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PULSE RADIOLYSIS STUDIES OF ENERGY TRANSFER REACTIONS FROM BENZENE EXCIMER TO PHOSPHINE OXIDES

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Acylphosphine oxides were tested as a new class of singlet indicators and the diphenyl phosphonyl radical was detected as a result of singlet energy transfer from benzene excimers to 2,4,6-trimethylbenzoyldiphenylphosphine oxide.

In the course of photochemical studies of acylphosphine oxides, we found that α-scission is one of the main photochemical reactions induced by 347 nm laser flashes.1) Among the resulting radicals, the diphenyl phosphonyl radical was shown to have a rather high extinction coefficient at its absorption maximum ($\varepsilon_{335\text{nm}}$ = 19000 $M^{-1}cm^{-1}$). Based on kinetic and mechanistic studies, the α-scission was found to occur exclusively from the excited singlet state, with a quantum yield of 0.5 in the case of 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMDPO).2) This finding and the strong ground state absorption of several acylphosphine oxides in the near UV region motivated us to test the possibility of singlet quenching by acylphosphine oxides.

Benzene excimers were chosen for energy transfer reactions because they have higher energy (emission maximum = 320 nm)3) than the first band of TMDPO (380 nm).

A nanosecond pulse radiolysis system with a 45 MeV electron linear accelerator was used to measure transient absorption spectra. The details of this system have been described elsewhere.4) TMDPO was obtained from BASF AG. Its synthesis has been described before.5) Samples were irradiated after bubbling with pure argon in a 1 cm rectangular quartz optical cell sealed with a teflon stopper. The absorbed dose was measured by the KCNS dosimeter6) (O.D. measurements at 475 nm).

Figure 1 shows absorption spectra observed immediately after the pulse. A weak absorption band peaked around 315 nm was observed in the case of neat benzene which should be due to the cyclohexadienyl radical.7) On addition of TMDPO, a new absorption band peaked at 335 nm was formed. With increasing the TMDPO concentration it became more and more difficult to observe the new absorption signal below 335 nm due to the strong ground state absorption of TMDPO. Nevertheless it is clear that the spectral shape of the new band is quite similar to that of the diphenyl phosphonyl radical.$^{1)}$ The rate of decay of this band fits second order kinetics as is illustrated in Fig. 2, the first halflife of the decay being proportional to the reciprocal initial optical density at 335 nm, i.e. to the reciprocal initial concentration of $O=\dot{P}(Ph)_2$ radicals. Irradiation of benzene produces excited singlet states with $\phi(S) = 1.6 \pm 0.2$.$^{8,9)}$ The picosecond pulse radiolysis of benzene showed that the excited singlet state reacts with ground state benzene resulting in singlet excimers, the formation time being about 10 ps.$^{10)}$ The excimer is characterized by an absorption band peaked at 500 nm$^{11)}$ and a lifetime of τ = 27 ns.$^{12)}$ Therefore, the fast decaying absorption observed at 500 nm in

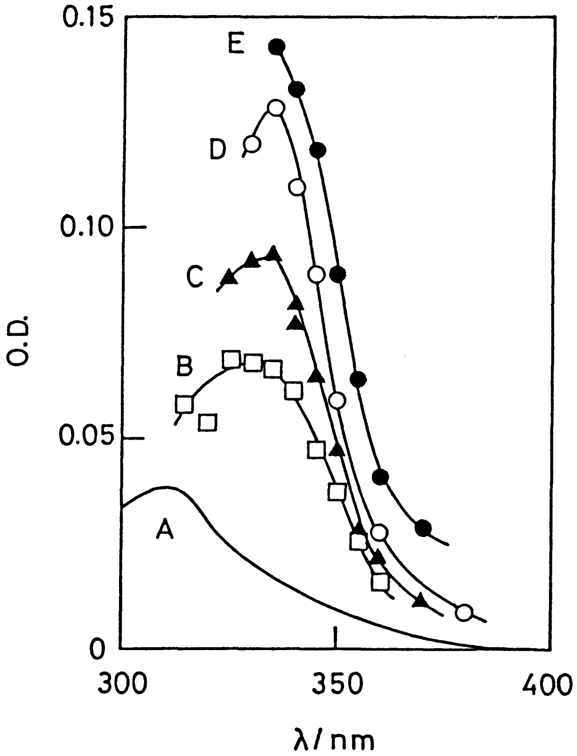

Fig. 1. End of pulse spectra of TMDPO in benzene. (A) 0 M; (B) 4.17 × 10^{-4} M; (C) 8.35 × 10^{-4} M; (D) 1.67 × 10^{-3} M; (E) 3.34 × 10^{-3} M.
Absorbed dose: 9.3 krad/pulse.

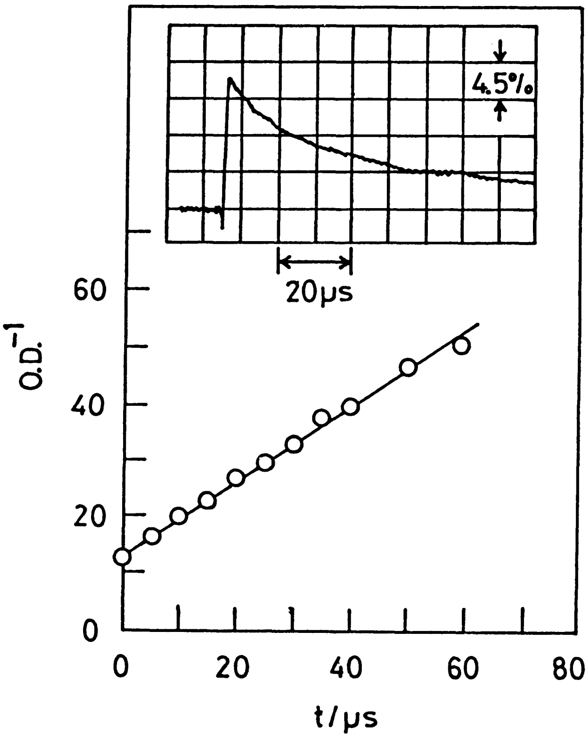

Fig. 2. Second-order kinetic plot of the decay of the optical density at 340 nm observed with 8.35 × 10^{-4} M TMDPO solution in benzene.
Insert: oscilloscope traces depicting changes in the optical absorption.

neat benzene (Fig. 3a) can be assigned to excimers. On addition of TMDPO, this absorption was displaced by an emission (Fig. 3b) which is ascribed to the fluorescence of excited singlet states of TMDPO.[2)] Based on these experimental results, it is concluded that energy transfer from excited benzene singlet excimers to TMDPO occurs and that diphenyl phosphonyl radicals are formed by subsequent α-scission. The yield of diphenyl phosphonyl radicals depends on the relative rates of two competing reactions; the rate of decay of the excimers, and the rate of energy transfer. Consequently, the yield of the diphenyl phosphonyl radical increases with the TMDPO concentration as shown in Fig. 4. A Stern-Volmer plot yielded the energy transfer rate constant $k_q = 5 \times 10^{10}\ M^{-1}s^{-1}$.

With increasing TMDPO concentration, the yield of the phosphonyl radical approaches a plateau value of G = 0.7. Considering ϕ(α-scission) = 0.5,[2)] the yield of benzene singlets can be calculated as 1.4 which is comparable with literature values.[8,9)]

Further studies on the energy transfer from singlet excimers to acylphosphine oxides in various aromatic solutions by pulse radiolysis are in progress.

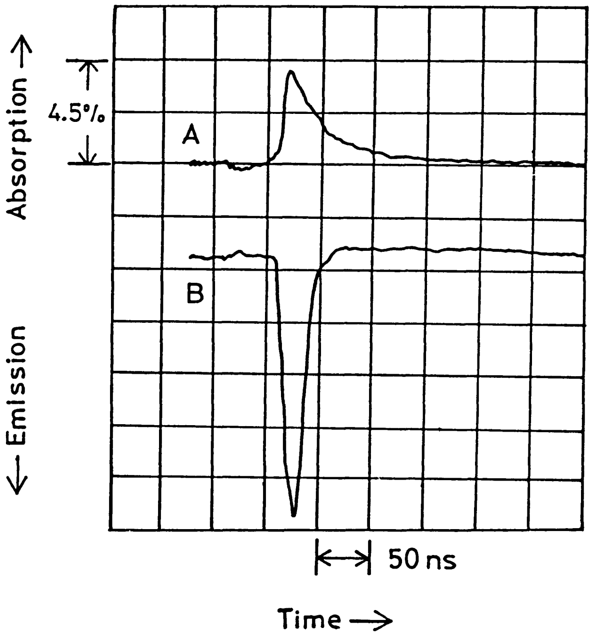

Fig. 3. Oscilloscope traces observed at 500 nm. (A) neat benzene, (B) 1.67×10^{-3} M TMDPO in benzene.

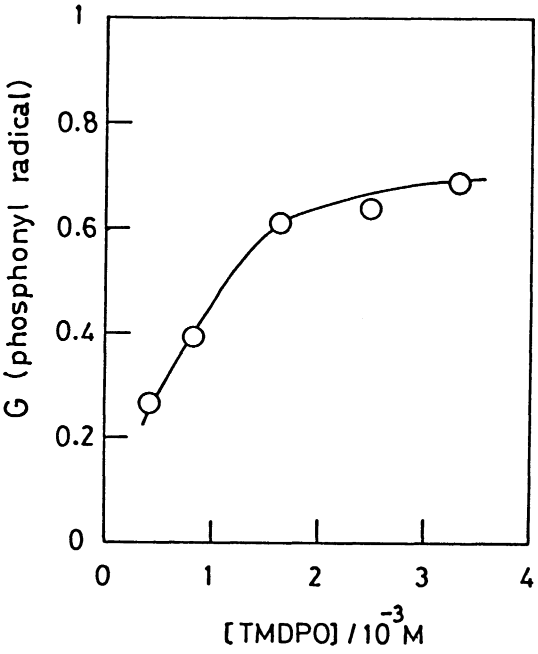

Fig. 4. Dependence of G(phosphonyl radical) on the TMDPO concentration.

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