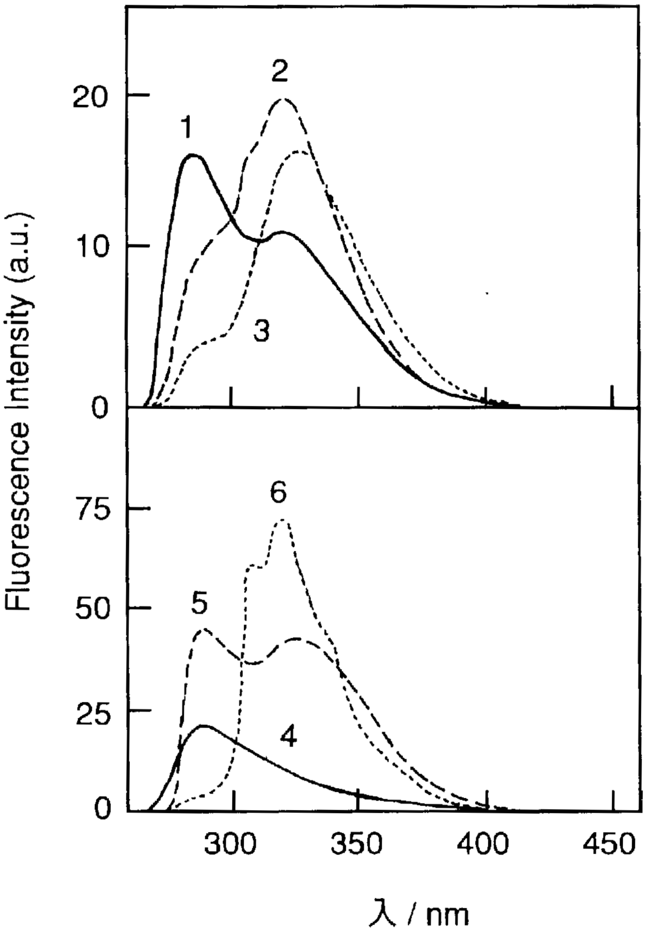


Figure 2. Emission spectra of ToTP (1), TmTP (2), TpTP (3), TooXP (4), TopXP (5) and TmpXP (6) in methanol ($\lambda_{ex.}$ = 254-nm, *d* = 0.61 ± 0.1).

those of phenyl acetate and TmpXP see Table IV. The $ø_{Fexcimer}$ value increased in the order: TooXP < ToTP < TmTP ~ TopXP < TpTP < TmpXP.

Quenching of Emissions by Oxygen. The fluorescence quenching of TAP was carried out in methanol to obtain information about the excited states by using oxygen as a quencher. A ratio of the fluorescence intensities (I_0/I) was plotted against oxygen concentration in methanol.[†] The symbols, I_0 and I, show the emission intensities in the absence and presence of oxygen, respectively. The fluorescence intensity measured at 290 nm for the monomer fluorescence and that at 350, 360, or 370 nm for the excimer fluorescence. Figure 3 shows the spectra, and Fig. 4 shows the Stern–Volmer plots for the TmTP fluorescence in the presence of oxygen. Good linear relations for both fluorescences were obtained for each TAP. The slopes of the plot [quenching rate] are about 1.1 × 10^2 M^{-1} for the monomer fluorescence and about 2.8 × 10^2 M^{-1} for the excimer fluorescence, as listed in Table IV.

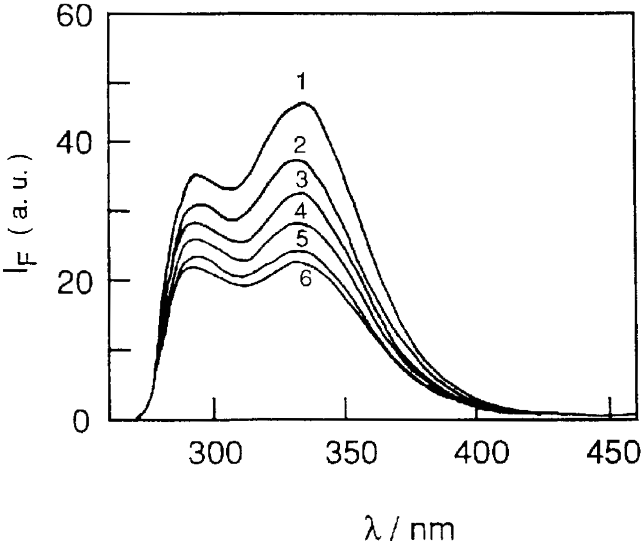


Figure 3. Emission spectra of TopXP in methanol. [O_2] = (from the top) 0.0 (1), 1.0 (2), 1.8 (3), 3.1(4), 4.1 (5) and 5.2 × 10^{-3} mol dm^{-3} (6).

Sensitivity. To make a thin photosensitive film, the grained aluminum plate was spin-coated with a solution of PSSt and TAP. After drying under vacuum, the coated film (film thickness: ca. 3 μm) was heated at 100°C (prebaking). The irradiation was carried out using a low-pressure Hg lamp. After irradiation, the film was heated at 100°C (post-baking). A 3% tetrabutylammonium hydroxide aqueous solution was used as the developer.

Sensitivities (*E*) were determined as the minimum energy necessary to deprotect the polymer. The results are listed in Table III. The *E* values related inversely with the $ø_{acid}$ values. The *E* value of PSSt–TmpXP film is the highest among the TAPs studied (*E* = 35 mJ cm^{-2}).

[†] Oxygen concentrations in methanol were assumed to be proportional to the ratio of oxygen gas in the mixed gas for the bubbling. Murov, S.L.; Camichael, I.; Hug, G.L., "Handbook of Photochemistry," second edition, revised and expanded, Marcel Dekker, Inc., New York, USA (1993) p. 291.

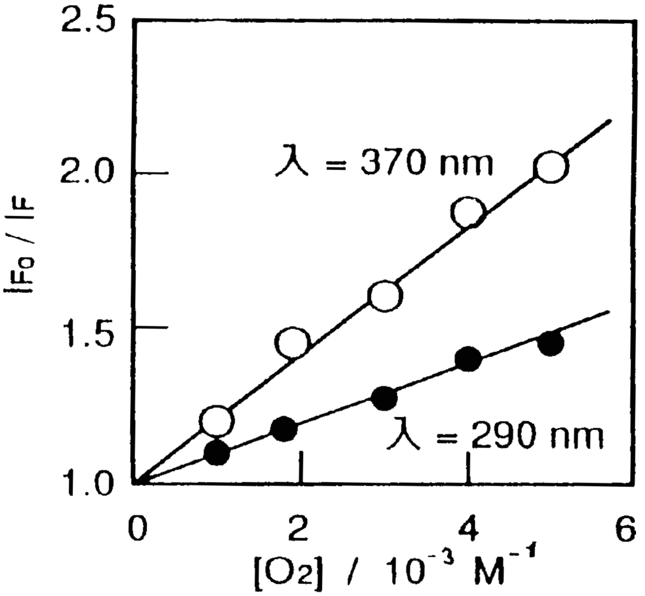
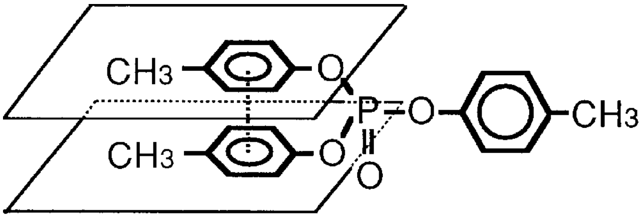


Figure 4. Plots of the ratios of the fluorescence intensities (I_{Fo} / I_F) versus oxygen concentration. The fluorescence intensities of TopXP were measured at 290-nm (●) and 370-nm (○).

Discussion

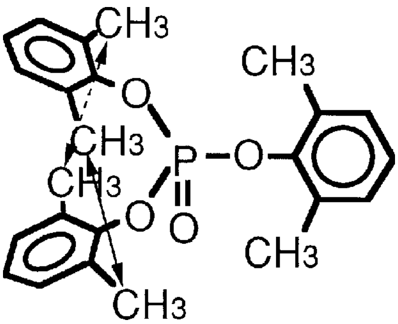
The photoreaction of TAP with 254-nm light yielded the biphenyl and monoaryl phosphate quantitatively. We concluded that the reaction proceeds by the way of the intramolecular excimer (IE) through the excited singlet state (^{1}TAP*), as seen[5] in the same reaction mechanism to that of TMP (Eq. 4).

$$\mathrm{TAP} \xrightarrow{h\nu} {}^1TAP^* \longrightarrow \text{intramolecular excimer (IE)}$$
$$\longrightarrow \text{bisaryl} + \text{monoaryl phosphate}. \qquad (4)$$



Scheme 2. Conformation of the intramolecular excimer (IE) for TpTP.

In the photoreactions of tris(4-substituted aryl) phosphate, the ϕ_{acid} value increased with decreasing σ_p value of the substituent.‡ It may reflect the π-electron density of the benzene ring. The reactivity of ToTP is anomalously smaller than those of TpTP and TmTP. The reaction of TAP proceeds through IE. It may be difficult to achieve the IE conformation owing to steric repulsions mainly between the methyl group and the methyl group belonging to the neighboring phenoxy group. Although the steric hindrance effects seem to decreases the reactivity effectively, that of TopXP is surprisingly high. Perhaps two methyl groups increase electron density of benzene ring enough, that small distortions of the IE conformation do not affect the reactivity of TAP. Indeed, the reactivity of TopXP is two to three times larger than that of TpTP. The ϕ_{Fex} value of TooXP is also smaller than those of TopXP and TmpXP. There are steric repulsions between the methyl group and the methyl group in the neighboring phenoxy groups. Scheme 3 shows a hypothetical conformation for TooXP, a typical compound. Steric repulsions between groups are indicated as fine-line type arrows. The reactivity of TooXP is too small to observe the steric hindrance effects described before. The order of the biphenyl yield agrees completely with that of the ϕ_{acid} value, as: ToTP < TmTP ~ TooXP < TpTP < TopXP < TmpXP. Although TmpXP is the most sensitive compound in the methyl-substituted TAPs studied, tris(3,4,5-trimethyl substituted phenyl) phosphate can be expected to be an even more sensitive compound than TmpXP owing to the effect of three methyl groups.



Scheme 3. Hypothetical conformation for TooXP. Fine-line type arrows show sterical repulsions between the methyl group and the methyl group of the neighboring phenoxy group.

To obtain information on ^{1}TAP* and IE, fluorescence quenching was carried out using oxygen gas. Both the fluorescences were quenched. Figure 4 shows the changes of ratios of the TopXP fluorescence intensities, I_{Fo}/I_F, in oxygen concentration monitored at 290- and 370-nm. The Stern–Volmer relation for the quenching of the monomer fluorescence is written as Eq. 5,

$$\phi_{Fmono,o} / \phi_{Fmono} = 1 + kqs\ \ \tau s[O_2], \qquad (5)$$

where $\phi_{Fmono,o}$ and ϕ_{Fmono} are the quantum yields of monomer fluorescence in the absence and presence of oxygen. The symbols, k_{qs} and τ_s, are the quenching rate constant for ^{1}TAP* and its life time. But the excimer fluorescence may be doubly quenched, because IE and its precursor, ^{1}TAP*, must be quenched by oxygen. The Stern–Volmer relation can then be written as Eq. 6,

$$\begin{aligned}\phi_{Fex,o} / \phi_{Fex} &= (1 + kqs\ \ \tau s[O_2])\ (1 + kqex\ \ \tau ex[O_2]) \\ &= 1 + (kqs\ \ \tau s + kqex\ \ \tau ex)[O_2] + kqs\ \ kqex\ \ \tau s\ \ \tau ex[O_2]^2, \qquad (6)\end{aligned}$$

where $\phi_{Fex,0}$ and ϕ_{Fex} are the excimer fluorescence quantum yields in the absence and presence of oxygen. The symbols, k_{qex} and τ_{ex} are the quenching rate constants and the life time of IE.

Because two good linear relations for the monomer fluorescence and for the excimer fluorescence are obtained in

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‡ In the photoreactions of tris(4-substituted aryl) phosphate,[5] when logarithmic ϕ_{acid} value was plotted against σ_p value of substituent group, a good linear relation was obtained.

each TAP, the last term in Eq. 6, $k_{qs}\ k_{qex}\ \tau_s\ \tau_{ex}\ [O_2]^2$, must be negligible. Then, the slope of the plot for the excimer fluorescence is the sum of quenching rates, $k_{qs}\tau_s + k_{qex}\tau_{ex}$. The quenching rate for the excimer, $k_{qex}\tau_{ex}$, can be estimated to be about $1.7 \times 10^2\ M^{-1}$ as a difference between the slopes. Both the life times may be estimated roughly by assuming diffusion-limited quenching rates and experimental rate constants determined for quenching of TMP fluorescences with oxygen [$k_q = 1.2 \times 10^{10}\ M^{-1}\ s^{-1}$ (monomer fluorescence), $1.7 \times 10^{10}\ M^{-1}\ s^{-1}$ (excimer fluorescence)[§]]. Although the lifetime of the singlet state is roughly constant in all TAPs (about 10 ns), that of the excimer changes [from 6 (TmpXP) to 10 ns (TpTP and TooXP)]. The latter life time seems to correlate with the reaction quantum yields.

The sensitivities of the thin films of PSSt and TAP were determined. The TmpXP film is the most sensitive ($E = 35$ mJ cm^{-2}). It can be concluded that the sensitivity is in proportion to the ϕ_{acid} value of TAP.

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[§] The quenching rate constants were calculated by means of quenching rates and lifetimes (τ_s and τ_{ex}) of tri(4-methoxyphenyl) phosphate in methanol.