

# ENERGY TRANSFER FROM MOLECULES IN THE TRIPLET STATE

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Unlike upper singlet states, the triplet states of molecules are readily observed by means of their absorption spectra using flash photolysis techniques. With the exception of the few molecules which have very short phosphorescence lifetimes, this is the only means available for the spectroscopic study of the triplet states of complex molecules in the gas phase or in solution.

The rate of decay of an excited molecule, in its lowest triplet level, is given by:

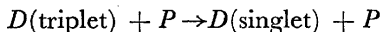
$$-\frac{d[T]}{dt} = k_0[T] + k_1[T] + k_2[T]^2 + k_3[T][G] + \sum_Q k_Q[T][Q]$$

where  $[T]$  is the triplet concentration,  $[G]$  is the concentration of the same species in the ground state and  $[Q]$  is the concentration of quenching molecules;  $k_0$  is the radiative decay constant (phosphorescence), and  $k_1$  is the constant for radiationless conversion to the ground state;  $k_2$  is the molecular quenching constant which, in the cases so far investigated, corresponds very nearly to unit encounter efficiency<sup>1</sup>;  $k_3$  is zero for aromatic hydrocarbons which have been studied kinetically<sup>2</sup>, but is significant in the case of chlorophyll<sup>3</sup>.

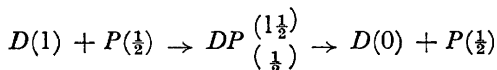
Three types of quenching have been distinguished which may contribute to  $k_Q$ :

*Heavy atom quenching*—Incorporation of heavy atoms into the solvent or into the molecule itself increases spin-orbit coupling and so increases  $k_0$ . This has a negligible effect on most triplet lifetimes in gases and liquids<sup>1,4</sup>.

*Paramagnetic quenching*—The process:



where  $P$  is a paramagnetic molecule, has been established<sup>2</sup> for  $O_2$  and  $NO$  and for a number of paramagnetic ions<sup>1</sup>. Triplet self quenching is also probably of this type. It is not a result of magnetic perturbation and there is no correlation with magnetic susceptibility. The spin restriction is removed by temporary association so that a doublet molecule, for example, acts as follows (spin given in brackets):



The paramagnetic molecule,  $P$ , is not generally changed in the process.

*Triplet energy transfer*—Singlet molecules cannot quench triplets in this way but may do so by the process:

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where  $D$  and  $A$  refer to donor and acceptor. This process was first illustrated in rigid media by Terenin and Ermolaev<sup>5</sup>, though very high concentrations of  $A$  were required. Porter and Wilkinson<sup>4</sup> have recently studied the process of triplet energy transfer in a wide variety of molecular pairs in fluid solvents. The occurrence of the process has been demonstrated unequivocally by observation of triplet absorption spectra of both donor and acceptor, and transfer probabilities have been studied as a function of energy level separations. No evidence is found, nor expected, for long range dipole-dipole transfer.

### References

- <sup>1</sup> G. Porter and M. R. Wright. *Discussions Faraday Soc.*, **27**, 18 (1959)
- <sup>2</sup> G. Porter and M. Windsor. *Proc. Roy. Soc.*, **A245**, 238 (1958)
- <sup>3</sup> H. Linschitz and K. Sarkanen. *J. Am. Chem. Soc.*, **80**, 4826 (1958)
- <sup>4</sup> G. Porter and F. Wilkinson. *Proc. Roy. Soc.*, **A264**, 1 (1961)
- <sup>5</sup> A. N. Terenin and V. L. Ermolaev. *Trans. Faraday Soc.*, **52**, 1042 (1956)