

THE PHOTOLYSIS OF ACYLPHOSPHINE OXIDES III: LASER FLASH PHOTOLYSIS STUDIES WITH PIVALOYL COMPOUNDS

T. SUMIYOSHI and W. SCHNABEL

*Hahn-Meitner-Institut für Kernforschung, Bereich Strahlenchemie, D-1000 Berlin 39,
Postfach 39 01 28 (F.R.G.)*

A. HENNE

BASF Aktiengesellschaft, D-6700 Ludwigshafen (F.R.G.)

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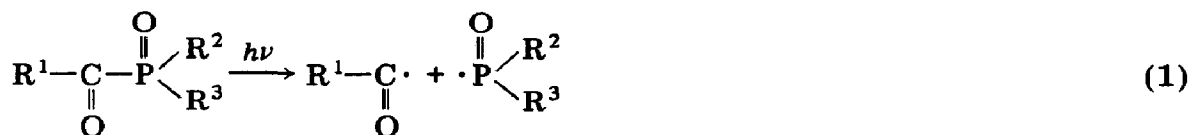
Summary

Argon-saturated dilute solutions of pivaloyldiphenylphosphine oxide (PDPO), dimethylpivaloyl phosphonate (PDME) and diethylpivaloyl phosphonate (PDEE) in various solvents were irradiated with 20 ns flashes of 347 nm light. All compounds underwent α scission from excited singlet states: $\Phi(\alpha) \approx 1$ (PDPO) and $\Phi(\alpha) \approx 0.3$ (PDME and PDEE). The singlet lifetimes (determined by single-photon counting) are 30 ns for PDPO and 11 ± 3 ns for PDME and PDEE. In the case of PDPO, singlet deactivation occurs predominantly via α scission. In the case of the phosphonates, triplets are also formed ($\Phi(T) = 0.6$; $\tau = 30$ ns) as revealed from quenching with naphthalene. Dimethoxyphosphonyl and diethoxyphosphonyl radicals reacted very effectively with styrene ($k_{R \cdot + St} = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), as was indicated by the formation of the characteristic absorption of adduct styryl radicals at 322 nm. In the case of diphenylphosphonyl radicals $k_{R \cdot + St}$ is about three times lower, which is thought to result from the rather flattened tetrahedral structure of this radical as compared with the pronounced tetrahedral structure of $\text{O}=\dot{\text{P}}(\text{OR})_2$ radicals. In the case of the phosphonates, the optical absorption spectra of three transients with different lifetimes were recorded which were tentatively assigned to biradicals, phosphonyl radicals and pivaloyl radicals. The extinction coefficient $\epsilon_{260 \text{ nm}}$ of pivaloyl radicals is $2.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

1. Introduction

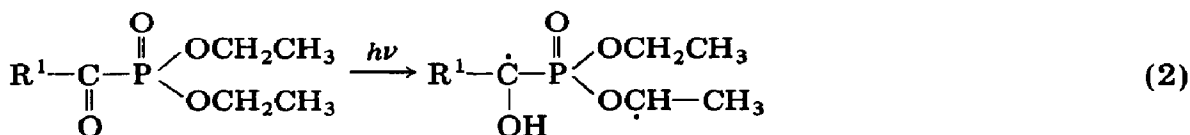
In parts I [1] and II [2] of this series it was shown that upon irradiation with UV light various acylphosphine oxides undergo α scission ac-

ording to

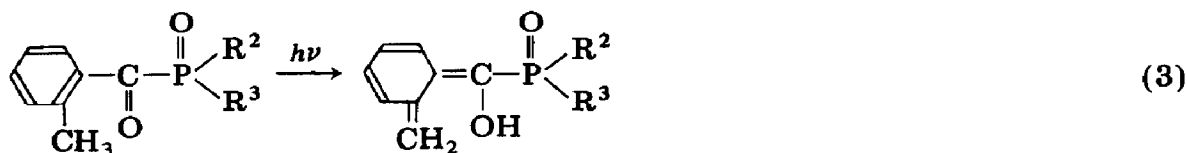


with quantum yields $\Phi(\alpha)$ in the range 0.5 - 1.0.

For those phosphonates with R^2 and R^3 being OCH_3 or OCH_2CH_3 , as well as α scission, intramolecular hydrogen abstraction leading to biradicals was observed according to the reaction

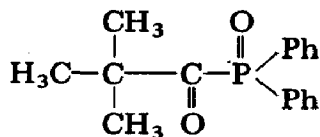


All compounds so far investigated have been aroylphosphine oxides[†] or aroyl phosphonates with R^1 being the phenyl group or a methyl-substituted phenyl group. Interestingly, some of the *o*-methyl-substituted compounds underwent an enolization process as well as α scission, *e.g.*

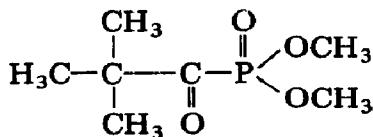


Whenever α scission was observed, it occurred very rapidly with a lifetime of a few nanoseconds or less and it was assumed that this reaction involved excited singlet states. However, biradical formation and enolization according to reactions (2) and (3) occurred with comparatively low rates and it was indicated in quenching experiments that excited triplet states were involved in these reactions.

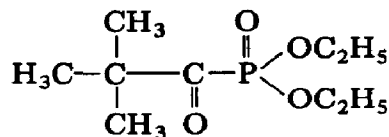
The objective of the work described in this paper was to investigate the behaviour of acylphosphine oxides and acylphosphonates (with R^1 being an aliphatic group) under the influence of UV irradiation. As typical representatives of this class of compounds the following pivaloyl compounds were investigated:



PDPO



PDME



PDEE

(PDPO, pivaloyldiphenylphosphine oxide; PDME, pivaloylphosphonic acid dimethyl ester; PDEE, pivaloylphosphonic acid diethyl ester.)

[†] Aroyl, $\text{R}-\text{C}(=\text{O})-$ group with $\text{R} \equiv \text{aryl}$.

2. Experimental details

2.1. Materials

PDPO, PDME and PDEE were synthesized as described previously [3]. Dichloromethane, methanol and cyclohexane, all of Uvasol quality, were obtained from E. Merck. They were used without further purification.

2.2. Irradiations

Dilute solutions of phosphine oxides, in most cases freed from oxygen by bubbling with purified argon, were irradiated in rectangular quartz cells. For the flash photolysis studies the irradiations were carried out at $\lambda = 347$ nm with a ruby laser operated in conjunction with a frequency doubler. The flash duration was about 20 ns.

Actinometry was performed with solutions of benzophenone (1.15×10^{-3} mol l⁻¹) containing naphthalene (1.03×10^{-1} mol l⁻¹). The absorbed dose per flash was calculated from the concentration of naphthalene triplets formed by energy transfer from benzophenone with $\epsilon_{T-T} = 1.32 \times 10^{-4}$ l mol⁻¹ cm⁻¹ at 425 nm and $\Phi(T) = 1.0$. The maximum laser output at $\lambda = 347$ nm was 8.4×10^{16} photons per flash.

Fluorescence spectra were recorded under continuous irradiation using a fluorescence spectrometer (MPF-4, Perkin-Elmer). Fluorescence lifetimes were determined using single-photon counting apparatus (199 M, Edinburgh Instruments).

3. Results

3.1. Emission measurements

Figure 1 shows absorption and emission spectra recorded with the three phosphine oxides: PDPO in methanol and PDME and PDEE in cyclohexane. The emission spectra possess maxima at about 430 nm and the excitation spectra resemble the absorption spectra with a red shift of 15 - 20 nm. Therefore it was concluded that the observed emission and absorption bands reflect S₀-S₁ transitions. From the intersection of the excitation and emission spectra at about 387 nm the singlet energy E_s (0-0 transition) of the phosphine oxides was estimated as about 310 kJ mol⁻¹.

Using the single-photon counting technique, rather long emission lifetimes were measured: $\tau_s = 30$ ns (PDPO); $\tau_s = 14$ ns (PDME); $\tau_s = 8$ ns (PDEE). From the kinetic traces presented in Fig. 2 it is seen that in all three cases the decay of the emission was single exponential, indicating the existence of only one excited fluorescing species. Phosphorescence was not detected.

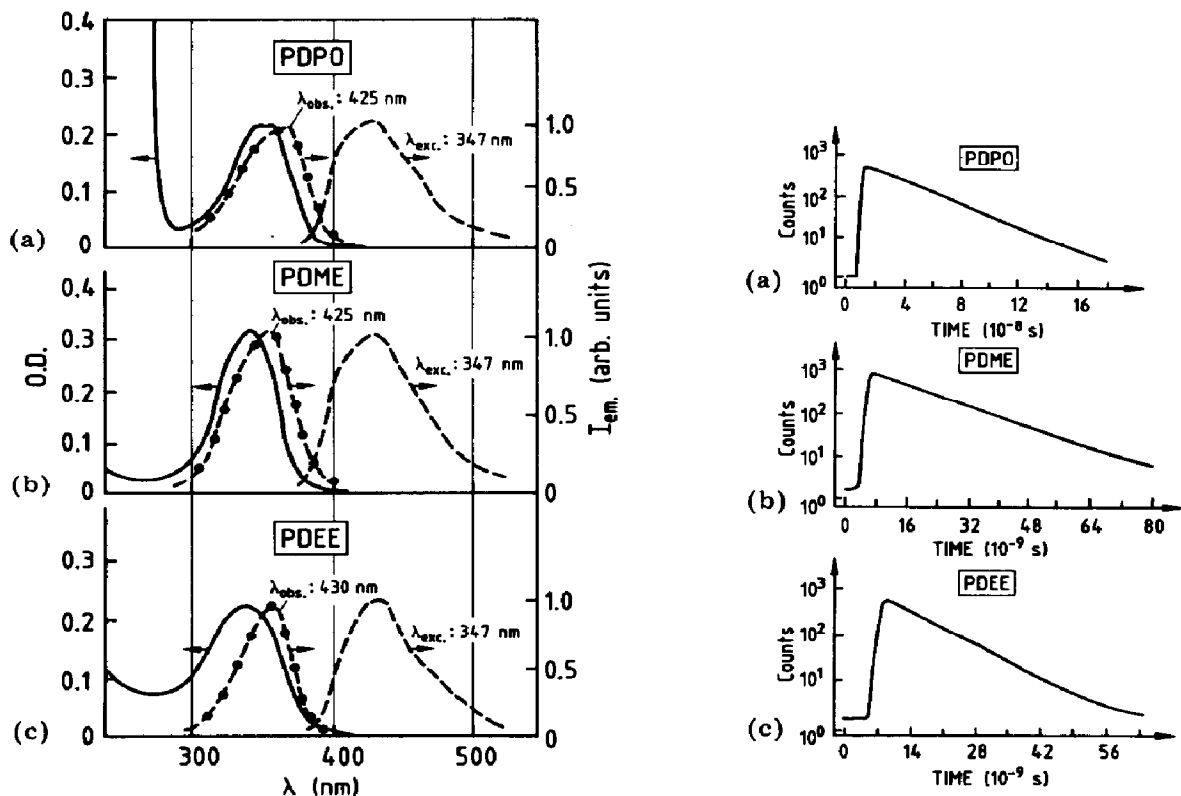


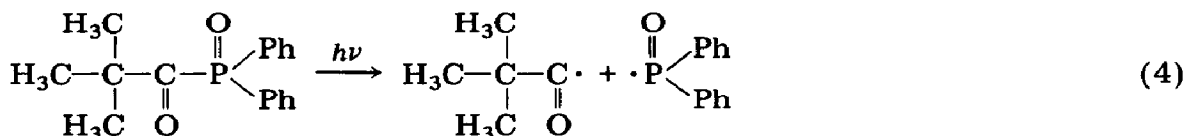
Fig. 1. Ground state absorption and emission spectra of pivaloylphosphine oxides recorded at room temperature: (a) [PDPO] = 7.8×10^{-4} M in methanol; (b) [PDME] = 6.6×10^{-3} M in cyclohexane; (c) [PDEE] = 3.6×10^{-3} M in cyclohexane; —, absorption spectra; ---, emission spectra; - · -, excitation spectra.

Fig. 2. Single-photon counting emission measurements in argon-saturated solutions of (a) PDPO, (b) PDME and (c) PDEE. For solvents and concentrations see caption to Fig. 1. $\lambda_{exc} = 347$ nm; $\lambda_{obs} = 425$ nm.

It is notable that in the case of benzoylphosphine oxides much shorter singlet lifetimes ranging from 0.3 to 0.7 ns were measured [1, 2].

3.2. Absorption measurements with PDPO

As was reported previously [1, 4], PDPO undergoes α scission quite effectively upon irradiation with 20 ns flashes of 347 nm light:



Diphenylphosphonyl radicals (see spectrum in Fig. 3(a)) were produced during and after the flash and the lifetime of formation is estimated to be about 30 ns on the basis of the grow-in curve shown in Fig. 3(b). This value

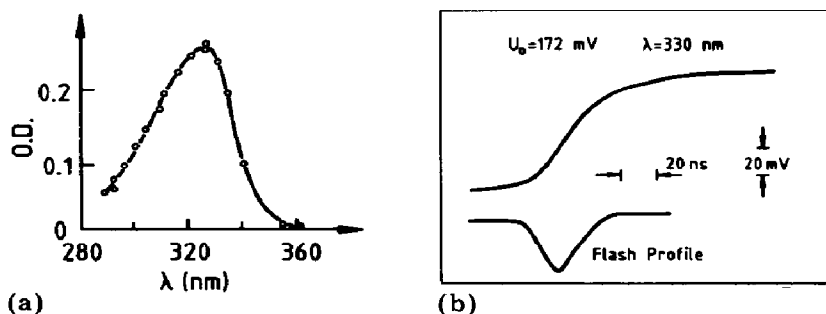


Fig. 3. Flash photolysis of PDPO in argon-saturated CH_2Cl_2 solution: (a) transient absorption spectrum recorded 100 ns after the flash ($[\text{PDPO}] = 7.8 \times 10^{-4} \text{ M}$; $D_{\text{abs}} = 3.6 \times 10^{-5} \text{ einstein l}^{-1}$); (b) oscilloscope traces illustrating the growing-in of the absorption at $\lambda = 330 \text{ nm}$ ($[\text{PDPO}] = 5 \times 10^{-4} \text{ M}$; $D_{\text{abs}} = 7.4 \times 10^{-5} \text{ einstein l}^{-1}$) (the lower trace depicts the flash profile).

correlates well with the singlet lifetime determined in the emission experiments (see above). It is therefore concluded that α scission according to reaction (4) occurs from the excited singlet states. From the optical density OD at 335 nm measured 100 ns after the flash the quantum yield $\Phi(\alpha)$ of α scission was estimated as being about 1 (with $\epsilon_{335\text{nm}} = 1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

The transient absorption decayed according to second-order kinetics indicating a self-reaction of the $\text{O}=\dot{\text{P}}(\text{Ph})_2$ radicals. The bimolecular rate constant $2k_s$ was estimated as $5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$.

3.3. Absorption measurements with PDME and PDEE

As can be seen from Fig. 4, three transient species were detected upon irradiating dilute solutions of PDME with 347 nm light flashes. The transients absorb light only weakly as expected for aliphatic compounds. Figure 4(a) shows three spectra measured at the end of the flash and 200 ns and 600 ns later. Difference spectra obtained by subtraction of the spectra in Fig. 4(a)

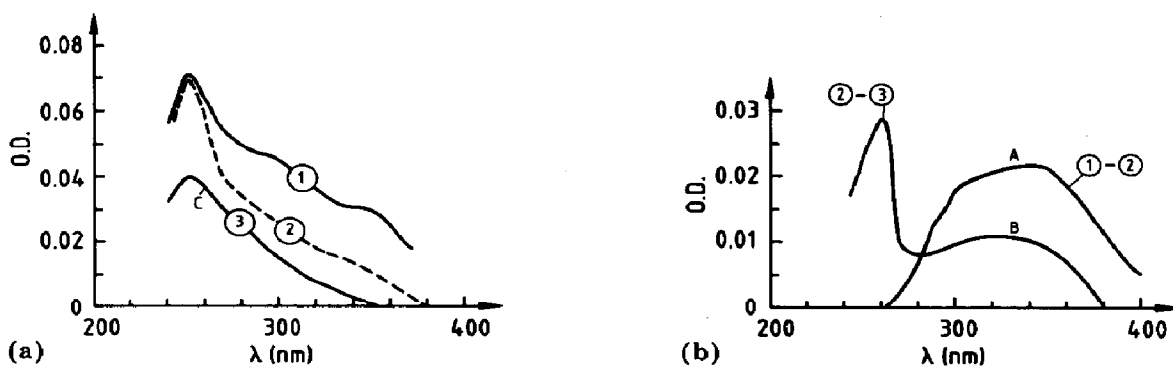


Fig. 4. Flash photolysis of PDME in argon-saturated CH_2Cl_2 solution ($[\text{PDME}] = 6.6 \times 10^{-3} \text{ M}$; $D_{\text{abs}} = 1.3 \times 10^{-4} \text{ einstein l}^{-1}$): (a) transient absorption spectra recorded at the end of the flash (curve 1), 200 ns (curve 2) and 600 ns (curve 3) after the flash; (b) difference spectra obtained by subtraction of the spectra in Fig. 4(a).

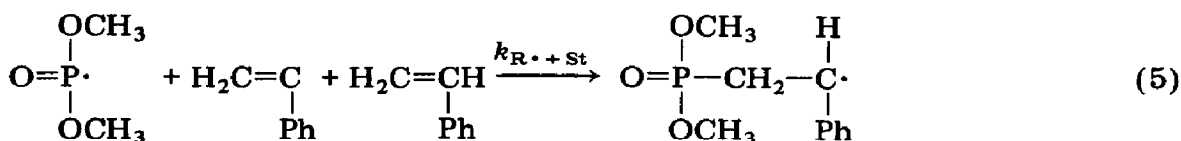
TABLE 1

Characteristic data for the transient species observed with PDME in cyclohexane or dichloromethane solution

Species	λ_{\max} (nm)	Lifetime	Remarks
A	330	100 - 200 ns	First-order decay
B	330 (260)	400 - 700 ns	First-order decay quenched by O ₂
C	260	0.4 - 1.1 μ s	Second-order decay

Fig. 4(a) are presented in Fig. 4(b). Characteristic data for the three species are compiled in Table 1.

The possibility that one of the three species is the PDME triplet can be excluded on the basis of results obtained with solutions containing naphthalene. The characteristic T-T absorption of naphthalene at 420 nm was evidence for the formation of naphthalene triplets, and the quenching rate constant $k_q = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ was determined from the grow-in curves. The lifetime τ_T of PDME triplets is about 30 ns and the quantum yield $\Phi(T)$ is about 0.6. Taking into account the rather short triplet lifetime, it becomes obvious that the three transients with lifetimes significantly longer than τ_T , that were observed by optical absorption measurements, are free radicals. It is interesting to note that the spectrum of the transient B was readily quenched by O₂. This finding suggests the possibility of assigning B to the phosphonyl radicals $\text{O}=\dot{\text{P}}(\text{OCH}_3)_2$ which should be very reactive towards oxygen, as concluded from the work with other phosphonyl radicals [1]. Additional evidence for the assignment of the transients was provided by experiments with solutions containing styrene. At styrene concentrations up to $2 \times 10^{-2} \text{ M}$, the rather intense absorption band of adduct styryl radicals with $\lambda_{\max} = 322 \text{ nm}$ (see Fig. 5(a)) was formed after the flash. A pseudo-first-order treatment of the measured grow-in rates yielded $k_{R\cdot + St} = 2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (in the case of PDEE, $k_{R\cdot + St} = 2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and $\tau_{R\cdot} = 4 \times 10^{-7} \text{ s}$ (see Fig. 5(b)). The latter value agrees well with the lifetime of species B (see Table 1) and the high value of $k_{R\cdot + St}$ suggests that B is not a carbon-centred radical but is a phosphorus-centred radical, *i.e.* the radical $\text{O}=\dot{\text{P}}(\text{OCH}_3)_2$ formed in reaction (1). Accordingly, the observed formation of styryl radicals reflects the occurrence of the reaction



In principle, the carbon-centred radicals generated in α scission can also react with styrene, forming adduct styryl radicals which also absorb at 320

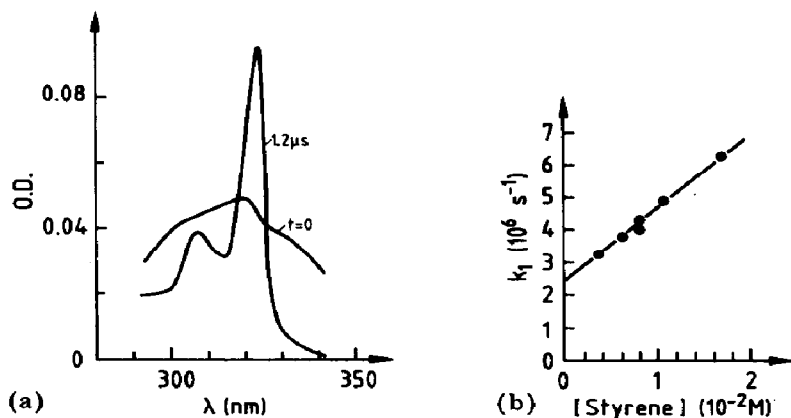


Fig. 5. Flash photolysis of PDME and PDEE in argon-saturated cyclohexane solution containing styrene: (a) transient absorption spectra recorded at the end of the flash and 1.2 μs later ($[\text{PDEE}] = 3.6 \times 10^{-3} \text{ M}$; $[\text{styrene}] = 1.4 \times 10^{-2} \text{ M}$; $D_{\text{abs}} = 1.1 \times 10^{-4} \text{ einstein l}^{-1}$); (b) pseudo-first-order rate constants for the formation of the absorption at 322 nm as a function of the styrene concentration ($[\text{PDME}] = 6.6 \times 10^{-3} \text{ M}$; $D_{\text{abs}} = 1.3 \times 10^{-4} \text{ einstein l}^{-1}$).

nm. However, the rate constants of these reactions are about two orders of magnitude lower than the rate constant of the reaction of phosphonyl radicals with styrene. At the relatively low styrene concentrations employed in these experiments ($[\text{St}] < 10^{-2} \text{ M}$), therefore, reactions of carbon-centred radicals with styrene could be neglected.

Hints for the assignment of species A were obtained from experiments with solutions containing large proportions of styrene. Figure 6 shows a plot of the pseudo-first-order rate constant of the decay of the absorption at 360 nm *versus* the styrene concentration, measured at concentrations up to 0.1 M. A second-order rate constant $k_{\text{A} + \text{St}} = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ is obtained from the slope of the straight line; the intercept coincides with the value of the rate constant measured with the styrene-free solution. On the basis of these findings A is tentatively attributed to a biradical formed by intramolecular hydrogen abstraction in triplet excited molecules according to reaction (2).

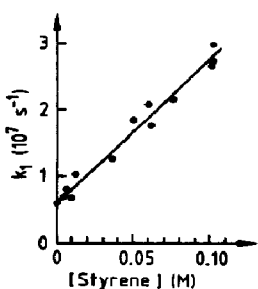
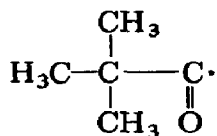


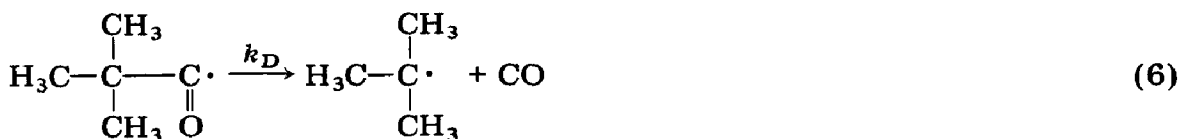
Fig. 6. Flash photolysis of PDME in argon-saturated cyclohexane solution: influence of styrene on the decay rate of the transient absorption at 360 nm ($[\text{PDME}] = 6.6 \times 10^{-3} \text{ M}$; $D_{\text{abs}} = 1.3 \times 10^{-4} \text{ einstein l}^{-1}$).

It still remains to discuss the nature of the long-lived species C having an absorption peak at 260 nm. It appears quite feasible to attribute this species to the pivaloyl radicals



that are generated by α scission according to reaction (1). Because adduct styryl radicals were easily detectable by their characteristic absorption band at 320 nm (see Fig. 5(a)) and because the extinction coefficient of styryl radicals is known [5] ($\epsilon_{322 \text{ nm}} = 5.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in cyclohexane at 25 °C) the quantum yield of α scission could be determined: $\Phi(\alpha) \approx 0.3$ was obtained for both PDME and PDEE.

Fischer *et al.* [6] have studied the kinetics of both the decarbonylation and the self-reaction of pivaloyl radicals in methylcyclopentane solution:



From the Arrhenius equations

$$\log k_D = 11.9 - \frac{9.3}{2.3RT} \quad (8)$$

and

$$\log 2k_S = 13.0 - \frac{3.6}{2.3RT} \quad (9)$$

given by these authors [6] (where R is in kilocalories per mole per kelvin), $k_D = 1.3 \times 10^5 \text{ s}^{-1}$ and $2k_S = 2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ are derived for $T = 298 \text{ K}$. The decay of the absorption of species C occurred definitely faster than expected from $\tau = 1/k_D \approx 8 \mu\text{s}$, which shows that species C cannot be assigned to *t*-butyl radicals. Moreover, the decay of the long-lived absorption followed second-order kinetics; as shown in Fig. 7, a plot of the first half-lives *versus* the reciprocal absorbed dose yields a straight line corresponding to

$$\tau_{1/2} = \frac{1}{2k_S[\text{R}\cdot]_0} = \frac{ed}{2k_S(\text{OD})_0} = \frac{1}{2k_S\Phi(\alpha)D_{\text{abs}}} \quad (10)$$

($d = 0.6 \text{ cm}$). It turns out that $2k_S = (2.0 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in accordance

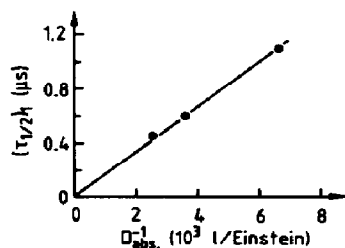


Fig. 7. Flash photolysis of PDME in argon-saturated cyclohexane solution: plot of the first second-order half-life of the decrease in the long-lived absorption (species C) at 260 nm vs. the reciprocal absorbed dose per flash ($[\text{PDME}] = 1.47 \times 10^{-2} \text{ M}$).

with the reported value, and that the extinction coefficient $\epsilon_{260 \text{ nm}}$ of pivaloyl radicals in cyclohexane is $2.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

It should be pointed out that with both PDME and PDEE quite similar results were obtained. Therefore, in most cases, results obtained with only one of the two, usually PDME, are presented in this paper.

4. Discussion

Conclusions concerning the mechanism of the photolysis of the two classes of phosphine oxides investigated during this work are depicted in Figs. 8 and 9. Contrary to the results for the aroylphosphine oxides, rather long-lived excited singlet states ($\tau_s \approx 10 \text{ ns}$) were detected with all three compounds. Regarding the singlet deactivation routes, however, significant differences were observed. In the case of PDPO, α scission (from singlet states) is the predominant deactivation route. With the pivaloylphosphonic acid esters PDME and PDEE, α scission also contributes significantly to the deactivation of the excited singlet states ($\Phi(\alpha) = 0.3$). However, intersystem crossing to the triplet manifold is the dominating singlet deactivation process in this case ($\Phi(T) = 0.6$). The results indicate that biradical formation plays

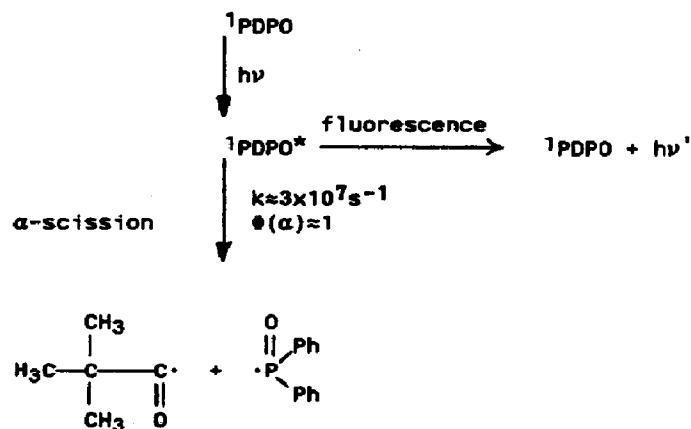


Fig. 8. Photolysis of solutions of PDPO in cyclohexane or CH_2Cl_2 .

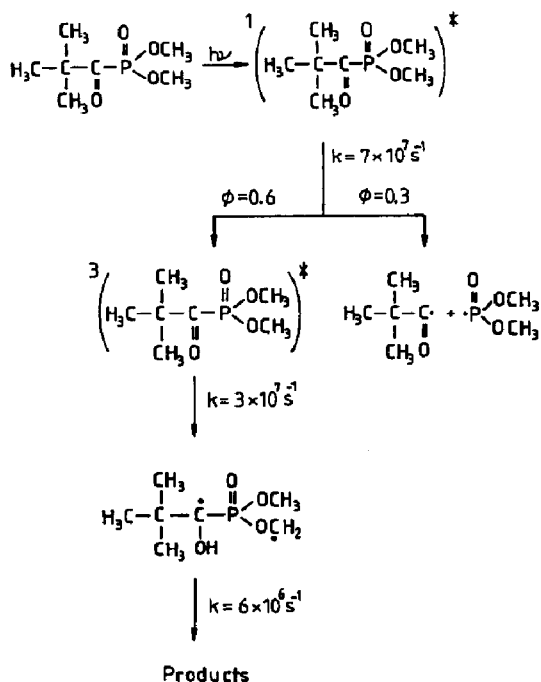


Fig. 9. Photolysis of solutions of PDME in cyclohexane or CH_2Cl_2 .

a role in the deactivation of the triplets. However, the extent to which this reaction occurs has not yet been determined.

Finally, the very high reactivity of dimethoxy- and diethoxyphosphonyl radicals towards styrene deserves some comment. The rate constants found in this work ($(2.2 - 2.5) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) are three to four times higher than the rate constant of the reaction of diphenylphosphonyl radicals ($\text{O}=\dot{\text{P}}(\text{Ph})_2$) with styrene. Whereas the high reactivities can be explained in terms of the pyramidal structure of the phosphonyl radicals, with the consequence that the unpaired electron is easily accessible to the reactants, the differences in reactivities of the different phosphonyl radicals can be understood on the basis of a pronounced tetrahedral structure in the case of dimethoxyphosphonyl and diethoxyphosphonyl radicals and the more flattened tetrahedral structure in the case of diphenylphosphonyl radicals [7, 8]. The more flattened the pyramid the lower is the reactivity of the phosphorus radical towards styrene. This aspect will be elaborated in more detail in a forthcoming paper [9].

Acknowledgments

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References

- 1 T. Sumiyoshi, W. Schnabel, A. Henne and W. Lechtken, *Polymer*, **26** (1985) 141.
- 2 T. Sumiyoshi, A. Henne and W. Schnabel, *J. Photochem.*, **32** (1986) 119.
- 3 P. Lechtken, I. Buethe and A. Henne (BASF AG), *Ger. Patent 2830927*, 1980.
P. Lechtken, I. Buethe, M. Jacobi and W. Trimborn (BASF AG), *Ger. Patent 2909994*, 1980.
M. Jacobi and A. Henne, *Radiat. Curing*, **10** (1983) 16.
- 4 T. Sumiyoshi, A. Henne, P. Lechtken and W. Schnabel, *Z. Naturforsch., Teil A*, **39** (1984) 434.
- 5 O. Brede, W. Helmstreit and R. Mehnert, *J. Prakt. Chem.*, **316** (1974) 402.
- 6 H. Schuh, E. J. Hamilton, Jr., H. Paul and H. Fischer, *Helv. Chim. Acta*, **57** (1974) 2011.
- 7 C. M. Kerr, K. Webster and Ff. Williams, *J. Phys. Chem.*, **79** (1975) 2650.
- 8 M. Geffroy and E. A. Lucken, *Mol. Phys.*, **22** (1971) 257.
- 9 T. Sumiyoshi and W. Schnabel, *Makromol. Chem.*, **186** (1985) 1811.