

## LASER FLASH PHOTOLYSIS OF ACYL PHOSPHONIC ACID ESTERS

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(Received September 7, 1984)

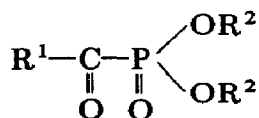
## Summary

Dilute solutions of 2,4,6-trimethylbenzoylphosphonic acid dimethyl ester (TMPDM), 2,4,6-trimethylbenzoylphosphonic acid diethyl ester (TMPDE) and benzoylphosphonic acid diethyl ester (BPDE) in various solvents were irradiated with 20 ns flashes of 347 nm light. TMPDE and TMPDM formed triplets ( $\phi(T) \approx 0.6$ ) which were readily converted to enol triplets ( $k_T^K \geq 5 \times 10^7 \text{ s}^{-1}$ ). The enol triplets relaxed to *Z* and *E* isomers ( $k_T^E = 1.7 \times 10^7 \text{ s}^{-1}$ ). The difference optical absorption spectra of the enol triplet and the (relaxed) enol isomers were recorded. The reketonization rate constants were found to depend on the nature of the solvent: they were higher for the *Z* isomer ( $(1.0 - 3.4) \times 10^6 \text{ s}^{-1}$ ) than for the *E* isomer ( $1 \times 10^3 - 7 \times 10^4 \text{ s}^{-1}$ ). The reketonization of the *E* isomers was accelerated by UV irradiation. Both TMPDE and TMPDM undergo  $\alpha$  scission mainly (if not exclusively) from singlet states as detected by the formation of adduct radicals ( $\phi = 0.3 \pm 0.1$ ) generated by reaction of dialkoxyphosphonyl radicals with benzene ( $k_{ad} = 4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ) and with styrene ( $k_{ad} = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). TMPDM is capable of acting as a photoinitiator for the free-radical polymerization of methyl methacrylate (MMA). BPDE formed triplets ( $\phi(T) = 0.9$ ) which were converted to biradicals by intramolecular hydrogen abstraction ( $k_T \approx 1.2 \times 10^7 \text{ s}^{-1}$ ). BPDE did not undergo  $\alpha$  scission and was found to be incapable of acting as a photoinitiator for the polymerization of MMA.

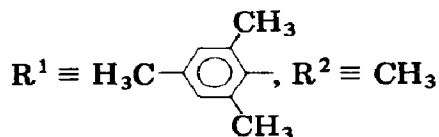
## 1. Introduction

Kinetic and mechanistic studies of the photolysis of some acyl phosphonates of the general structure

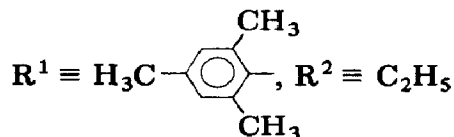
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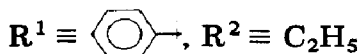
2,4,6-trimethylbenzoylphosphonic acid dimethyl ester (TMPDM):



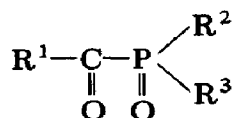
2,4,6-trimethylbenzoylphosphonic acid diethyl ester (TMPDE):



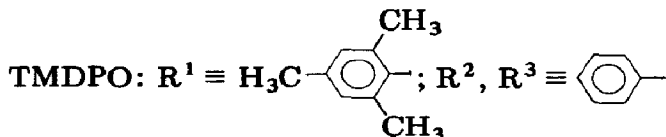
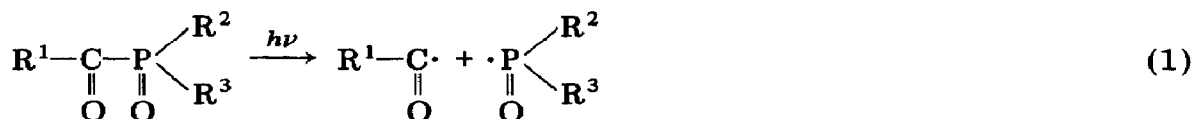
benzoylphosphonic acid diethyl ester (BPDE):



are reported in this paper. Both acyl phosphonates and acylphosphine oxides of the general structure



have been reported to be capable of acting as photoinitiators for the free-radical polymerization of olefinic compounds [1 - 4]. It has recently been shown by Sumiyoshi *et al.* [5, 6] that the pronounced initiator efficiency of 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMDPO) is essentially due to the high quantum yield (0.5 - 0.7) of radical formation via the reaction

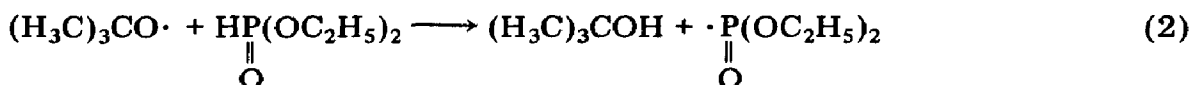


and the high reactivity of diphenylphosphonyl radicals towards olefinic compounds.

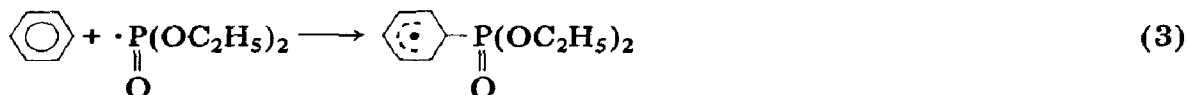
The existence of two intermediates with absorption maxima at about 380 nm and with lifetimes of several hundred nanoseconds and several

microseconds respectively was inferred from preliminary flash photolysis experiments with TMPDM and TMPDE [6]. Because a straightforward assignment of these species was not possible, additional experiments with the two trimethyl-substituted compounds (TMPDM and TMPDE) and the non-methyl-substituted compound (BPDE) were carried out. With all three compounds another short-lived species ( $\tau \approx 50$  ns) was detected which was ascribed to triplet excited molecules. Moreover it was evident that in the photolysis of TMPDM and TMPDE  $\alpha$  scission became operative simultaneously with an intramolecular rearrangement process. In the case of BPDE  $\alpha$  scission could not be detected and it appeared that the major route of deactivation of excited states was radiationless transition to the ground state.

In connection with the present investigation previous work by Griller and coworkers [7, 8] and Anpo *et al.* [9] is noteworthy. These workers used electron paramagnetic spectroscopy to study the reactions of diethoxyphosphonyl radicals that were generated by the reaction of *tert*-butoxyl radicals with diethyl phosphite:



The observed addition of diethoxyphosphonyl radicals to benzene, leading to the substituted cyclohexadienyl radical



was particularly relevant to the present work in which it served as a probe reaction for detecting  $\alpha$  scission (reaction (1)) of the acylphosphonates under investigation. As has been reported by Griller *et al.* [8] the rate constant of reaction (3) in iso-octane solution at room temperature is  $2.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . The absorption spectrum of the resulting cyclohexadienyl radical possesses a rather narrow band with a maximum at 326 nm ( $\epsilon = 2.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). In earlier work performed by Terauchi and Sakurai [10] it was found that BPDE formed a cyclic trimer upon irradiation with light with  $\lambda > 320$  nm in cyclohexane solution. The quantum yield of disappearance of BPDE was found to be 1.85. These workers [10] claimed that the photochemical reactions of benzoylphosphonates proceed via excited triplet states and that  $\alpha$  scission according to reaction (1) does not occur. Ketyl radicals formed by hydrogen abstraction from the solvent or from non-excited phosphonate molecules were postulated as intermediates. Work on light-induced addition reactions of diethylphosphites to olefins at temperatures between 100 and 110 °C was reviewed by Sosnovsky [11]. It was assumed that free phosphonyl radicals were involved in these reactions. A survey of work on phosphonyl radicals and other phosphorus-centred radicals which had been performed up to about 1971 was given by Bentrude in ref. 12. To the best of our knowledge the photochemical reactions of trimethyl-substituted benzoylphosphonates such as TMPDM and TMPDE have not been investigated systematically up to now.

## 2. Experimental details

### 2.1. Materials

TMPDM, TMPDE and BPDE were synthesized as described previously [1, 2, 4]. Benzene (E. Merck pro analysi grade (purity, 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, dichloromethane, tetrachloromethane and cyclohexane (all Uvasol grade obtained from E. Merck) were used as received. Styrene and methyl methacrylate (E. Merck pro synthesis grade) were freed from the stabilizer by repetitive washing with NaOH solution and water. After drying over  $CaCl_2$  and  $CaH_2$  they were distilled over a fractionation column. *trans*-Piperylene (*trans*-1,3-pentadiene) (EGA (purity, 99%)) was used as received. Naphthalene (E. Merck scintillation grade) and benzophenone (Aldrich (purity, 99%)) were recrystallized from ethanol and heptane solutions respectively.

### 2.2. Irradiation

Dilute solutions of phosphonates from which oxygen had been removed by bubbling with purified argon were irradiated in rectangular quartz cells. The irradiations were carried out at 347 nm with the aid of a ruby laser operated in conjunction with a frequency doubler. The duration of the flash was about 20 ns (halfwidth). The formation and decay of the transients were monitored by optical absorption measurements. As can be seen from Fig. 1, the absorption spectra of the three phosphonates possess maxima in the range between 350 and 380 nm corresponding to  $S_0 \rightarrow S_1$  transitions as shown by fluorescence excitation spectra. Accordingly, irradiation with light with  $\lambda_{inc} = 347$  nm produced mainly vibronically excited states of the first electronically excited singlet state.

The fluorescence spectra were recorded under continuous irradiation using a spectrofluorometer (Perkin-Elmer MPF-4). The fluorescence

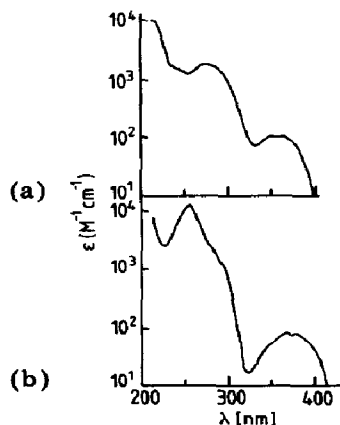


Fig. 1. Ground state absorption spectra of (a) TMPDE and (b) BPDE recorded in cyclohexane solutions at 23 °C.

lifetimes were determined using a single-photon-counting apparatus (Edinburgh Instruments 199M).

### 2.3. 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 (concentration,  $1.15 \times 10^{-3}$  mol l<sup>-1</sup>) at  $[Naph] = 1.03 \times 10^{-1}$  mol l<sup>-1</sup> was measured at  $\lambda = 425$  nm ( $\epsilon_{T-T} = 1.32 \times 10^4$  l mol<sup>-1</sup> cm<sup>-1</sup> [13];  $\phi(T) = 1.0$ ). The maximum laser output at  $\lambda = 347$  nm was  $5.7 \times 10^{16}$  photons per flash corresponding to an absorbed dose per flash  $D_{abs}$  of  $3.6 \times 10^{-5}$  einsteins l<sup>-1</sup> at an optical density (OD) of 0.1.

### 2.4. Bulk polymerization experiments

Methyl methacrylate and styrene containing  $1.1 \times 10^{-3}$  M TMPDM or BPDE were irradiated at 20 °C in glass ampoules under argon using a high pressure mercury lamp (Original Hanau TQ 718-600 W). The solutions were protected against light with  $\lambda < 300$  nm by a Duran glass shield 7 mm thick. The polymer generated during the irradiation was precipitated from acetone solution with methanol. The monomer conversion, which was determined gravimetrically, exhibited a linear dependence on the absorbed dose up to conversions of about 4%.

## 3. Results

### 3.1. Experiments with 2,4,6-trimethylbenzoylphosphonic acid dimethyl ester and 2,4,6-trimethylbenzoylphosphonic acid diethyl ester

#### 3.1.1. Emission measurements

Emission and excitation spectra recorded on continuous irradiation of TMPDM in cyclohexane solution are presented in Figs. 2(a) and 2(b). The emission spectrum possesses a maximum around 440 nm and the excitation spectrum strongly resembles the absorption band between 330 and 400 nm (see Fig. 1(a)). It is therefore concluded that this absorption band corresponds to the  $S_0 \rightarrow S_1$  transition. The singlet energy  $E_S$  was evaluated as about 308 kJ mol<sup>-1</sup>. Flash excitation at 347 nm yielded a similar emission spectrum. The emission formed and decayed during the flash (halfwidth, about 20 ns). With the aid of the single-photon-counting technique the singlet lifetime  $\tau_S$  was determined to be 0.7 ns. A longer-lived emission was not detectable. As analogous results were obtained from emission measurements with TMPDE in cyclohexane solution they are not described here in detail.

#### 3.1.2. Transient absorption spectra

Dilute solutions of TMPDM and TMPDE in benzene, tetrachloromethane, dichloromethane and methanol were irradiated with 20 ns flashes

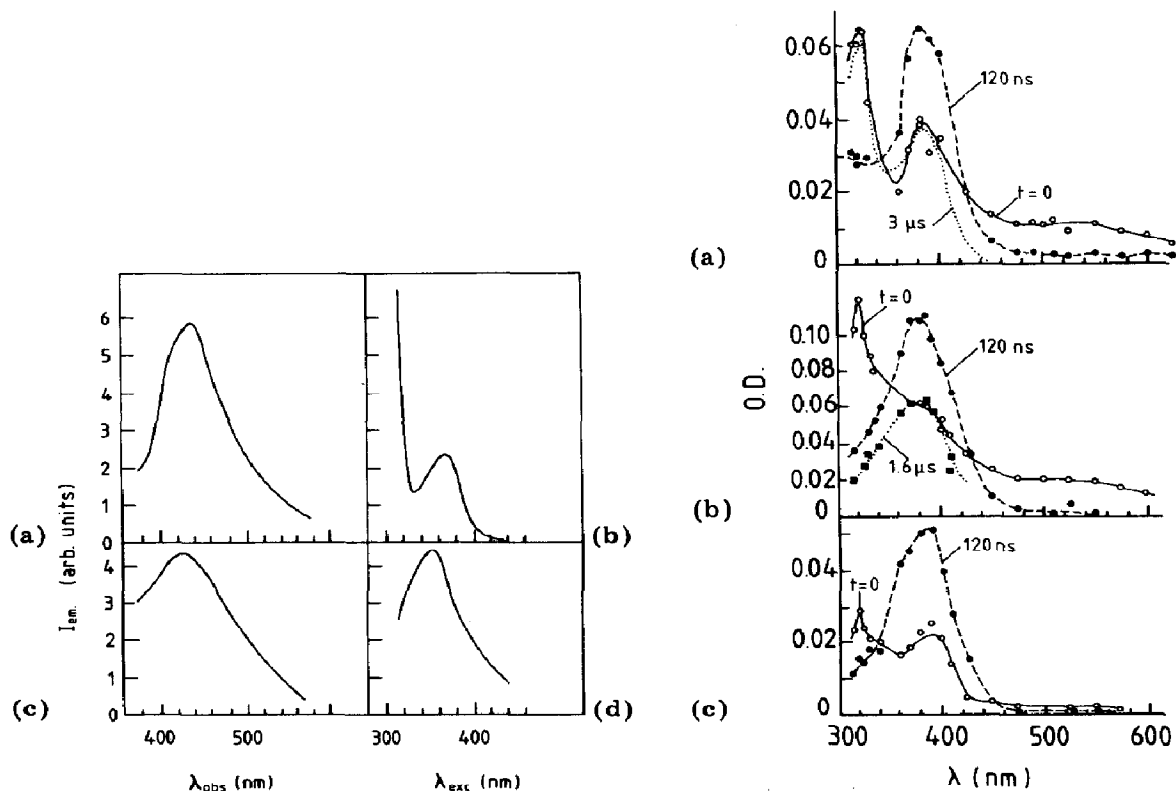
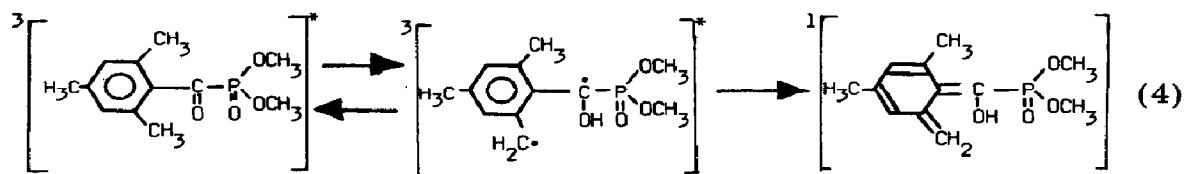


Fig. 2. Emission and excitation spectra of TMPDM and BPDE in cyclohexane solution recorded under continuous irradiation ( $[TMPDM] = 2.6 \times 10^{-3}$  M;  $[BPDE] = 3.8 \times 10^{-3}$  M): (a) fluorescence emission spectrum of TMPDM ( $\lambda_{exc} = 347$  nm); (b) excitation spectrum of TMPDM ( $\lambda_{obs} = 440$  nm); (c) fluorescence emission spectrum of BPDE ( $\lambda_{exc} = 347$  nm); (d) excitation spectrum of BPDE ( $\lambda_{obs} = 440$  nm).

Fig. 3. Transient absorption spectra recorded at various times after the flash for TMPDM in argon-saturated solutions of various solvents: (a)  $2 \times 10^{-3}$  M TMPDM in benzene,  $D_{abs} = 2.0 \times 10^{-5}$  einsteins  $l^{-1}$ ; (b)  $2.5 \times 10^{-3}$  M TMPDM in tetrachloromethane,  $D_{abs} = 5.2 \times 10^{-5}$  einsteins  $l^{-1}$ ; (c)  $1.8 \times 10^{-3}$  M TMPDM in dichloromethane,  $D_{abs} = 3.5 \times 10^{-5}$  einsteins  $l^{-1}$ .

of 347 nm light. Inspection of the spectral changes in the solutions as a function of time after the flash showed that four different transient species, designated below as A, B, C and D, could be discriminated. Figure 3 shows typical transient spectra obtained with TMPDM. In all solvents a spectrum with a strong maximum at 320 nm and a much weaker maximum at 520 nm was formed during the flash, and this was ascribed to species A. From the results of quenching experiments with naphthalene and piperylene it was inferred that species A corresponds to triplet-excited TMPDM molecules, *i.e.* the spectrum formed during the flash is a triplet-triplet (T-T) absorption spectrum. In all solvents this spectrum decayed by a first-order process with lifetimes ranging from 45 to 60 ns. Simultaneously with the decay of species A a new absorption spectrum was formed with a maximum at about 380 nm, and this is ascribed to species B. The spectra recorded 120 ns

after the start of the flash are also shown in Fig. 3. They show two decay modes indicating the existence of another species C. The first-order lifetimes measured in solutions of various solvents ranged from 290 to 1000 ns (rapid mode, species B) and from 15 to 870  $\mu$ s (slow mode, species C). All the kinetic data are compiled in Table 1. Because both absorption decay modes at 380 nm followed first-order kinetic laws and because the decay rates were independent of the absorbed dose rate and the phosphonate concentration the corresponding processes seem to be attributable to intramolecular reactions. Comparison of methyl-substituted benzoylphosphonates with methyl-substituted acetophenones and benzophenones capable of undergoing photoenolization [14 - 21] suggests that the intramolecular processes observed in this work could be assigned to enolizations proceeding according to the following mechanism:



According to reaction (4) hydrogen abstraction occurs in triplet excited molecules of TMPDM, *i.e.* ketone triplets are converted to biradicals which can be ascribed to enol triplets [21]. The question now arises as to whether the transient absorption spectrum observed at the end of the 20 ns flash is due to ketone triplets or enol triplets. Transient absorption spectra quite similar to those recorded for TMPDM and TMPDE were observed by Haag *et al.* [18] for 2-methylacetophenone and related compounds. These workers assigned the spectrum formed during the 20 ns flash ( $\lambda_{\text{max}} = 320$  nm) to enol triplets and the spectrum formed subsequently ( $\lambda_{\text{max}} = 380$  nm) to ground state enols. By analogy with these assignments the three species observed with TMPDM and TMPDE could be attributed to the enol triplet (A) (*i.e.* the biradical) and to the two isomers of the enol in the ground state, *i.e.* the *Z* isomer (B) and the *E* isomer (C):

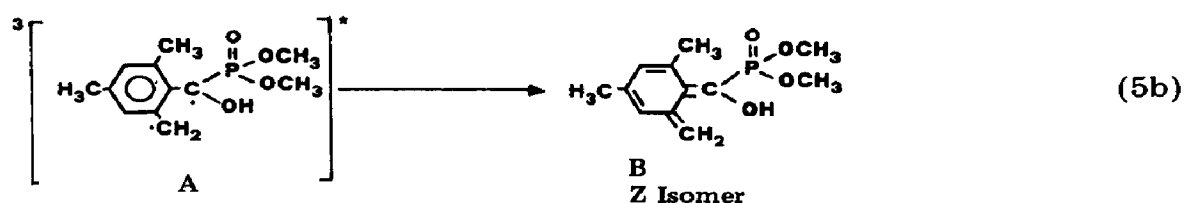
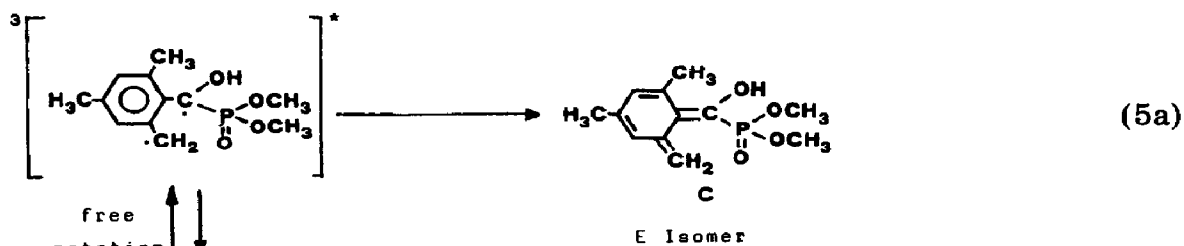
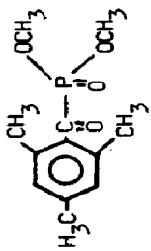
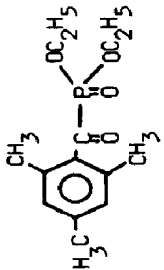
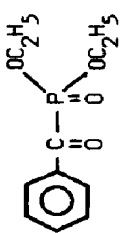


TABLE 1

First-order lifetimes of the decay of transient species observed on flash photolysis of 2,4,6-trimethylbenzoylphosphonic acid dimethyl ester, 2,4,6-trimethylbenzoylphosphonic acid diethyl ester and benzoylphosphonic acid diethyl ester in various solvents at 23 °C

	Species A		Species B		Species C	
	$\tau$ (ns)	$\lambda$ (nm)	$\tau$ ( $\mu$ s)	$\lambda$ (nm)	$\tau$ ( $\mu$ s)	$\lambda$ (nm)
TMPDM 	57 (CCl <sub>4</sub> )	320	1.00 (CCl <sub>4</sub> )	380	116 (CCl <sub>4</sub> )	380
	50 (CH <sub>2</sub> Cl <sub>2</sub> )	520	0.29 (CH <sub>2</sub> Cl <sub>2</sub> )		480 (CH <sub>2</sub> Cl <sub>2</sub> )	
	43 (C <sub>6</sub> H <sub>6</sub> )		0.29 (CH <sub>3</sub> OH)		15 (CH <sub>3</sub> OH)	
			0.70 (C <sub>6</sub> H <sub>6</sub> )		870 (C <sub>6</sub> H <sub>6</sub> )	
TMPDE 	50 (CH <sub>2</sub> Cl <sub>2</sub> )	320	0.45 (CH <sub>2</sub> Cl <sub>2</sub> )	380		380
			1.26 (C <sub>6</sub> H <sub>6</sub> )			
BPDE 	87 (CCl <sub>4</sub> )	320	—		—	
	72 (CH <sub>2</sub> Cl <sub>2</sub> )	450				
	87 (C <sub>6</sub> H <sub>12</sub> )					
	77 (C <sub>6</sub> H <sub>6</sub> )					



This assignment, which is based on the assumption that the ketone triplets of TMPDM and TMPDE are very short lived ( $\tau_T < 10$  ns) and therefore are not observable with 20 ns flashes, is affirmed by the fact that B and C have identical absorption spectra which differ from that of A.

In benzene solution, and in dichloromethane solutions containing styrene, an additional species D was detected by the formation of an absorption band with a maximum around 325 nm. The spectrum of species D recorded 3  $\mu$ s after the start of the flash is shown in Fig. 3(a). As can be seen from the oscilloscope trace in Fig. 4(b), species D is formed subsequent

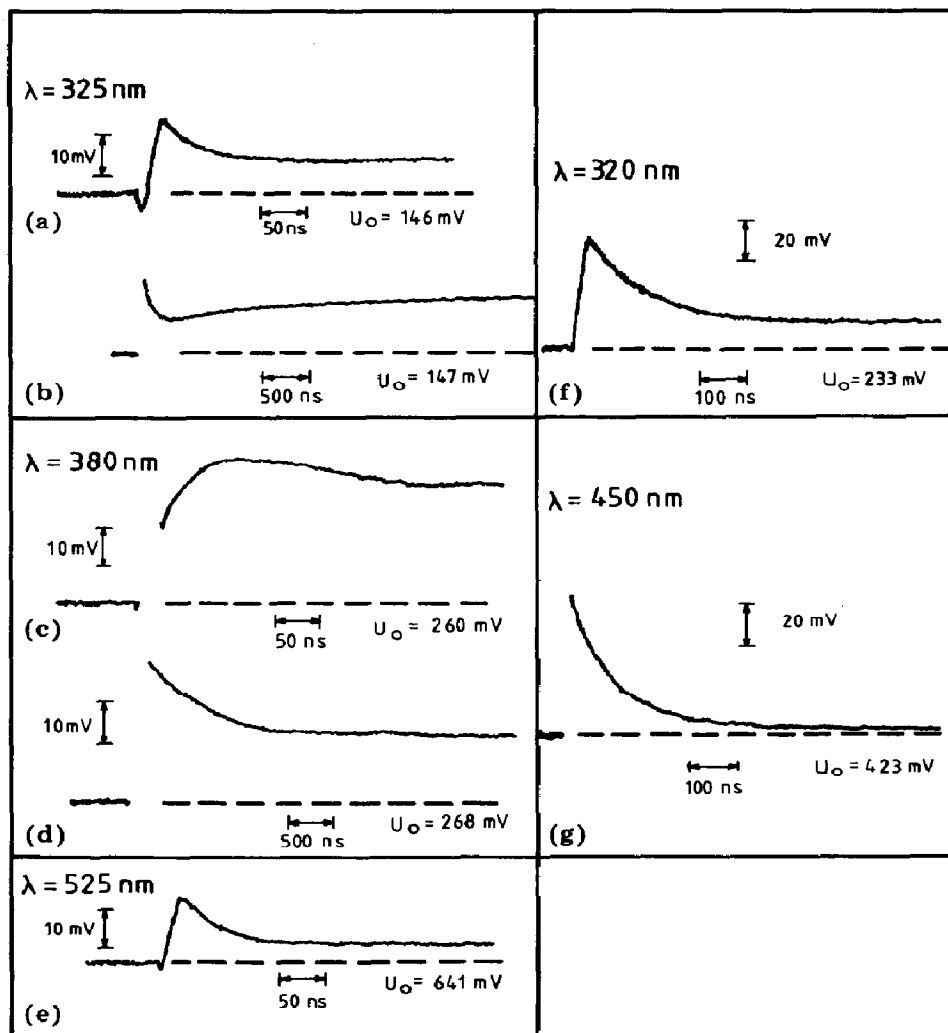


Fig. 4. Oscilloscope traces illustrating changes of the transient absorption with time at various wavelengths. (a) - (e)  $2.0 \times 10^{-3}$  M TMPDM in argon-saturated benzene solution,  $D_{\text{abs}} = 3.8 \times 10^{-5}$  einsteins  $l^{-1}$ ; (f), (g)  $4.8 \times 10^{-3}$  M BPDE in argon-saturated benzene solution,  $D_{\text{abs}} = 2.0 \times 10^{-5}$  einsteins  $l^{-1}$ .

to the decay of species A and the formation of B. The kinetics of the formation of D and the decay of B are not correlated. Moreover the absorption of D was not observed with solutions of TMPDM in the other non-aromatic solvents. It is therefore concluded that D is generated by a reaction of the aromatic compound with a primary product of the photolysis of TMPDM which absorbs only weakly between 300 and 600 nm and therefore could not be detected directly by spectroscopy. Because the absorption spectrum of D strongly resembles that of the cyclohexadienyl radicals observed by Griller *et al.* [8] on addition of diethoxyphosphonyl radicals to benzene it is assumed that this primary product is identical with the dimethoxyphosphonyl radical ( $\cdot\text{P}(\text{O})(\text{OCH}_3)_2$ ) which is generated by  $\alpha$  scission according to reaction (1). The dimethoxyphosphonyl radicals add to benzene thus forming cyclohexadienyl radicals in an analogous manner to reaction (3). From the measured rate of formation of cyclohexadienyl radicals the rate constant  $k[\text{benzene} + \cdot\text{P}(\text{O})(\text{OCH}_3)_2] = (4.1 \pm 0.4) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  was evaluated and, by using  $\epsilon_{326 \text{ nm}} = 2.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  [8], a value of about  $0.3 \pm 0.1$  was obtained for the quantum yield of the cyclohexadienyl radicals. This value can be set equal to  $\phi[\cdot\text{P}(\text{O})(\text{OCH}_3)_2]$  on the assumption that all dimethoxyphosphonyl radicals underwent addition to benzene according to reaction (3).

Experiments with TMPDM in dichloromethane solutions containing various amounts of styrene yielded spectral changes similar to those observed in benzene solution. However, the rate constant for the formation of adduct radicals was found to be several orders of magnitude higher than that for the reaction of dimethoxyphosphonyl radicals with benzene (see Table 2). It should be noted that dimethoxyphosphonyl radicals can react with both the olefinic group and the phenyl ring of styrene, and it appears that the high rate constant reflects the occurrence of the reaction with the olefinic group. Radicals of the type  $(\text{C}_6\text{H}_5)\text{CHCH}_2\text{R}$  absorb strongly at 320 nm [22, 23] and have an absorption spectrum similar to that of the cyclohexadienyl radicals. In this connection the work of Brede *et al.* [24] on the adduct of OH radicals with styrene should be noted; these workers reported  $\lambda_{\text{max}} = 345 \text{ nm}$  with  $\epsilon = (8 \pm 2) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for the radical  $\cdot(\text{C}_6\text{H}_5\text{OH})-\text{CH}=\text{CH}_2$  and  $\lambda_{\text{max}} = 320 \text{ nm}$  with  $\epsilon = 6.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  for the radical  $(\text{C}_6\text{H}_5)-\dot{\text{C}}\text{H}-\text{CH}_2\text{OH}$ .

TABLE 2

Bimolecular rate constants of the reactions of dimethoxyphosphonyl and diethoxyphosphonyl radicals with benzene and styrene at 23 °C

	Rate constant ( $\text{M}^{-1} \text{ s}^{-1}$ )	
	Benzene	Styrene
$\cdot\text{P}(\text{O})(\text{OCH}_3)_2$	$(4.1 \pm 0.4) \times 10^4$	$(1.7 \pm 0.2) \times 10^8$
$\cdot\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	$(4.1 \pm 0.4) \times 10^4$	$(1.3 \pm 0.2) \times 10^8$

Investigations with TMPDE yielded results analogous to those obtained with TMPDM, and the kinetic data are given in Table 1. Therefore it is concluded that the photochemistry of the trimethylbenzoylphosphonates does not depend on the nature of the ester group as far as methyl and ethyl esters are concerned.

### 3.1.3. Quenching experiments with *trans*-piperylene, naphthalene and styrene

*trans*-Piperylene quite effectively inhibited the formation of the absorption at 325 nm (species A) during the flash and consequently also the extent of the absorption at 380 nm (species B and C). Moreover it accelerated the rate of decay of the absorption at 325 nm as can be seen from Fig. 5 where oscilloscope traces depicting the changes in the OD at 325 and 380 nm are shown. It is interesting to note that the fractions of the fast and slow modes of the decrease in OD at 380 nm remained constant although the total OD decreased with increasing concentration of *trans*-piperylene. These results can be interpreted in terms of *trans*-piperylene accepting energy by transfer from the ketone triplets. Consequently the yield of enol triplets and therefore the yield of enol is reduced. Moreover, *trans*-piperylene reacts with enol triplets; as is shown in Fig. 5(a) the rate of decay of the OD at 325 nm is accelerated on addition of *trans*-piperylene. Because the lifetimes did not differ significantly from the duration of the flash the rate constant of the reaction of *trans*-piperylene with enol triplets could be estimated only roughly as  $k_q \approx 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . If the OD at 325 nm is taken as a measure of the formation of enols in the absence and presence of *trans*-piperylene ( $\text{OD}_{[\text{PIP}]} = 0$  and  $\text{OD}_{[\text{PIP}]}$  respectively), the quenching efficiency of *trans*-piperylene with respect to its reaction with ketone triplets is demonstrated in Fig. 6(a) by the Stern–Volmer plot

$$\frac{\text{OD}_{[\text{PIP}] = 0}}{\text{OD}_{[\text{PIP}]}} = 1 + \frac{k_q [\text{PIP}]}{k_T^K} \quad (6)$$

where  $k_T^K$  is the first-order rate constant of the decay of ketone triplets. A value of  $3 \times 10^8 \text{ s}^{-1}$  for  $k_T^K$  was obtained from the slope of the straight line in Fig. 6(a) by assuming  $k_q = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

In solutions of TMPDM and TMPDE containing naphthalene the characteristic absorption of naphthalene triplets was observed during the

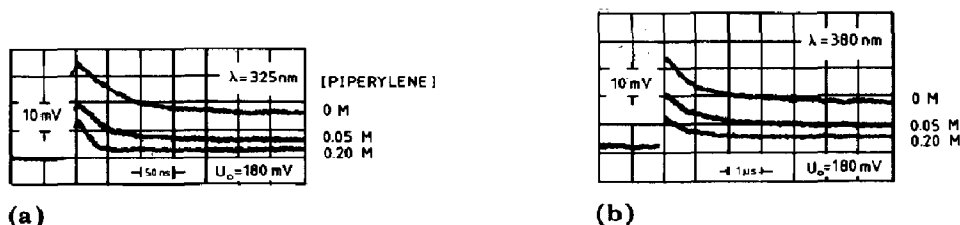


Fig. 5. Influence of piperylene on the formation and decay of the absorption of (a) species A at 325 nm and (b) species B at 380 nm in an argon-saturated solution of  $2.5 \times 10^{-3} \text{ M}$  TMPDM in tetrachloromethane ( $D_{\text{abs}} = 5.2 \times 10^{-5} \text{ einsteins l}^{-1}$ ).

flash. At all naphthalene concentrations the build-up rate was so fast that  $k_q$  could not be measured. A Stern–Volmer plot based on measurements at 425 nm is shown in Fig. 6(b). A value of  $5 \times 10^7 \text{ s}^{-1}$  for  $k_T^K$  was obtained from the slope of the straight line

$$\frac{\text{OD}_{\text{total}}}{\text{OD}} = 1 + \frac{k_T^K}{k_q [\text{Naph}]} \quad (7)$$

by assuming  $k_q = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . In eqn. (7)  $\text{OD}_{\text{total}}$  is the optical density at 425 nm measured at the naphthalene concentration  $[\text{Naph}]_{\text{total}}$  where all phosphonate triplets were quenched and OD is the optical density at 425 nm measured at  $[\text{Naph}] < [\text{Naph}]_{\text{total}}$ . The quantum yield of triplet formation  $\phi(T)$  for both TMPDM and TMPDE was calculated to be  $0.6 \pm 0.1$  from the naphthalene triplet concentration measured at  $[\text{Naph}]_{\text{total}}$ . A value of  $1.32 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  was assumed for  $\epsilon_{425 \text{ nm}}$  in benzene [13].

Although the values of  $k_T^K$  evaluated for the two quenchers do not agree very well they are appreciably higher than  $k_T^E = 1.7 \times 10^7 \text{ s}^{-1}$  measured for the decay of the absorption at 325 nm. This confirms the postulate that species A has a precursor with a lifetime significantly shorter than the flash length.

Styrene also quenched the formation of the absorption at 380 nm, *i.e.* the formation of B and C, in a similar manner to *trans*-piperylene. The slope of the straight line in the Stern–Volmer plot was about the same as that for *trans*-piperylene. It should be noted that the extent of the absorption at 325 nm due to adduct radicals generated by the reaction of dimethoxyphosphonyl radicals with styrene was independent of the styrene concentration in the range  $(1 - 5) \times 10^{-2} \text{ M}$ , whereas the formation of the absorption at 380 nm was strongly quenched. This result indicates that ketone triplets, which are quenched by styrene, should not be considered as major precursors of dimethoxyphosphonyl radicals.

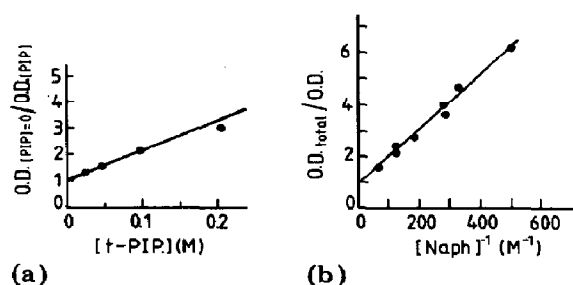


Fig. 6. Quenching experiments with *trans*-piperylene (PIP) and naphthalene (Naph): (a) ratio of the optical density  $\text{OD}_0$  at 325 nm recorded 120 ns after the flash in the absence of PIP to the optical density OD recorded under the same conditions in the presence of PIP vs. the concentration of PIP ( $[\text{TMPDM}] = 2.5 \times 10^{-3} \text{ M}$  in argon-saturated tetrachloromethane solution; absorbed dose per flash,  $5.2 \times 10^{-5} \text{ einsteins l}^{-1}$ ); (b) ratio of  $\text{OD}_{\text{total}}$  (which corresponds to  $[\text{Naph}]_{\text{total}}$  where all phosphonate triplets are quenched) to OD (which corresponds to  $[\text{Naph}] < [\text{Naph}]_{\text{total}}$ ) vs.  $1/[\text{Naph}]$  at 425 nm ( $[\text{TMPDM}] = 1.0 \times 10^{-3} \text{ M}$  in argon-saturated dichloromethane solution). Measurements with solutions of TMPDE ( $1.8 \times 10^{-3} \text{ M}$ ) and BPDE ( $2.8 \times 10^{-3} \text{ M}$ ) in dichloromethane solutions also fitted the straight line shown in (b).

### 3.1.4. Polymerization experiments

Styrene and methyl methacrylate containing  $1.1 \times 10^{-3}$  M TMPDM were continuously irradiated with light from a high pressure mercury lamp in the absence of air at 20 °C. Under the experimental conditions the radiation at 313 and 366 nm was absorbed in about equal amounts by the initiator. As can be seen in Table 3 TMPDM initiated the polymerization of methyl methacrylate quite effectively, *i.e.* the rate of monomer conversion in the presence of TMPDM was about six times higher than that in its absence. In the case of styrene, however, the rate of monomer conversion was increased by only a factor of about 2.

TMPDE exhibited similar behaviour to that of TMPDM. In the polymerization of methyl methacrylate the rate of monomer conversion in the presence of the initiator was about ten times higher than that in its absence.

TABLE 3

Rate  $\nu$  of the bulk polymerization of methyl methacrylate and styrene initiated by irradiation with light of wavelength 313 and 366 nm at 20 °C

Initiator	$\nu$ ( $\times 10^5$ M s $^{-1}$ )	
	Methyl methacrylate	Styrene
TMPDM ( $1.1 \times 10^{-3}$ M)	5.10	0.82
TMPDE ( $1.5 \times 10^{-3}$ M)	8.70	
BPDE ( $1.1 \times 10^{-3}$ M)	0.98	
None	0.87	0.36

Incident intensity,  $1.7 \times 10^{-5}$  einsteins cm $^{-2}$  s $^{-1}$ .

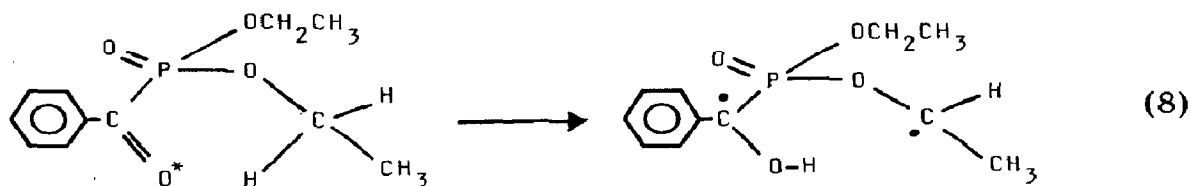
## 3.2. Experiments with benzoylphosphonic acid diethyl ester

### 3.2.1. Emission measurements

Emission and excitation spectra recorded on continuous irradiation of BPDE in cyclohexane solution are shown in Figs. 2(c) and 2(d). The emission spectrum has a maximum around 430 nm and the excitation spectrum strongly resembles the absorption band between 330 and 400 nm (see Fig. 1(b)). Therefore, as in the case of TMPDM and TMPDE, it is concluded that this absorption band corresponds to the  $S_0 \rightarrow S_1$  transition. The singlet energy  $E_S$  was found to be 300 kJ mol $^{-1}$ . On flash photolysis of BPDE in cyclohexane solution the emission spectrum formed and decayed during the flash (halfwidth, about 20 ns), indicating a singlet lifetime in the nanosecond range or less.

### 3.2.2. Transient absorption spectrum

Figure 7 shows the difference absorption spectrum observed at the end of the flash in argon-saturated carbon tetrachloride solution. It possesses two maxima: one at 310 nm and the other around 450 nm. Similar spectra were recorded in dichloromethane, cyclohexane and benzene solutions. In all cases these spectra decayed according to first-order kinetics with lifetimes between 72 and 87 ns (see Table 1 and Figs. 4(f) and 4(g)) leaving a permanent difference absorption spectrum with a maximum around 340 nm which is also shown in Fig. 7 (in this case it was recorded 500 ns after the flash). The latter spectrum was assigned to a reaction product which has not yet been identified. On the basis of quenching experiments with naphthalene, the transient absorption spectrum was not assigned to the triplet state of BPDE but to a reaction product of the short-lived triplet. It is feasible that excited carbonyl groups abstract hydrogen atoms from the ethyl groups thus forming a biradical whose spectrum is recorded at the end of the flash:



It should be noted that a transient absorption at 325 nm corresponding to a radical of the cyclohexadienyl type was not formed in the benzene solution. From this result it is inferred that BPDE does not undergo significant  $\alpha$  scission (reaction (1)) as is observed with the methyl-substituted phosphonates TMPDM and TMPDE.

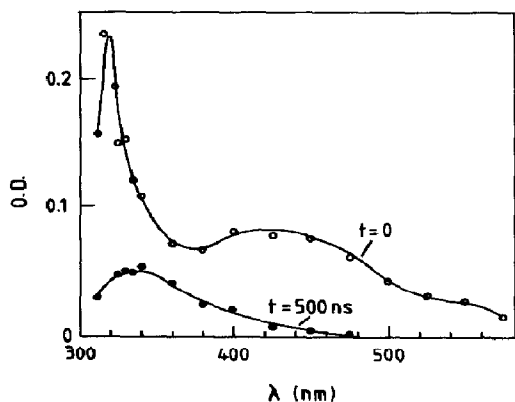


Fig. 7. Difference absorption spectra recorded at the end of the flash and 500 ns later for BPDE in argon-saturated carbon tetrachloride solution ( $D_{\text{abs}} = 3.5 \times 10^{-5}$  einsteins  $\text{l}^{-1}$ );  $[\text{BPDE}] = 4.8 \times 10^{-3}$  M.

### 3.2.3. Quenching experiments

In the presence of naphthalene the formation of its T-T absorption spectrum was observed after the flash. The quenching rate constant  $k_q$  was determined from the build-up rates at  $[\text{Naph}] > [\text{Naph}]_{\text{total}}$  to be  $(4 \pm 1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . On plotting  $\text{OD}_{\text{total}}/\text{OD}$  (measured at 425 nm) versus  $[\text{Naph}]^{-1}$  according to eqn. (7) a straight line with the same slope as that found with TMPDM and TMPDE was obtained. From the slope and  $k_q$  a value of  $(4.2 \pm 1.0) \times 10^7 \text{ s}^{-1}$  was obtained for  $k_T$ . This value is definitely greater than  $k = (1.25 \pm 0.15) \times 10^7 \text{ s}^{-1}$  found for the decay of the transient absorption in the absence of naphthalene. Therefore it is concluded that this transient absorption is not due to the triplet but to a product formed by its decay. This conclusion is confirmed by the fact that naphthalene did not affect the decay rate of the transient absorption at 320 nm.

The quantum yield  $\phi(T)$  of triplet formation was found to be 0.90 by assuming  $\epsilon_{425 \text{ nm}} = 1.32 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for naphthalene triplets [13].

### 3.2.4. Polymerization experiments

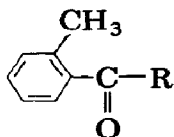
On continuous irradiation of methyl methacrylate containing  $1.1 \times 10^{-3} \text{ M}$  BPDE with light from a high pressure mercury lamp under the same conditions as those described in Section 3.1.4 the rate of monomer conversion was almost the same as that obtained in the absence of BPDE (see Table 3). Thus it appears that BPDE is not capable of initiating the polymerization of methyl methacrylate in agreement with the observation that BPDE triplets do not undergo  $\alpha$  scission and are unlikely to form ketyl radicals, which could initiate radical chain reactions, by intermolecular hydrogen abstraction.

## 4. Discussion

The results obtained during this work show clearly that, under the influence of UV light, the trimethyl-substituted benzoylphosphonates TMPDM and TMPDE exhibit quite different behaviour from that observed with the non-substituted analogue BPDE. Elementary reactions involving transients detected with TMPDM are shown in Scheme 1. An analogous scheme would be obtained for TMPDE. From the results obtained in the presence of styrene, it was inferred that route c is not important for the generation of phosphonyl radicals. Thus it is concluded that excited singlet states undergo a significant amount of  $\alpha$  scission (route b') and a large fraction of singlets concurrently undergo intersystem crossing (route b) as indicated by the rather high quantum yield of triplets ( $\phi(T) \approx 0.6$ ).

These results lead to the conclusion that the formation of TMPDM triplets is followed by a sequence of intramolecular processes (routes c', d,

d', e and e') involving enolization in the triplet state. The photoenolization of aromatic ketones



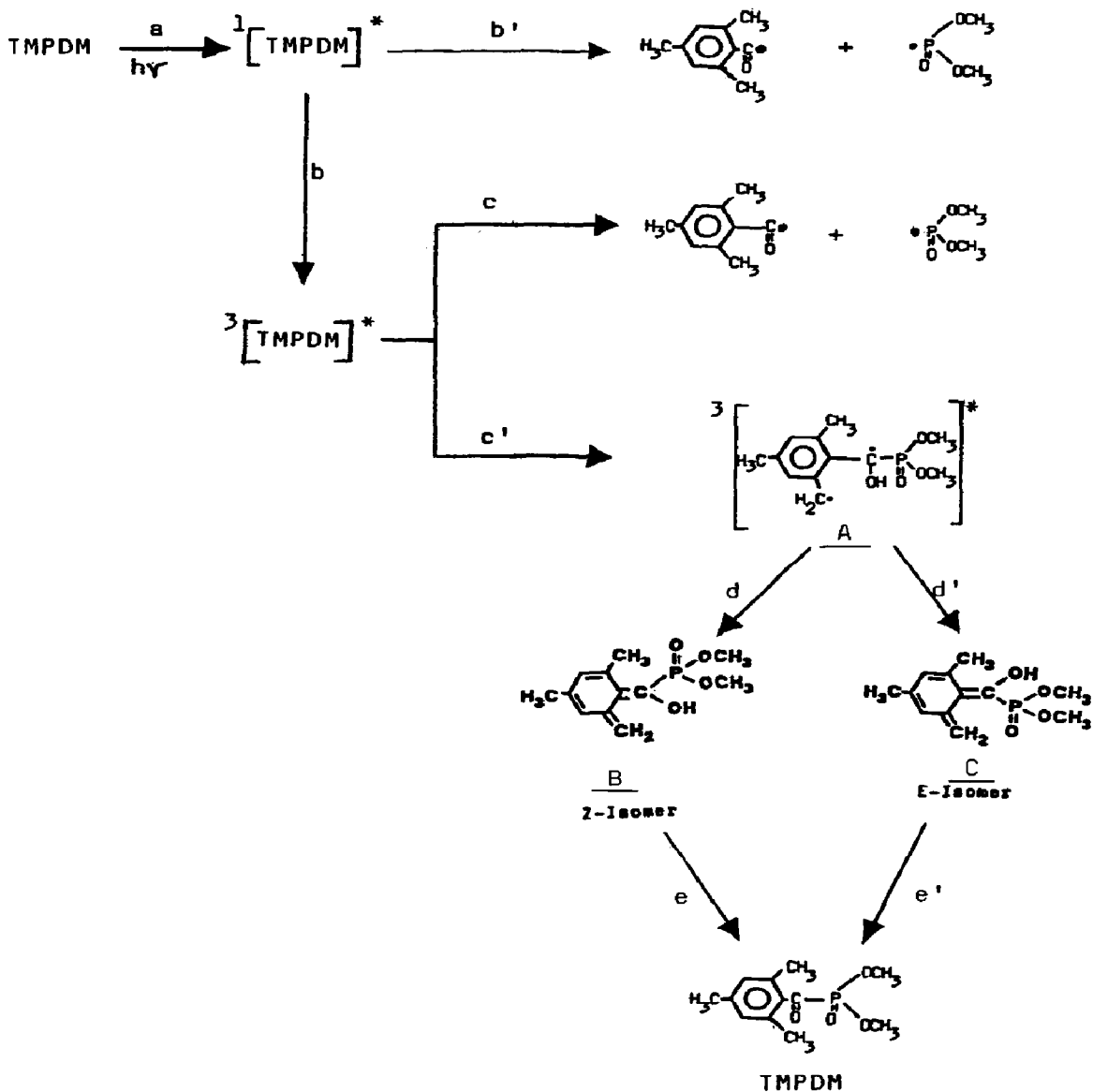
with a methyl group in the ortho position relative to the carbonyl and with R  $\equiv$  methyl, phenyl etc. has been intensively studied during the last two decades [14-21] and it appears quite feasible that methyl-substituted benzoylphosphonates behave similarly. In fact the photochemical behaviour of TMPDM and TMPDE strongly resembles that of 2-methylacetophenone [18] as far as the short lifetime of the ketone triplets ( $\tau_T^K < 20$  ns) and the shape of the spectra of the enol triplets (species A) and of the relaxed enol isomers are concerned.

The lifetimes of species B and C were found to depend on the chemical nature of the solvent as can be seen from Table 1. Most of these measurements were carried out with TMPDM, and it was found that the lifetimes of B (0.7  $\mu$ s and 1.0  $\mu$ s respectively in the non-polar solvents benzene and tetrachloromethane) were longer than in the polar solvents methanol and dichloromethane ( $\tau \approx 0.3$   $\mu$ s). The lifetime of C is not correlated with the polarity of the solvent. Hydrogen bonding and/or complexation appear to determine the rate of reketonization in this case. The shortest lifetime was found in methanol which probably interacts with the enol via hydrogen bonding. However, species C lived longest in benzene, a solvent which does not interact specifically strongly with particular functional groups as does methanol and probably the halogenated hydrocarbons. It should be noted here that the assignment of species B and C to the *Z* and *E* isomers of the enol is based on their lifetimes. The configuration of the *E* isomer suggests that reketonization is more complicated than in the case of the *Z* isomer. The strong light sensitivity of C agrees with this proposal: when the intensity of the analytical light was increased by a factor of 10, the lifetime of C was reduced by a factor of about 4.

In addition to enolization,  $\alpha$  scission is another major process induced by UV irradiation of TMPDM and TMPDE. Dimethoxyphosphonyl and diethoxyphosphonyl radicals formed by  $\alpha$  scission do not appear to absorb light to a detectable extent in the wavelength range investigated (300 - 600 nm). However, it has been shown above that phosphonyl radicals can readily be detected via adduct radicals formed by the addition of phosphonyl radicals to styrene. This process can be used as a reference reaction for studies concerning the reactivity of dialkoxyphosphonyl radicals [25]. As far as BPDE is concerned  $\alpha$  scission was not detected by the formation of adduct radicals during photolysis in the presence of benzene or styrene. In accordance with this result BPDE proved ineffective as a photoinitiator for the polymerization of methyl methacrylate, in contrast with TMPDM and TMPDE which acted quite effectively as initiators in the



polymerization of this monomer. It is interesting to note that BPDE triplets which are formed with high yields ( $\phi(T) = 0.9$ ) are converted quite rapidly by intramolecular hydrogen abstraction to biradicals, which subsequently form products which have not yet been identified. In this respect BPDE did not serve as a reference compound incapable of undergoing intramolecular hydrogen abstraction, as was originally anticipated. Both TMPDE and BPDE undergo intramolecular hydrogen abstraction, although of a quite different nature. However, it follows from comparison of the two compounds that methyl groups at the benzoyl moiety strongly enforce  $\alpha$  scission.



Scheme 1. Photoreactions of TMPDM.

## Acknowledgments

The authors are grateful to Dr. G. Beck for maintaining the laser flash photolysis equipment. Mrs. U. Fehrmann contributed to this work by carrying out the polymerization experiments. One of the authors (T.S.) was financially supported by a grant from the Nishina Memorial Foundation which is gratefully acknowledged.

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