

On the photolysis of acylphosphine oxides: 1. laser flash photolysis studies with 2,4,6-trimethylbenzoyldiphenylphosphine oxide

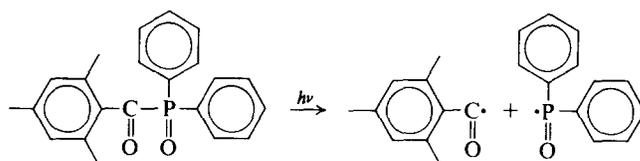
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(Received 27 February 1984)

2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMDPO) was irradiated in dilute solutions of benzene, methanol and dichloromethane with 20 ns flashes of 347 nm light. By optical absorption measurements, a transient spectrum with a maximum at about 330 nm detected at the end of the flash was ascribed to the diphenyl phosphonyl radical $(\text{Ph})_2\dot{\text{P}}=0$. This radical is formed by the reaction.

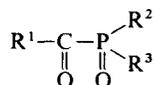


Evidence was obtained for fragment radicals being formed, to some extent at least, from triplet states. Both the singlet and the triplet lifetimes were estimated as $\tau < 1$ ns. The singlet energy was estimated as 288 kJ mol^{-1} . In the absence of radical scavengers $(\text{Ph})_2\dot{\text{P}}=0$ radicals undergo a self reaction ($2k_2 \approx 5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$). Rather high rate constants (in $\text{l mol}^{-1} \text{ s}^{-1}$) were found for reactions of $(\text{Ph})_2\dot{\text{P}}=0$ radicals with olefinic compounds: 6.0×10^7 (styrene), 6.0×10^7 (methyl methacrylate), 2.3×10^7 (methacrylate), 1.8×10^7 (acrylonitrile), 5.0×10^6 (t-butyl vinyl ether), 2.0×10^6 (vinyl acetate). The quantum yield of radical formation is $\phi(-\text{TMDPO}) = 0.5$ to 0.7 . These results clearly show why TMDPO is highly appropriate to be applied as an initiator for photocuring of coatings of various compositions.

(Keywords: photoinitiators; acylphosphine oxides; diphenylphosphonyl radicals; absorption spectra; reactivity towards olefinic compounds)

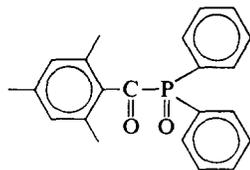
INTRODUCTION

Recently, acylphosphine oxides of the general structure



have been developed as a new class of u.v. photoinitiators¹.

Compounds with $\text{R}^1 = 2,4,6$ -trisubstituted benzoyl and R^2 and $\text{R}^3 = \text{phenyl}$, such as 2,4,6-trimethylbenzoyl diphenyl phosphine oxide (TMDPO)



were shown to be particularly suitable initiators for photocuring compositions based on acrylates of styrene-containing UP resins. TMDPO, as well as other acylphosphine oxides, exhibits a characteristic absorption in the near u.v. range with a maximum at $380 \text{ nm}^{2,3a}$ as can be seen from Figure 1. This absorption at relatively long wavelengths makes TMDPO particularly suitable for the initiation of photopolymerization in TiO_2 -pigmented coatings² and of thick-walled glass fibre-reinforced polyesters^{3b}.

In toluene or methanol solution, the quantum yield of TMDPO decomposition is 0.6 – 0.7 . Photolysis in methanol/ H_2O_2 gave strong evidence for α -scission to occur as is depicted in Scheme 1^{3a}.

In the presence of hydrogen peroxide the fragment radicals were converted to diphenylphosphinic acid (IV) and 2,4,6-trimethylbenzoic acid (V).

The present work is aimed at elucidating kinetics and mechanism of the photolysis of TMDPO in the presence of unsaturated compounds capable of undergoing radical polymerization. It was intended to measure the lifetime of the excited species giving rise to α -scission and, in

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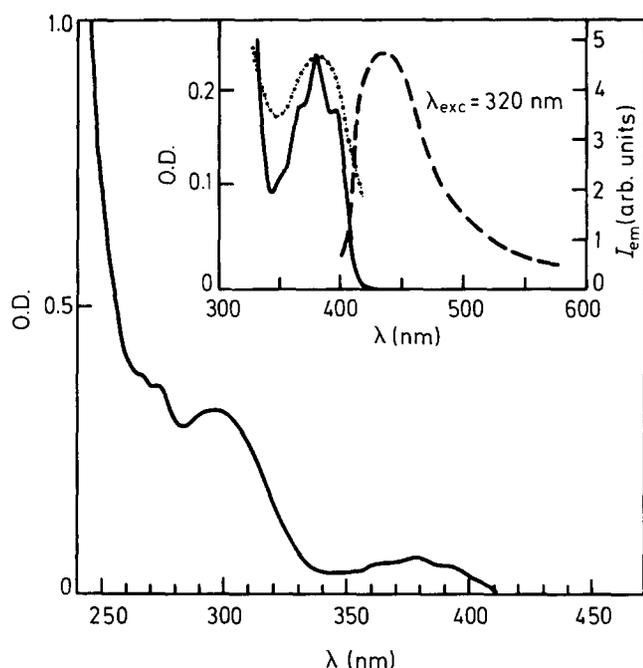
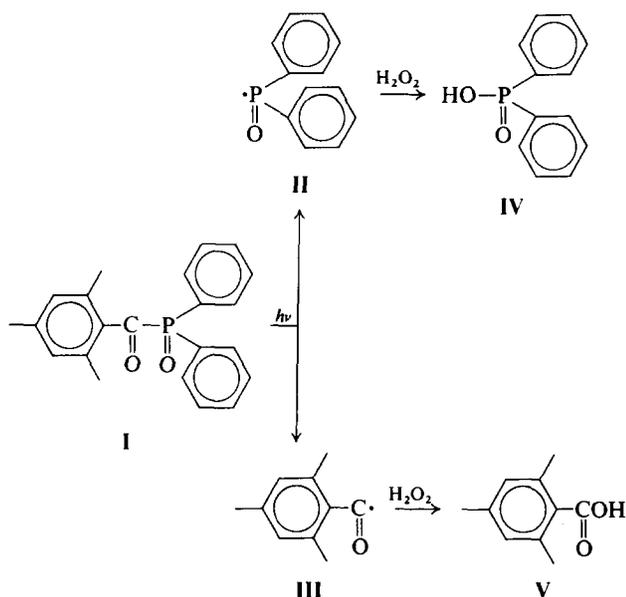


Figure 1 Ground state absorption spectrum of TMDPO (1.0×10^{-4} mol l^{-1}) in solution of CH_2Cl_2 recorded at 23°C. Inset: Ground state absorption spectrum (—), excitation (•••••) and emission (----) spectrum in benzene solution of TMDPO (4.2×10^{-4} mol l^{-1}). The excitation spectrum was recorded at $\lambda_{exc} = 440$ nm. The ground state absorption spectra in benzene and CH_2Cl_2 above 300 nm were identical



Scheme 1 Photolysis of TMDPO in methanolic solution containing hydrogen peroxide

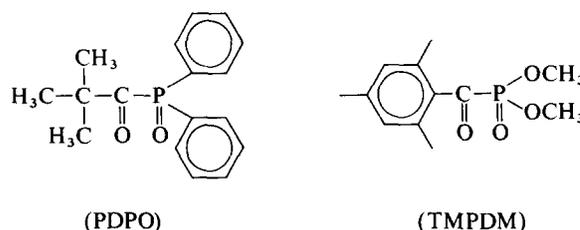
addition, to evaluate rate constants of the reaction of excited initiator molecules and/or of fragment radicals with various monomers.

EXPERIMENTAL

Materials

2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMDPO) was recrystallized from ether solution before use. Its synthesis was described previously^{1,2}. In a similar manner, pivaloyldiphenylphosphine oxide (PDPO) and

2,4,6-trimethylbenzoylphosphonic acid dimethylester (TMPDM) were synthesized.



Benzene (E. Merck, p.a. 99.5%) was washed with concentrated H_2SO_4 , dried over $CaCl_2$ and sodium, and subsequently distilled over a fractionation column (Fischer, Bonn). Methanol (E. Merck, Uvasol[®]) and dichloromethane (E. Merck, p.a.) were used as received.

The following monomers were used: methyl methacrylate (MMA), methyl acrylate (MA), styrene (St), acrylonitrile (AN), vinylacetate (VAc) and t-butyl vinyl ether (BVE). They were freed from stabilizers as has been described before⁴.

Irradiations

Dilute solutions of the initiator were irradiated in rectangular quartz cells, which were freed from oxygen by bubbling with purified argon. Irradiation was carried out at 347 nm with the aid of a ruby laser in conjunction with one frequency doubler. The duration of the flash was about 20 ns (halfwidth). Formation and decay of transients were followed by optical absorption and emission measurements. In addition, photocurrent measurements were conducted in order to test whether ionic intermediates were formed during or after the flash. The sensitivity of the set-up was checked with Ar-saturated solutions of anthracene (3×10^{-5} M) in methanol, where ions are readily formed upon irradiation with light of $\lambda_{inc} = 347$ nm⁵.

As can be seen from Figure 1, the absorption spectrum of TMDPO possesses two absorption bands with maxima at about 380 and 295 nm, which probably correspond to $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions. Accordingly, irradiation of TMDPO with light of $\lambda_{inc} = 347$ nm produces mainly vibronically excited states of the first excited singlet state.

Fluorescence spectra were recorded under continuous irradiation with the aid of a spectrofluorimeter (MPF-4, Perkin-Elmer). Fluorescence lifetimes were determined with a single photon counting apparatus (199M, Edinburgh Instruments).

Actinometry

In the flash photolysis experiments at $\lambda_{inc} = 347$ nm, the absorbed dose per flash was determined as follows: the optical absorption of naphthalene triplets formed by energy transfer from benzophenone (1.15×10^{-3} mol l^{-1}) at $[Naph] = 1.03 \times 10^{-1}$ mol l^{-1} , was measured at $\lambda = 425$ nm ($\epsilon_{T-T} = 2.3 \times 10^4$ l mol⁻¹ cm⁻¹, $\phi(T) = 1.0$). The maximum laser output at $\lambda = 347$ was 5.7×10^{16} photons per flash corresponding to an absorbed dose per flash, at O.D. = 0.1, of $D_{abs} = 3.6 \times 10^{-5}$ einstein l^{-1} .

RESULTS

Emission measurements with TMDPO

The emission spectrum shown in the inset of Figure 1 was recorded upon continuous irradiation of a benzene

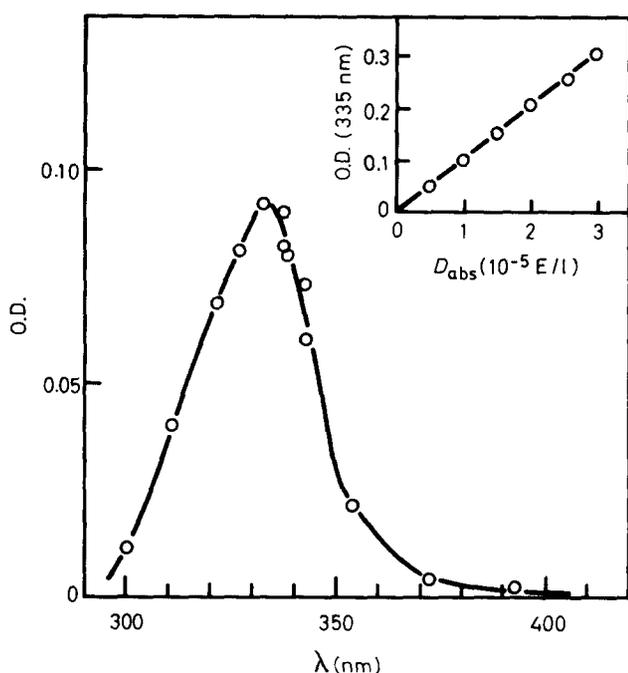


Figure 2 Transient absorption spectrum recorded immediately at the end of the laser flash with an Ar-saturated solution of TMDPO in CH_2Cl_2 ($4.2 \times 10^{-4} \text{ mol l}^{-1}$). $D_{\text{abs}} = 9.4 \times 10^{-6} \text{ Einstein l}^{-1}$. Inset: the optical density measured at the end of the flash as a function of the absorbed dose per flash

solution of TMDPO at $\lambda_{\text{exc}} = 320 \text{ nm}$. It possesses a maximum at about 440 nm . A similar emission spectrum was obtained with a CH_2Cl_2 solution. The inset of *Figure 1* also shows the excitation spectrum recorded at $\lambda = 440 \text{ nm}$. It is seen that excitation and absorption spectra are identical. Therefore, it is concluded that the emission band corresponds to the ground state absorption band due to the $S_0 \rightarrow S_1$ transition ($\lambda_{\text{max}} = 380 \text{ nm}$). From the intersection of the two spectra at 415 nm the singlet energy (o-o transition) of TMDPO was estimated as ca. 290 kJ mol^{-1} .

Upon flash irradiation at $\lambda_{\text{exc}} = 347 \text{ nm}$ a quite similar emission spectrum was observed. The emission formed and decayed during the flash (halfwidth ca. 20 ns). In order to search for a long-lived emission, a photomultiplier system (RCA, type 1P28) operated initially with two dynodes and, after a delay time of 400 ns , with 9 dynodes, was employed. However, a long-lived emission was not detected. The single photon counting technique also did not reveal a long-lived emitting transient. The kinetic analysis of the decay of the luminescence showed that about 99% of the emission decayed exponentially with a lifetime of about 0.3 ns . These results show that excited singlet states of TMDPO are very short-lived.

Absorption measurements with TMDPO

Upon irradiation of TMDPO in dilute solution with 20 ns flashes of $\lambda_{\text{inc}} = 347 \text{ nm}$ a transient difference spectrum in the wavelength range between 280 and 380 nm was observed. The difference spectrum was built up during the flash. In the absence of scavengers it decayed with 1st half-lives between 5 and $20 \mu\text{s}$ depending on the absorbed dose per flash. A typical difference spectrum ($\lambda_{\text{max}} = 331 \text{ nm}$) recorded with a CH_2Cl_2 solution is shown in *Figure 2*. Similar transient differential spectra were observed with solutions of TMDPO in benzene ($\lambda_{\text{max}} = 336 \text{ nm}$) and methanol ($\lambda_{\text{max}} = 328 \text{ nm}$). From the

inset in *Figure 2* it is seen that the transient optical density measured at the end of the flash increased linearly with increasing absorbed dose. In *Figure 3* the ground state absorption spectra of unirradiated and irradiated TMDPO are compared. Obviously the photolysis of TMDPO leads to products with absorption spectra different from that of TMDPO. The isobestic point at about 330 nm is identical to the maximum of the transient difference spectrum (see *Figure 2*). Therefore, this wavelength was considered quite appropriate for kinetic measurements (*vide infra*). At wavelengths of maximum difference, on the other hand, e.g. at 295 nm and 380 nm , the quantum yield of the conversion of TMDPO could be estimated. The value obtained, $\phi(-\text{TMDPO}) \approx 0.5-0.6$ compares satisfactorily with the value obtained at a much lower absorbed dose rate in solution of toluene and methanol, namely $\phi(-\text{TMDPO}) \approx 0.6-0.7^{3a}$.

With respect to the assignment of the transient absorption formed during the flash, the question arose whether bond cleavage according to *Scheme 1* occurred directly from excited singlet states or whether triplet states formed by intersystem crossing were involved. Evidence for the formation of triplets was obtained from experiments with benzene solutions of TMDPO containing naphthalene. At naphthalene concentrations greater than 0.5 mol l^{-1} the absorption spectrum of naphthalene triplets ($\lambda_{\text{max}} = 425 \text{ nm}$) was observed. Typical data are shown in *Table 1*. Concurrently with the formation of the absorption at 425 nm the maximum at 336 nm decreased. It appears that naphthalene triplets were formed by energy transfer from TMDPO triplets to naphthalene in competition with fragmentation into radicals according to reaction (2)

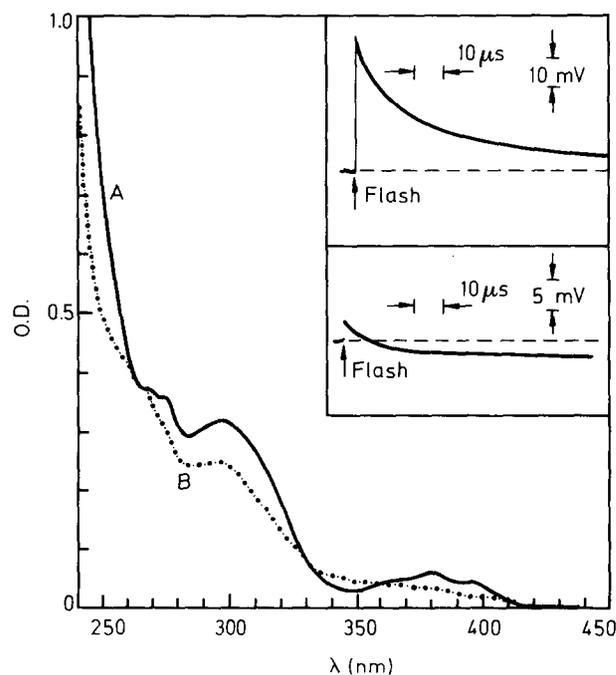
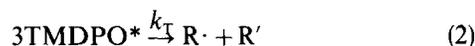


Figure 3 Ground state absorption spectra of TMDPO in Ar-saturated CH_2Cl_2 solution (A) before and (B) after irradiation with a laser flash of 347 nm light ($D_{\text{abs}} = 5.2 \times 10^{-5} \text{ Einstein l}^{-1}$). Optical density at $d = 1.0 \text{ cm}$ vs. wavelength. Inset: oscilloscope traces depicting the change of the O.D. at $\lambda = 335 \text{ nm}$, $U_0 = 104 \text{ mV}$ and $\lambda = 380 \text{ nm}$, $U_0 = 152 \text{ mV}$

Table 1 Transient absorption (at $\lambda = 425$ nm) observed at the end of the flash due to naphthalene triplets. TMDPO (4.2×10^{-4} mol l⁻¹) in Ar-sat. benzene solution, $D_{\text{abs}}: 1.9 \times 10^{-5}$ einstein l⁻¹

[Naph] (mol l ⁻¹)	O.D. ($\lambda = 425$ nm)
0.5	0.006
1.0	0.01
2.0	0.02



By considering the two reactions, the O.D. of naphthalene triplets observed at the end of the flash should depend on the naphthalene concentration according to equation (3)

$$\frac{(\text{O.D.})_{\text{total}}}{(\text{O.D.})} = 1 + \frac{k_T}{k_Q[\text{Q}]} \quad (3)$$

where $(\text{O.D.})_{\text{total}}$ is the optical density that would be observed if all TMDPO triplets were quenched by naphthalene. With the data of Table 1 the lifetime of TMDPO triplets is estimated as 0.3 ns by assuming $k_Q = 1 \times 10^9$ l mol⁻¹ s⁻¹, i.e. the lifetime is much shorter than the duration of the flash (ca. 20 ns). This result implies that the absorption band at 336 nm observed at the end of the flash is to be attributed to fragment radicals. The triplet energy of TMDPO must be greater than that of naphthalene, i.e. $E_T(\text{TMDPO}) > 251$ kJ mol⁻¹.

In this connection it has to be considered (a) that naphthalene does not absorb light at $\lambda = 347$ nm, and (b) that singlet quenching can be excluded for energetical reasons ($E_S(\text{Naph}) = 385$ kJ mol⁻¹ > $E_S(\text{TMDPO}) \approx 290$ kJ mol⁻¹). Because it was not possible for practical reasons to employ naphthalene concentrations high enough to suppress the formation of the transient absorption at 336 nm completely it cannot be decided whether bond breakage according to Scheme 1 involves both singlet- and triplet-excited or just triplet excited states of TMDPO. However, it is obvious that triplet states are involved in bond breakage.

The assignment of the absorption band at 336 nm observed with TMDPO solutions at the end of the flash to fragment radicals was affirmed by the following findings: The rate of decay of the transient O.D. is significantly increased by O₂ and unsaturated compounds capable of reacting with free radicals (*vide infra*). In the absence of scavengers, the decrease of the transient O.D. follows 2nd order kinetics as can be seen from Figure 4, where the reciprocal half-life is plotted vs. the initial O.D. (measured at the end of the flash). A linear relationship between these two parameters is expected on the basis of equation (4)

$$(\tau_{1/2})^{-1} = 2k_R[\text{R} \cdot]_0 \quad (4)$$

which is derived from equation (5)

$$\frac{1}{[\text{R} \cdot]_t} = \frac{1}{[\text{R} \cdot]_0} + 2k_R t \quad (5)$$

where $[\text{R} \cdot]_0 (\propto (\text{O.D.})_0)$ is the initial concentration of radicals and k_R is the bimolecular rate constant for the reaction $\text{R} \cdot + \text{R} \cdot$. The possibility of an assignment of the

transient differential absorption spectrum to ionic intermediates can be discarded because experiments with methanolic solutions of TMDPO showed that neither during nor after the flash a photocurrent was formed.

Reactions of radicals produced from TMDPO with oxygen and unsaturated compounds

As has been mentioned above, the transient absorption decayed very rapidly in the presence of O₂. By recording the decrease of the absorption in benzenic solution of TMDPO, at $\lambda_{\text{obs}} = 335$ nm, at two oxygen concentrations (1.9×10^{-3} and 9.5×10^{-3} mol l⁻¹) a bimolecular rate constant $k_{\text{R} \cdot + \text{O}_2} = 2.5 \times 10^9$ l mol⁻¹ s⁻¹ was determined.

The reactivity of initiator radicals towards various unsaturated compounds was investigated by measuring the rate of the decrease of the O.D. at $\lambda_{\text{obs}} = 335$ nm with Ar-saturated benzene solutions containing 4.2×10^{-4} mol l⁻¹ TMDPO and, in addition, a monomer at a concentration greater than 10^{-2} mol l⁻¹. Under this condition pseudo-1st order kinetics prevailed:

$$-\frac{d[\text{R} \cdot]}{dt} = k_{\text{R} \cdot + \text{M}}[\text{M}][\text{R} \cdot] = k_1[\text{R} \cdot] \quad (6)$$

with $k_1 = k_{\text{R} \cdot + \text{M}}[\text{M}]$ and $(\tau_{1/2})^{-1} = \frac{k_1}{\ln 2}$

In Figure 5 the reciprocal half-life is plotted vs. the monomer concentration. Bimolecular rate constants obtained from the slopes of the straight lines are compiled in Table 2.

For comparison, Table 2 also contains values of rate constants $k_{\text{R} \cdot + \text{M}}$ which were determined in former work with 1-phenyl-2-hydroxy-2-methyl-propanone-1 (PHMP)⁷ and benzoinmethylether (BME)⁸. These compounds also undergo α -scission upon irradiation with u.v.-light:

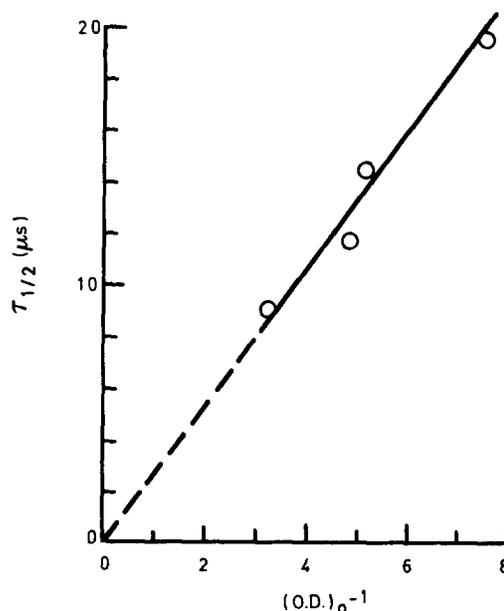
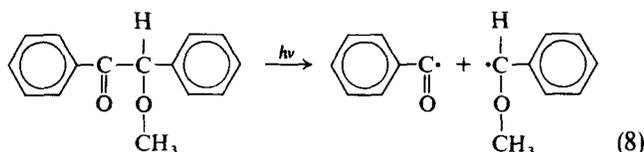
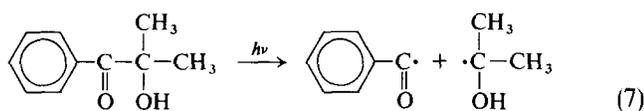


Figure 4 Plots of first 2nd order half-lives vs. the reciprocal initial optical density, measured with Ar-saturated solutions at the end of the flash at different absorbed doses per flash at $\lambda_{\text{obs}} = 335$ nm in benzene at 23°C. $[\text{TMDPO}] = 4.2 \times 10^{-4}$ mol l⁻¹



The rate constants compiled in Table 2 are, in principle, composite rate constants comprising the reactions of both fragment radicals with the respective monomer. A comparison of the values reveals that the radicals produced by the photolysis of TMDPO are much more reactive towards monomers than the radicals generated from the other two initiators. If it is taken into account, moreover, that PHMP and BME form benzoyl-type radicals as well as does TMDPO, it becomes obvious that the very high reactivity of radicals stemming from TMDPO must be

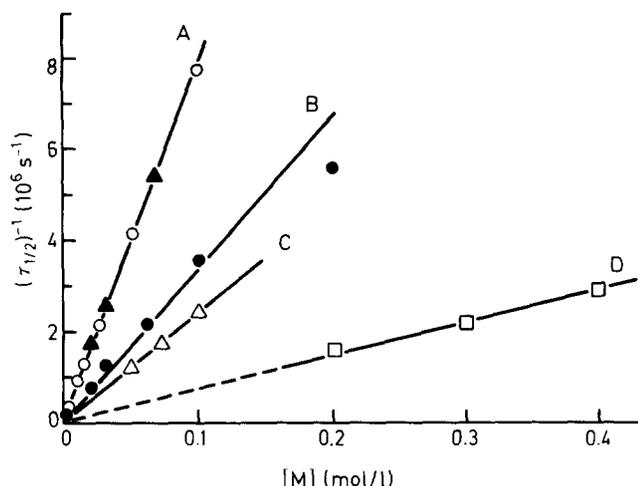
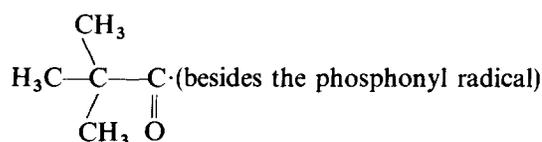


Figure 5 Reciprocal pseudo-1st order half-lives as a function of the monomer concentration $[M]$. The measurements were carried out in Ar-saturated benzene solutions at $\lambda_{\text{obs}} = 335 \text{ nm}$ at an absorbed dose of $2.2 \times 10^{-5} \text{ Einstein l}^{-1}$. $[\text{TMDPO}] = 4.2 \times 10^{-4} \text{ mol l}^{-1}$. Curve (A) = St MMA; curve (B) = MA; curve (C) = AN; curve (D) = BVE

due to the reactivity of radicals of the type $(\text{Ph})_2\text{P}=\text{O}$ (Ph = phenyl), and that these radicals must be much more reactive than the partner radicals, i.e. 2,4,6-trimethylbenzoyl radicals, that are generated simultaneously. Following this line, it turns out that the transient absorption observed in the flash photolysis of TMDPO is essentially due to the absorption of radicals of the type $(\text{Ph})_2\text{P}=\text{O}$. This point will be dealt with in more detail in the next section.

Experiments with PDPO and TMPDM

These two compounds were studied in order to substantiate the assumption that the transient absorption spectrum observed with TMDPO was essentially due to the absorption of phosphonyl radicals $(\text{Ph})_2\text{P}=\text{O}$. As a matter of fact, PDPO yielded almost the same transient absorption spectrum with $\lambda_{\text{max}} = 325 \text{ nm}$ as TMDPO upon irradiation in Ar-saturated methanolic solution. In this case, α -scission causes the generation of the radical



which possesses a much lower absorptivity in the wavelength range between 300 and 350 nm than the benzoyl radical, which is produced in the photolysis of TMDPO. Because the same transient absorption spectrum (of comparable intensity) was generated both with PDPO and TMDPO, it is concluded that this spectrum can be attributed to the phosphonyl radical $(\text{Ph})_2\text{P}=\text{O}$.

A quite different situation was encountered with TMPDM. After the rapid decay of the absorption of a short-lived species ($\tau_{1/2}$: 30–40 ns) a long-lived transient absorption spectrum with a maximum at a significantly longer wavelength, i.e. at 380 nm, was detected upon irradiation of TMPDM in solution of methanol, dichloromethane and benzene. It decayed with a lifetime much longer than that measured in the cases of TMDPO and PDPO. This finding indicates that, provided dimethoxy phosphonyl radicals, $(\text{H}_3\text{CO})_2\text{P}=\text{O}$, were formed, their absorptivity is much lower than that of $(\text{Ph})_2\text{P}=\text{O}$ radicals. The possibility of assigning this

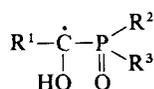
Table 2 Bimolecular rate constants (in $\text{l mol}^{-1} \text{ s}^{-1}$) of the reaction of initiator radicals with various monomers

Monomer	TMDPO	PHMP*	BME**
Styrene	$(6.0 \pm 0.3) 10^7$	4.7×10^5	1.6×10^5
Methyl methacrylate	$(6.0 \pm 0.3) 10^7$	6.3×10^5	0.9×10^5
Methylacrylate	$(2.3 \pm 0.2) 10^7$		
Acrylonitrile	$(1.8 \pm 0.2) 10^7$	1.6×10^6	0.2×10^5
t-Butylvinyl ether	$(5.0 \pm 0.3) 10^6$		
Vinyl acetate	$(2.0 \pm 0.2) 10^6$		1.5×10^5

* 1-Phenyl-2-hydroxy-2-methylpropanone-1⁷

** Benzoinmethylether⁸

transient absorption spectrum to ketyl radicals of the structure



is discarded because similar results were obtained in different solvents. Ketyl radicals could be formed via hydrogen abstraction from solvent molecules by excited TMPDM molecules. This reaction should be much less probable in benzene than in the other two solvents. The fact that no solvent effect was observed indicates that photoreduction does not occur to a detectable extent¹³.

With respect to the assignment of the transient optical absorption found with TMDPO, similar conclusions were arrived at by experiments with other acylphosphine oxides having different substituents. Details will be reported in a forthcoming paper.

DISCUSSION

The important results of this paper concern (a) the assignment of the transient absorption spectrum with its maximum around 330 nm, detected during the flash photolysis of TMDPO to diphenyl phosphonyl radicals, $(\text{Ph})_2\dot{\text{P}}=\text{O}$, and (b) the finding that these radicals are of relatively high reactivity towards compounds having olefinic double bonds.

The assignment of the transient absorption spectrum is essentially based on the fact that the extinction coefficient of $(\text{Ph})_2\dot{\text{P}}=\text{O}$ radicals around 330 nm is significantly higher than that of the partner radicals, generated simultaneously with the diphenylphosphonyl radicals. While this fact became obvious by comparing the transient absorption spectra observed with TMDPO and PDPO it can also be substantiated by results obtained with other compounds yielding benzoyl radicals upon photolysis by u.v. light. Such compounds are, e.g., pivalophenone⁹, poly(phenyl isopropenyl ketone)⁹ and hydroxyalkyl phenones¹⁰. In these cases, transient absorption spectra with maxima around 340, 370 and 410 nm, which were assigned to benzoyl radicals, were observed. However, the extinction coefficients were, generally, very low and amounted at the maxima only to a few hundred $\text{l mol}^{-1} \text{cm}^{-1}$. A much higher ϵ value is estimated, for example, from the transient optical density $(\text{O.D.})_0 = 0.09$ recorded at 335 nm with a solution of TMDPO in benzene at the end of the flash at $D_{\text{abs}} = 9.4 \times 10^{-6}$ einstein/l. From equation (9)

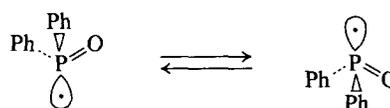
$$\epsilon_{335} = \frac{(\text{O.D.})_0}{D_{\text{abs}}\phi(\text{R}\cdot)d} \quad (9)$$

one obtains, with $d = 1$ cm, $\epsilon_{335} = 9.6 \times 10^3 / \phi(\text{R}\cdot)$. Because of the uncertainty about the exact value of $\phi(\text{R}\cdot)$, a lower and an upper limit of ϵ can be given, only: with $\phi(\text{R}\cdot) = 1.0$: $\epsilon_{335} = 9.6 \times 10^3 \text{ l mol}^{-1} \text{cm}^{-1}$ (lower limit), and with $\phi(\text{R}\cdot) = 0.5$: $\epsilon_{335} = 1.92 \times 10^4 \text{ l mol}^{-1} \text{cm}^{-1}$ (upper limit). Therefore, it is concluded that the transient absorption spectrum observed in the present work with TMDPO dissolved in various solvents is to be assigned to diphenylphosphonyl radicals.

The high reactivity of diphenylphosphonyl radicals towards olefinic compounds is remarkable. Indeed, the

biomolecular rate constants compiled in Table 2 demonstrate that, due to the high reactivity of $(\text{Ph})_2\dot{\text{P}}=\text{O}$ radicals, TMDPO is most appropriate among other initiators to initiate the free radical polymerization of various monomers.

It has been pointed out by Bentrude¹¹ that phosphonyl radicals of the general structure $\text{R}_2\dot{\text{P}}=\text{O}$ are expected to dimerize readily. This becomes feasible since e.s.r. investigations¹² revealed a pyramidal configuration of $\text{Ph}_2\dot{\text{P}}=\text{O}$ and similar radicals with a high degree of spin density on phosphorus:



This expectation was substantiated in this work. The kinetic analysis of the decay of the absorption at $\lambda = 335$ nm resulted in $2k_2/\epsilon = 3.8 \times 10^5 \text{ s}^{-1}$ (in benzene solution at 23°C). With the aid of the extinction coefficient of $\text{Ph}_2\dot{\text{P}}=\text{O}$ (*vide ante*) at 335 nm one obtains $2k_2 = 3.6 \times 10^9 - 7.3 \times 10^9 \text{ l mol}^{-1} \text{s}^{-1}$, i.e. k_2 refers to an encounter-controlled reaction.

ACKNOWLEDGEMENTS

The authors are grateful to Dr G. Beck for maintaining the ruby laser and to Dr R. B. Frings for carrying out the fluorescence lifetime measurements. The experiments with vinyl acetate were carried out by Mr W. K. Wong. One of the authors (T.S.) expresses his thanks to the Nishina Memorial Foundation for supporting him financially.

Note added in proof

The long-lived absorption is due to the triplet of an enol generated by intramolecular hydrogen abstraction.

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