

The Role of the Triplet State in Dye Photochemistry*

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Two excited electronic states are of principal importance in dye photochemistry—the lowest excited singlet S_1 and the lowest triplet T_1 . The former usually determines the colour of the dye whilst the triplet state has no effect on colour since radiative transitions from the ground state are forbidden. Higher singlet and triplet states are not normally populated by visible light and, even if excitation to these states does occur, radiationless conversion to S_1 or T_1 is usually very rapid.¹

The important photochemical reactions of dyes are those which result in fading or phototendering of the fabric. These reactions may proceed from either the S_1 or T_1 states and in principle such reactions may be prevented by increasing the probability of radiationless transitions. If S_1 is responsible we shall wish to increase the probability of the $S_1 \rightarrow S_0$ or $S_1 \rightarrow T_1$ crossings whilst if T_1 is responsible we must increase the probability of the $S_1 \rightarrow S_0$ or $T_1 \rightarrow S_0$ crossings. Research in this field is therefore concerned with two main questions:

- 1) In any particular dye reaction what part is played by the S_1 and T_1 states?
- 2) What factors determine the radiationless transition probabilities of the crossings $S_1 \rightarrow S_0$, $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ and by what means can these transitions be enhanced?

* Dieser Vortrag ist nur als Zusammenfassung eingegangen, da der Inhalt praktisch vollständig in den nebenstehend zitierten Arbeiten enthalten ist.

On the first question very little work has yet been carried out on actual dye molecules but the experimental methods for solution of the problem are available and have been used for the detailed study of several model systems. The quinones, and duroquinone in particular, have been investigated by flash photolysis methods² and it has been shown that attack on the substrate by excited duroquinone occurs via the S_1 state and not via T_1 . This must not be assumed to be generally the case and it is known that the similar reaction of aromatic ketones, such as benzophenone, proceeds via the T_1 state.³

Considerable progress has been made recently in studies of the second problem and particularly of the factors affecting the $T_1 \rightarrow S_0$ radiationless transition.⁴ Deactivation of the triplet state can be brought about by paramagnetic molecules or ions and also by transfer to a molecule with a lower triplet level.^{3,6} In many cases such energy transfer processes are very efficient and photochemical reaction of a molecule can be completely suppressed by addition of a small amount of quenching substance.

¹ G. PORTER, *Proc. Chem. Soc.*, Tilden Lecture 1959, 291.

² K. BRIDGE and G. PORTER, *Proc. Roy. Soc. A244* (1958) 259, 276.

³ G. PORTER and F. WILKINSON, to be published.

⁴ G. PORTER and M. W. WINDSOR, *Proc. Roy. Soc. A245* (1958) 238.

⁵ G. PORTER and M. R. WRIGHT, *Faraday Soc. Disc.* 27 (1959) 18.

⁶ A. TEREININ and V. ERMOLAEV, *Trans. Faraday Soc.* 52 (1956) 1042.