The Photo-induced Cleavage of Acylphosphine Oxides

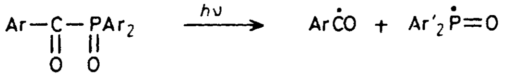
Jane E. Baxter,[a] R. Stephen Davidson,[a]* Hendrik J. Hageman,[b] Keith A. McLauchlan,[c] and David G. Stevens[c]

[a] *Department of Chemistry, The City University, Northampton Square, London EC1V 0HB, U.K.*
[b] *Akzo Research, Corporate Research Department, 6800 Arnhem, The Netherlands*
[c] *Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, U.K.*

By the use of chemically induced dynamic electron polarisation acylphosphine oxides have been shown to undergo the Type I fission reaction from their triplet states.

Acylphosphine oxides have a relatively strong absorption band in the 300—400 nm ($\varepsilon < 1000$ dm^3 mol^{-1} cm^{-1}) region, which is somewhat reminiscent of that exhibited by 1,2-dicarbonyl compounds. Recently it has been claimed that acylphosphine oxides[1] and related compounds[2] readily undergo the Type I cleavage reaction (1) which is in marked contrast with the lack of evidence supporting the view that 1,2-dicarbonyl compounds undergo a similar reaction in the solution phase[2] with similar facilities.[3]

That photolysis of acylphosphine oxides leads to radicals capable of initiation of polymerisation has been shown by Schnabel *et al.*[2,4] ourselves, and Timpe.[5] Evidence that the radicals are generated by a Type I process has been deduced from studies using the technique of laser flash photolysis.[1,2,4] Unequivocal identification of the radicals using this technique is difficult since the absorption spectrum of the phosphorus radical is broad, relatively featureless, and is in the region of wavelength for laser excitation. E.s.r. is a much more powerful technique for identifying radicals and the flash photolysis e.s.r. method together with chemically induced dynamic electron polarisation (CIDEP) has proved invaluable in sorting out the mechanisms of photochemical reactions leading to a radical production.[6,7] We now report upon a study of the photolysis of acylphosphine oxides using this method to



$$\mathrm{Ar{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{P}}Ar_2} \xrightarrow{h\nu} \mathrm{Ar\dot{C}O} + \mathrm{Ar'_2\dot{P}{=}O} \quad (1)$$

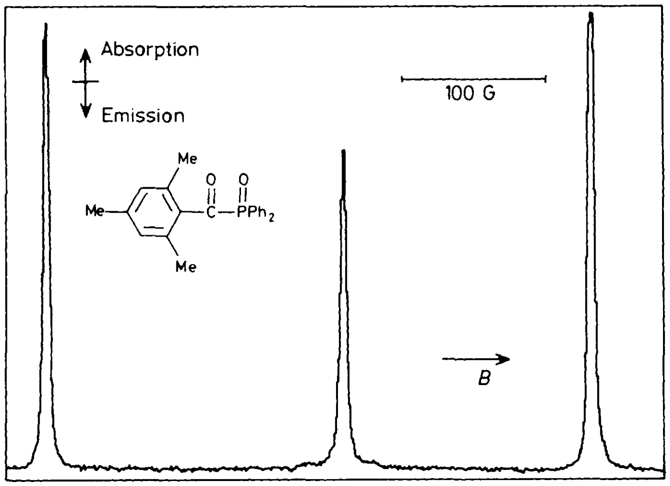


Figure 1. The TIS spectrum of radicals produced by photolysis of the 2,4,6-trimethylphenylacyl derivative. The outermost lines result from phosphorus-centred radical and the innermost one from the carbon-centred radical. The spectrum exhibits absorptive TM electron-spin polarization.

identify the radicals and in addition demonstrate that they are predominantly produced from the triplet state.

Two closely-related compounds in this series have been studied, the 2,4,6-trimethylphenyl- and the 2,6-dimethoxyphenyl-acyl derivatives of the diphenylphosphine oxide compound. These were dissolved in propan-2-ol and subjected to laser photolysis at 308 nm. Spectra were obtained using the time-integration spectroscopy (TIS) technique;[8] this involves sampling and integrating numerically the e.s.r. signal observed, after each laser pulse, over a chosen time interval and at a specific value of the external magnetic field. This is then repeated for successive field values. In this study the signals varied rapidly in time and unusually short sample periods were used. Experiments were conducted at room temperature on flowing deoxygenated samples.

The spectrum of the radicals produced on photolysis of the 2,4,6-trimethylphenyl compound is shown in Figure 1, with the signal integrated between 0.12 and 0.24 μs after the photolysis pulse. It consists of three lines, the outer two of which are due to the phosphorus-centred radical, being split by a phosphorus coupling of 372.7 gauss (1 G = 10^{-4} T). The central line is from the carbon-centred radical, whose small couplings are not resolved on the wide sweep (and limited number of field points) used to construct the spectrum. No other C-centred radical was observed, *e.g.* the $Me_2\dot{C}OH$ radical produced by hydrogen abstraction from the solvent.† This spectrum shows conclusively that the radicals are produced as a result of a Type I cleavage. The spectrum is highly spin-polarized, in enhanced absorption, at this early time. This is due to the action of the triplet mechanism (TM) of CIDEP and it is remarkable in a system wherein a large hyperfine coupling would be expected to produce strong geminate radical pair mechanism (RPM) polarization that more is not observed:[7] the intensities of the low and high field lines are almost identical and show only a very slight distortion due to emission/absorption (E/A) RPM polarization. As time evolves such distortions quickly affect the spectrum, as is shown for the other system, discussed below. The observation of the TM polarization demonstrates unequivocally that the observed radicals result from the reaction of the triplet state of the precursor.

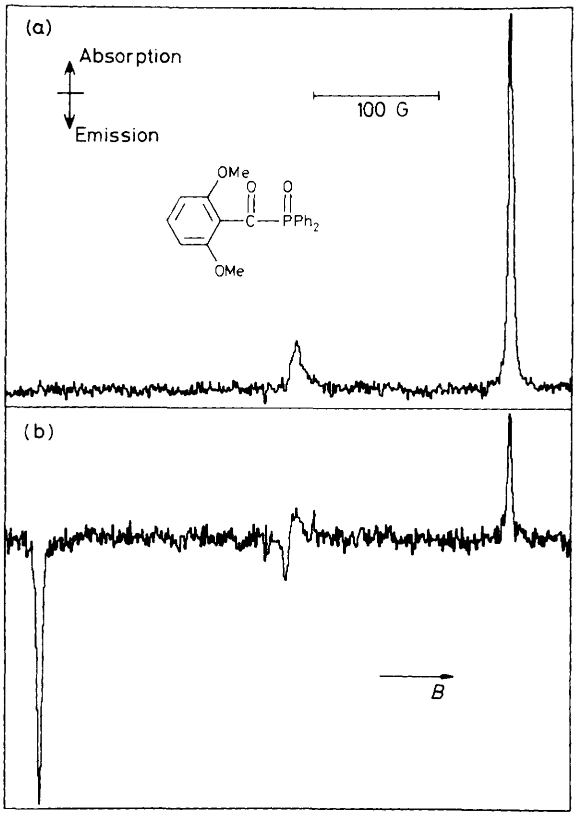


Figure 2. The TIS spectrum of radicals produced by photolysis of the 2,6-dimethoxylphenylacyl derivative with time integration (a) between 0.1 and 0.3 μs and (b) between 0.5 and 1.0 μs post flash. The latter shows a spectrum of three lines, due to phosphorus and carbon-centred radicals as before, but now dominated by E/A RPM spin polarization. The former shows that an absorptive TM contribution is evident at earlier times and produces a distorted spectrum due to its addition to a simultaneous geminate RPM spectrum.

The spectrum of radicals produced by photolysis of the 2,6-dimethoxyphenyl compound is shown at two different times after the flash in Figures 2(a) and 2(b). In Figure 2(b), obtained with sampling between 0.5 and 1.0 μs after the photolysis flash, again a basic three line pattern is apparent, although now some lines are in opposite phases. Once again the outer lines emanate from the phosphorus centred radical, with a coupling of 372.7 gauss, and the inner one from the carbon-centred one, showing that Type I cleavage has occurred. Unlike the previous case, this spectrum is dominated by RPM polarization, and shows the emission at low field, absorption at high (E/A) characteristics of geminate radicals formed from the excited triplet state of their precursor. The TM polarization is evidently much weaker in this system (or spin relaxation is much faster) and the spectrum shows little evidence of a TM contribution. However in Figure 2(a), obtained with integration between 0.1 and 0.3 μs after the flash, a TM contribution (as shown for the other compound in Figure 1) adding to an E/A RPM contribution [as shown in Figure 2(b)]. The TM contribution is sufficient at

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† Chemical trapping of the photogenerated radicals has been carried out using TMPO (2,2,4,4-tetramethylpiperidinyloxyl). No evidence could be found for the formation of the $Me_2\dot{C}OH$ radical and the same results were obtained when the reactions were run in either benzene or propan-2-ol solution. J. E. Baxter, R. S. Davidson, and H. J. Hageman, to be published.

this early time just to make the lowest field line visible in absorption, to make the central line in absorption and to enhance the high-field one. The observation of the TM contribution confirms the triplet nature of the precursor.

In conclusion, it has been shown by direct observation that in propan-2-ol solution the two acylphosphine oxides studied dissociate through their excited triplet states to produce radicals *via* a Type I cleavage.

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