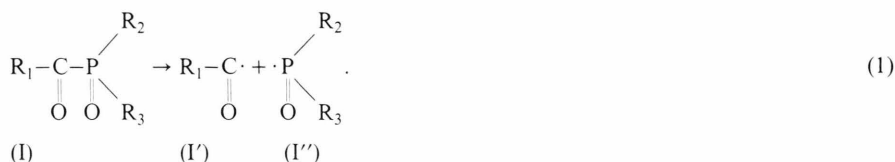


Optical Absorption Spectra of Phosphonyl Radicals

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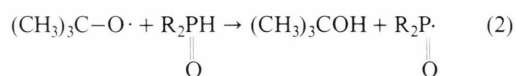
Upon UV-irradiation, various phosphine oxides of the general structure I were found to be fragmented readily into free radicals I' and I'':



Laser flash photolysis studies revealed that radicals of type I'' with R₂ and/or R₃ being phenyl groups possess a strong absorption band with a maximum around 330 nm. $\epsilon_{335\text{ nm}} = 1.9 \times 10^4 \text{ l/mol cm}$ was estimated for diphenyl phosphonyl radicals (Ph₂P=O).

Phosphonyl radicals of the general structure R₂R₃P=O can be produced directly by UV irradiation of various acyl phosphine oxides according to reaction (1) (cf. Abstract). This reaction proceeds rather fast if R₂ and/or R₃ are phenyl groups. Actually, compounds such as 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (TMDPO) are used technically to initiate free radical chain reactions, e.g., during photocuring of coatings [1].

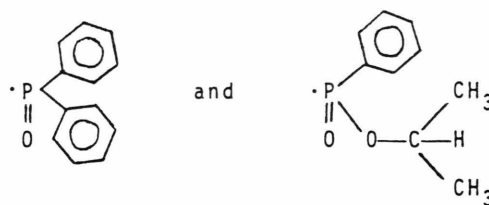
It is noteworthy that, up till now, indirect methods were used to generate phosphonyl radicals [2, 3]: frequently, tert-butoxyl-radicals (CH₃)₃CO·, formed by photolysis of di-tert-butyl peroxide, were allowed to react with phosphites:



Because the rate constants of such reactions are relatively low [2a] (10⁵ to 10⁶ l/mol s), physical properties and chemical reactivities of phosphonyl radicals produced via indirect action could not be studied readily and, commonly, continuous irradiation techniques were employed such as in the

EPR studies of Anpo et al. [2], and of Roberts and Singh [3]. Absorption spectra of phosphonyl radicals have not yet been reported.

In this paper, we wish to describe flash photolysis studies of the direct photolysis of the compounds listed in Table I by light of 347 nm which was produced by a ruby laser (J. K. Lasers Ltd.) in conjunction with a frequency doubler. The transient absorption spectra shown in Fig. 1 were recorded 50 to 100 ns after the flash (halfwidth ca. 20 ns). They are very similar and are attributed to the respective phosphonyl radicals produced according to reaction (1):



The assignment of the transient spectra to free radicals results from the fact that, in the cases of TMDPO and TMPPI the lifetime of the precursors, i.e. electronically excited states, is less than one ns. In the case of PDPO the fluorescence lifetime is about 30 ns. This value is still low compared to the time after the start of the flash (about 100 ns) at which the transient spectra were recorded.

Product analyses carried out after continuous irradiation of TMDPO in solution and measurements of the decrease of the ground state absorption

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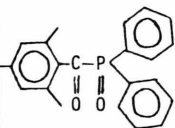
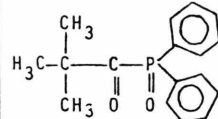
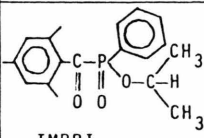
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Table I. Absorption and emission of transients produced during the photolysis of acyl phosphine oxides.

Compound	Emission			Absorption	
	λ_{exc} (nm)	λ_{max} (nm)	lifetime at λ_{max} (ns)	λ_{max} (nm)	(O.D.) [*] (O.D.) _{rel}
 TMDPO	320	420	0.5	336 (benzene)	0.55
	360	420	0.3	331 (CH ₂ Cl ₂) 328 (CH ₃ OH)	
 PDPO	286	425	30	332 (CH ₂ Cl ₂)	1.00
	347	425	30	325 (CH ₃ OH)	
 TMPPI	310	440	0.6	327 (CH ₃ OH)	0.24
	380	440	0.4		

* Initial optical density of R₂P=O radicals relative to that observed with PDPO.

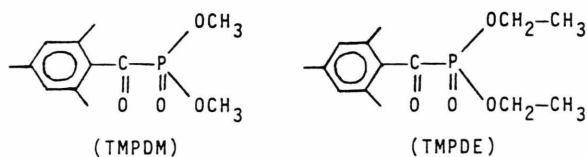
after flash photolysis resulted in a quantum yield of total decomposition Φ (–TMDPO) \approx 0.5. Assuming a similar value for fragmentation into radicals, an extinction coefficient of $\epsilon_{335\text{nm}} = 1.9 \times 10^4$ (l/mol cm) was estimated. Taking into account that 2,4,6-trimethylbenzoyl radicals (similar to benzoyl radicals) were found to possess an extinction coefficient of only a few hundred (l/mol cm) and that (CH₃)₃C–C=O radicals are absorbing even less in this wavelength range, it is concluded that the spectra shown in Fig. 1 are due to the radicals Ph₂P=O and Ph(C₃H₇O)P=O.

In this connection it is interesting to note that diphenylphosphinyl radicals (Ph₂P·) were reported [4] to possess an absorption spectrum with a maximum around 330 nm.

With respect to the question as to whether the precursors of the free radicals are singlet- or triplet-excited states, it can be concluded from the results of quenching experiments with naphthalene that at

least to some extent triplets are involved in the fragmentation process.

With 2,4,6-trimethylbenzoylphosphonic acid dimethylester (TMPDM) and with 2,4,6-trimethylbenzoylphosphonic acid diethylester (TMPDE)



a short-lived absorption ($\lambda_{\text{max}} = 380$ nm, $\tau_{1/2} < 1$ μ s) was observed at the end of the flash. After its decay a rather long-lived absorption band ($\lambda_{\text{max}} = 370$ nm) remained. Further work will reveal whether the short-lived absorption is due to triplets and whether the long-lived absorption can be ascribed to diacylphosphonyl radicals or radicals of another structure. A forthcoming paper will report on the

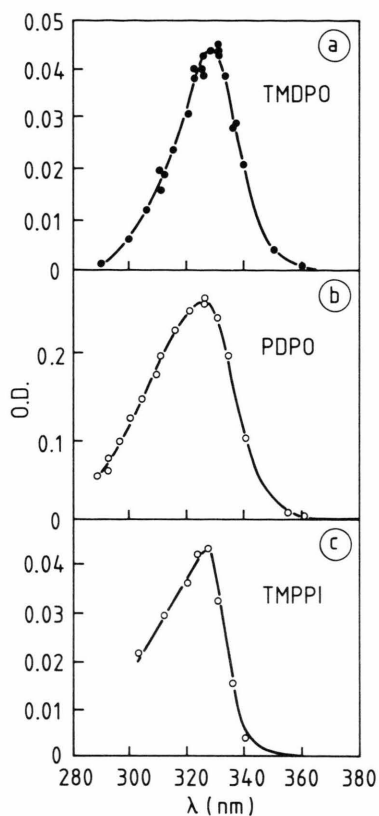


Fig. 1. Transient difference absorption spectra recorded 50 to 100 ns after irradiation of acyl phosphine oxides in argon-saturated methanol solution by a 20 ns flash of 347 nm light. (a) TMDPO (4.0×10^{-4} mol/l), (b) PDPO (7.8×10^{-4} mol/l), (c) TMPPI (4.6×10^{-4} mol/l). Absorbed dose per flash (in Einstein/l): 1.0×10^{-5} (a), 3.6×10^{-5} (b) and 2.4×10^{-5} (c).

reactivity of diphenylphosphonyl radicals which was found to be unusually high towards olefinic compounds.

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