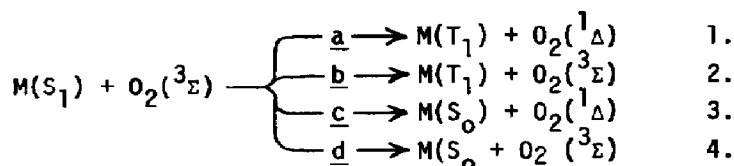# $O_2{}^1\Delta g$ QUENCHING BY THE TRIPLET STATE OF 1, 3-DIPHENYLISOBENZOFURAN IN SOLUTION

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If the singlet (S_1)-triplet (T_1) energy separation of an aromatic sensitizer M exceeds the excitation energy ($\sim$8000cm^{-1}) of $O_2{}^1\Delta_g$, processes 1-4 may contribute to the overall quenching of $M(S_1)$ by the $O_2{}^3\Sigma_g$ ground state with respective probabilities a,b,c and d.

$$M(S_1) + O_2(^3\Sigma) \begin{cases} \underline{a} \longrightarrow M(T_1) + O_2(^1\Delta) & 1. \\ \underline{b} \longrightarrow M(T_1) + O_2(^3\Sigma) & 2. \\ \underline{c} \longrightarrow M(S_0) + O_2(^1\Delta) & 3. \\ \underline{d} \longrightarrow M(S_0 + O_2\ (^3\Sigma) & 4. \end{cases}$$

If each triplet state subsequently produces $O_2{}^1\Delta$ in the energy transfer process

$$M(T_1) + O_2(^3\Sigma) \longrightarrow M(S_0) + O_2(^1\Delta) \qquad 5.$$
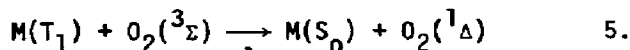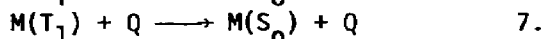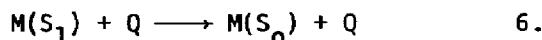
the overall quantum yield of $O_2(^1\Delta)$ is given by

$$\gamma_\Delta = \gamma_{IS} + K[O_2](2\underline{a} + \underline{b} + \underline{c} - \gamma_{IS})/(1 + K[O_2]) \qquad I$$

where γ_{IS} and K denote the intersystem crossing efficiency and Stern Volmer oxygen quenching constant for $M(S_1)$ respectively. For M=1,3-diphenylisobenzofuran (DPBF) in benzene

$$\gamma_{IS} = 0.06 \pm 0.03$$
$$2\underline{a} + \underline{b} + \underline{c} = 1.3_3 \pm 0.15$$

The addition of azulene (Q) to this system introduces the additional processes

$$M(S_1) + Q \longrightarrow M(S_0) + Q \qquad 6.$$
$$M(T_1) + Q \longrightarrow M(S_0) + Q \qquad 7.$$

which reduce the quantum yield of $O_2{}^1\Delta$ formation to $\gamma_\Delta{}^Q$ where

$$\left\{ \frac{\gamma_\Delta}{\gamma_\Delta{}^Q (1 + K_Q[Q])^{-1}} \right\}^{-1} = A + \frac{k_5[O_2]}{k_7[Q]} \left\{ 1 + A \right\} \qquad II$$

and $A = (\underline{a} + \underline{c}) K[O_2]/\left\{ (a + b) K[O_2] + \gamma_{IS} \right\}$

(K_Q is the Stern-Volmer quenching constant associated with process 6). For DPBF in benzene A = 0.29 $\pm$ 0.05 which with the condition

$a + b + c + d = 1$ provides the alternatives

$\underline{a}$	$\underline{b}$	$\underline{c}$	$\underline{d}$
0.3	0.6_3	0.07	0
0.3_7	0.5_6	0	0.07

It is proposed that the partitioning of products from the quenching process $M(S_1) + O_2(^3\Sigma)$ arises from the primary process 1, the products of which undergo successive reactive re-encounters with each other to generate the products of processes 2 and 3 as shown in the sequence

$$M(S_1) + O_2(^3\Sigma) \longrightarrow \begin{array}{l} M(T_1) + O_2(^1\Delta) \\ M(T_1) + O_2(^3\Sigma) \\ M(S_0) + O_2(^1\Delta) \\ M(S_0) + O_2(^3\Sigma) \end{array} \quad \begin{array}{l} \underline{a} = 1-p_T \\ \underline{b} = p_T(1-p_\Delta) \\ \underline{c} = p_T p_\Delta \\ \underline{d} = 0 \end{array}$$

In this case the partitioning factors are related to the re-encounter probabilities p_T and p_Δ as shown, or since

$$2\underline{a} + \underline{b} + \underline{c} = 1.33 = 2-p_T$$
$$p_T = 0.6_7 \text{ and } p_\Delta = \underline{c}/p_T \approx 0.1$$

For two dynamically equivalent processes (between identical solute molecules in the same solvent) the rate constants k_i and k_j are related to the appropriate reactive re-encounter probabilities by[1]

$$k_i(1-p_i)/p_i = k_j(1-p_j)/p_j$$

For the reaction

$$DPBF(S_0) + O_2(^1\Delta) \longrightarrow DPBFO_2$$

in benzene it has been found that[1,2]

$$k = 7 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \text{ and } p = 0.067$$

hence for any other bimolecular process between these molecules in this solvent

$$k(1-p)/p = 1.0 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$$

whence for reactions

$$M(T_1) + O_2(^1\Delta) \longrightarrow M(T_1) + O_2(^3\Sigma)$$
$$p_T = 0.6_7 \text{ and } k = 2.0 \times 10^{10}\text{M}^{-1}\text{s}^{-1}$$

and

$$M(T_1) + O_2(^3\Sigma) \longrightarrow M(S_0) + O_2(^1\Delta)$$
$$p_\Delta \approx 0.1 \text{ and } k = 1.1 \times 10^9\text{M}^{-1}\text{s}^{-1}$$

which are consistent with theoretical expectation[3,4]

With the experimental values of p and derived rate constants k, the Noyes pair model formulation[5]

$$k = k^{O}(1-p)$$

provides estimates of the equilibrium statistical rate constant k^{O} which describes the relaxation of the appropriate complex states $^{1,3}\Gamma_i(M,O_2)$ shown in the accompanying scheme.

References

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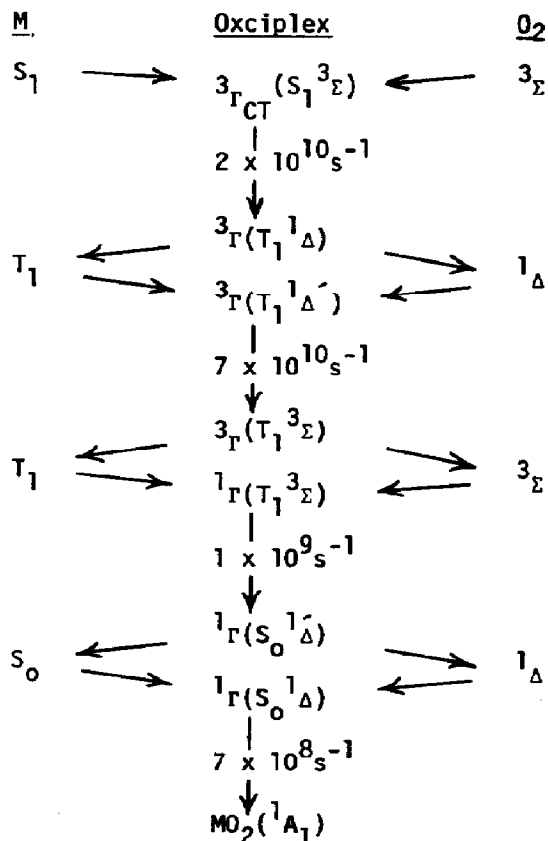
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