

THE EFFICIENCY OF TRIPLET ENERGY TRANSFER TO $O_2(^3\Sigma_g^-)$: SENSITIZER AND MEDIUM DEPENDENCE[†]

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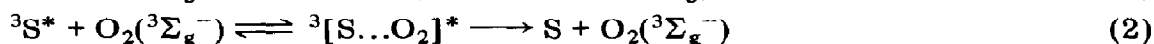
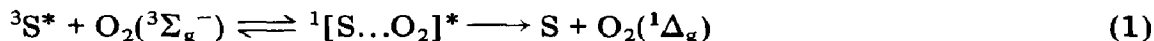
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The efficiency of formation of $O_2(^1\Delta_g)$ in the process whereby electronically excited triplet states are quenched by $O_2(^3\Sigma_g^-)$ has been a matter of some debate. The two spin-allowed processes



proceed via the singlet and triplet manifolds respectively of the encounter complex. Quenching via the quintet manifold



is forbidden. The rate constants for oxygen quenching of triplet states do not generally exceed about one-ninth of the diffusion-controlled value and it has naturally been concluded that quenching is restricted to the singlet manifold and that each quenching act leads to a molecule of $O_2(^1\Delta_g)$ [1]. The validity of this conclusion has been seriously questioned as a result of pulse radiolysis [2] and pulsed laser [3] studies which in turn have themselves been the subjects of criticism based on steady state experiments [4].

In the work to be described a series of sensitizers in aerated media have been subjected to pulsed laser excitation at 355 nm. In each case, the sensitizer triplet yield and the $O_2(^1\Delta_g)$ emission intensity have been monitored by kinetic absorption and kinetic emission spectroscopy respectively. This has allowed determination of S_{Δ}^{ac} values, the fraction of quenchings of each sensitizer triplet by oxygen which leads to $O_2(^1\Delta_g)$ relative to the corresponding value for acridine, the most efficient sensitizer examined. The values for benzene as solvent reproduced in Table 1 clearly demonstrate (a) that S_{Δ} values may vary significantly from unity and (b) that benzophenone, as proposed previously [2, 3], is particularly inefficient in this respect.

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TABLE 1

<i>Sensitizer</i>	S_{Δ}^{ac} in benzene
Acridine	1.0
Anthracene	0.8
Fluorenone	0.8
2-Acetonaphthone	0.7
Benzophenone	0.3

References

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