Thiophosphonyl Radicals

Photolytic Generation and Reactivity Towards Olefinic Compounds

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Upon irradiation with UV light ($\lambda = 347$ nm), 2,4,6-trimethylbenzoyldiphenylphosphine sulfide was found to be fragmented into free radicals by α-scission ($\Phi(\alpha) = 0.3 \pm 0.1$):

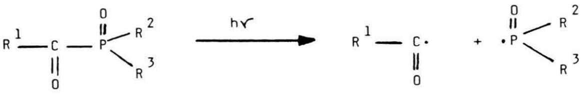
(1)

Flash photolysis studies revealed that the optical absorption spectrum of diphenylthiophosphonyl radicals, $S = \dot{P}(Ph)_2$, possesses a strong band with $\lambda_{max} = 340$ nm and a somewhat weaker band with $\lambda_{max} \approx 500$ nm ($\varepsilon_{340\,nm} = (1.2 \pm 0.2) \cdot 10^4$ l/mol cm).

The reactivity towards olefinic compounds, M, is 10 to 30 times lower than in the case of $O = \dot{P}(Ph)_2$ radicals. Typical bimolecular rate constants (in l/mol s) of the reaction of $S = \dot{P}(Ph)_2$ with M are: 4×10^6 (styrene), 6.2×10^5 (methylacrylate), 4.2×10^4 (vinyl acetate).

Optical Absorption Spectra and Quantum Yields of α-Scission

It has been reported previously [1 – 3] that phosphonyl radicals can be generated by light-induced α-scission of acyl phosphine oxides according to the reaction (2)



In the case of 2,4,6-trimethylbenzoyldiphenylphosphine oxide, diphenyl phosphonyl radicals, $O = \dot{P}(Ph)_2$, are produced with $k_\alpha > 10^9\ s^{-1}$ ($\Phi(\alpha) = 0.4$).

We have now shown that thiophosphonyl radicals of the structure $S = \dot{P}(R)_2$ can be generated similarly. According to (1) (cf. abstract), the photolysis of 2,4,6-trimethylbenzoyldiphenyl sulfide (TMDPS) yields diphenylthiophosphonyl radicals, $S = \dot{P}(Ph)_2$.

TMDPS, whose ground state and emission spectra are shown in Fig. 1 a, was irradiated in Ar-saturated CH_2Cl_2 solution by 347 nm flashes produced by a ruby laser (J. K. Lasers Ltd.) operated in conjunction with a frequency doubler. At the end of the 20 ns flash, the absorption spectrum shown in Fig. 1b was recorded. It exhibits maxima at 340 and 500 nm. This transient spectrum, which decays at all wave lengths with the same rate according to 2nd order kinetics is attributed to diphenylthiophosphonyl radicals on the basis that it is very smilar to the absorption spectrum of diphenyl phosphonyl radicals, $O = \dot{P}(Ph)_2$. The latter is shown in Figure 1 c.

In the presence of styrene, the absorption spectrum of adduct styryl radicals, peaked at 325 nm, was built-up simultaneously with the decay of the transient spectrum assigned to the thiophosphonyl radicals. This is depicted in Figure 2. Using the extinction coefficient of styryl radicals reported by Brede et al. [4], $\varepsilon_{320\,nm} = 5.8 \times 10^3$ l/mol cm, the concentration of diphenylthiophosphonyl radicals was estimated for the case that all of them were scavenged by styrene. Actually, this case was approximated only roughly, because even at rather high styrene concentrations part of the thiophosphonyl radicals underwent other reactions, especially radical-radical reactions. Moreover, trimethylbenzoyl radicals generated according to (1) are also expected to react with styrene forming adduct styryl radicals. Since the rate constant of this reaction (estimated as 5×10^5 l/mol s) is about 10 times lower than that of the reaction of $S = \dot{P}(Ph)_2$

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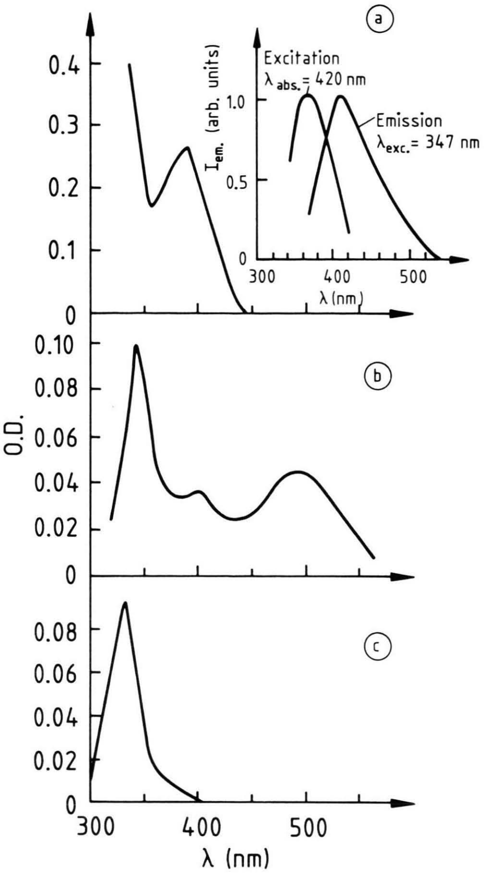

Fig. 1. (a) Ground state absorption spectrum of TMDPS in CH_2Cl_2 solution. Inset: emission and excitation spectra. (b) and (c) Difference absorption spectra recorded after irradiation of TMDPS (b) and TMDPO (c) in Ar-saturated CH_2Cl_2 solution by a 20 ns flash of 347 nm light. [TMDPS] = 3.6×10^{-4} mol/l; [TMDPO] = 4.0×10^{-4} mol/l. $D_{abs.}$: 2.9×10^{-5} (b) and 2.2×10^{-5} Einstein/l (c). These spectra were recorded at the end of the flash.

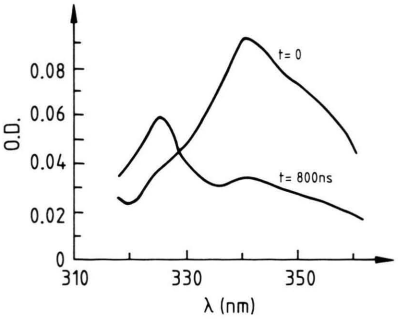

Fig. 2. Transient absorption spectra recorded with an Ar-saturated solution of TMDPS (3.6×10^{-4} mol/l) containing styrene (0.44 mol/l). $D_{abs.}$: 3.1×10^{-5} Einstein/l.

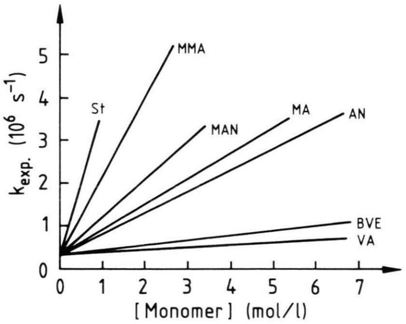

Fig. 3. Reaction of $S = \dot{P}(Ph)_2$ radicals with various monomers. Experimental 1st order rate constants of the decay of the transient absorption at $\lambda = 500$ nm vs. the monomer concentration. TMDPS in Ar-saturated CH_2Cl_2 solution (8.2×10^{-4} mol/l). $D_{abs.} = 2.9 \times 10^{-5}$ Einstein/l.

radicals with styrene (vide infra), the reaction of benzoyl radicals with styrene could be ignored by measuring the styryl radical concentration at a time after the flash when thiophosphonyl radicals were almost totally consumed but trimethylbenzoyl radicals only to a small extent.

Being aware of these restraints, the extinction coefficient of $S = \dot{P}(Ph)_2$ radicals and the quantum yield of α-scission were estimated: $\varepsilon_{340\,nm} = (1.2 \pm 0.2) \times 10^4$ l/mol cm and $\Phi(\alpha) = 0.3 \pm 0.1$. For comparison, data obtained with CH_2Cl_2 solutions of both 2,4,6-trimethylbenzoylphosphine oxide (TMDPO) and TMDPS are listed in Table 1.

It should be noted that, in the evaluation of the ε-values of the radicals $S = \dot{P}(Ph)_2$ and $O = \dot{P}(Ph)_2$, the absorption of the trimethylbenzoyl radicals was neglected. This is justifiable because benzoyl radicals absorb light at $\lambda > 300$ nm relatively weakly (ε is in the order of a few hundred only). According to Fischer et al. [5] $\varepsilon \leqq 320$ l/mol cm at $\lambda = 370$ nm in 3-methyl-3-pentanol solution at 22 °C.

Reactions with Olefinic Compounds

The reactivity of diphenylthiophosphonyl radicals towards various olefinic compounds was investigated

Table 1. Experimental condition for the determination of $\Phi(\alpha)$ and of the extinction coefficients of the radicals $O=\dot{P}(Ph)_2$ and $S=\dot{P}(Ph)_2$ in CH_2Cl_2 solution.

Compound	TMDPO	TMDPS
Concentration (mol/l)	4.4×10^{-4}	7.2×10^{-4}
O.D. at 347 nm	0.142	0.204
Absorbed dose (Einstein/l)	2.1×10^{-5}	2.9×10^{-5}
Radical	$O=\dot{P}(Ph)_2$	$S=\dot{P}(Ph)_2$
$\Phi(\alpha)$	0.4 ± 0.1	0.3 ± 0.1
λ_{max} (nm)	330	340
ε_{max} (l/mol cm)	$(1.6 \pm 0.2) \times 10^4$	$(1.2 \pm 0.2) \times 10^4$

Table 2. Bimolecular rate constants $k_{R^\cdot+M}$ of the reaction of the radicals $O=\dot{P}(Ph)_2$ and $S=\dot{P}(Ph)_2$ with various monomers (in l/mol s).

	$O=\dot{P}(Ph)_2$	$S=\dot{P}(Ph)_2$
Styrene (St)	4.6×10^7	4.0×10^6
Methylmethacrylate (MMA)	4.1×10^7	1.9×10^6
Methacrylonitrile (MAN)	1.9×10^7	9.1×10^5
Methylacrylate (MA)	1.7×10^7	6.2×10^5
Acrylonitrile (AN)	1.3×10^7	5.2×10^5
n-Butylvinylether (BVE)	5.0×10^6	1.5×10^5
Vinylacetate (VA)	1.4×10^6	4.2×10^4

by measuring the decay of the absorption of the radicals at $\lambda = 500$ nm. Solutions of TMDPS in CH_2Cl_2 containing various amounts of the unsaturated compound were irradiated with 347 nm light flashes. Figure 3 shows plots of 1st order decay rate constants vs. the monomer concentration. From the slope of the straight lines bimolecular rate constants of the reaction

$$S=\dot{P}(Ph)_2 + M \rightarrow \text{Products} \qquad (3)$$

were calculated according to the equation

$$k_{exp} = \sum k + k_{R^\cdot+M}[M] . \qquad (4)$$

$\sum k$ denotes the sum of rate constants of reactions which, in addition to reaction (3), contribute to the decay of the radicals. In the absence of additives, $S=\dot{P}(Ph)_2$ radicals were mainly deactivated by a self-reaction with $2k_S = 1.9 \times 10^{10}$ l/mol s. The values of the rate constants $k_{R^\cdot+M}$ obtained for the radicals $S=\dot{P}(Ph)_2$ and $O=\dot{P}(Ph)_2$ are listed in Table 2. $S=\dot{P}(Ph)_2$ radicals are 10 to 30 times less effective in the reaction with olefinic compounds than $O=\dot{P}(Ph)_2$ radicals. Principally, the differences in reactivity can be caused both by geometrical factors and by differences in the electron density distribution in the two radicals. To our knowledge, nothing is known, up to now, about the latter point. With respect to steric effects, it might be noted that the high reactivity of the phosphonyl radicals was explained in terms of its rather pronounced tetrahedral structure, which alleviates the accessibility to approaching reactants [2]. Replacement of the oxygen atom in the phosphonyl radical by the more voluminous sulfur atom brings about a structural alteration with the consequence of a reduced accessibility of the site of the unpaired electron.

Acknowledgements

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[5] C. Huggenberger, J. Lipscher, and H. Fischer, J. Phys. Chem. **84**, 3467 (1980).