The Quenching of Excited Singlet States of Rose Bengal by Bifunctional Compounds

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Summary The quenching of the fluorescence of Rose Bengal by α,ω-diaminoalkanes, α,ω-dinaphthylalkanes, and naphthylalkylamines is extremely efficient and is dependent upon the nature of the terminal groups in the bifunctional compounds and the length of chain which links the two groups.

We report[1] upon the quenching of the fluorescence of Rose Bengal by bifunctional molecules and note that the efficiency of quenching is dependent upon (a) the length of chain linking the two groups in the quenched molecule, and (b) the type of complex formed in the quenching process. Rate constants for the quenching of the fluorescence of Rose Bengal are summarised in the Figure.

It is strikingly obvious that the quenching by diaminoalkanes is most effective when the number of methylene groups in the chain varies from 2 to 5, whilst the quenching efficiency of the α,ω-dinaphthylalkanes and the naphthylalkylamines is at a minimum when the two groups in the quencher are linked by three methylene groups. However, in all cases the efficiency of quenching by these bifunctional molecules is much greater than that for the appropriate monofunctional compounds (*i.e.* triethylamine and 1- and 2-methylnaphthalene). Furthermore, the efficiency is greater than the statistical factor of 2.

Quenching of the fluorescence of dyes by amines in polar solvents has been attributed to an electron transfer process although no spectroscopic evidence is available to support the postulated formation of radical ions.[2] It is also possible that the quenching process involves the formation of contact or encounter charge transfer complexes and at present there is no evidence to show which is the more favoured of the two processes.

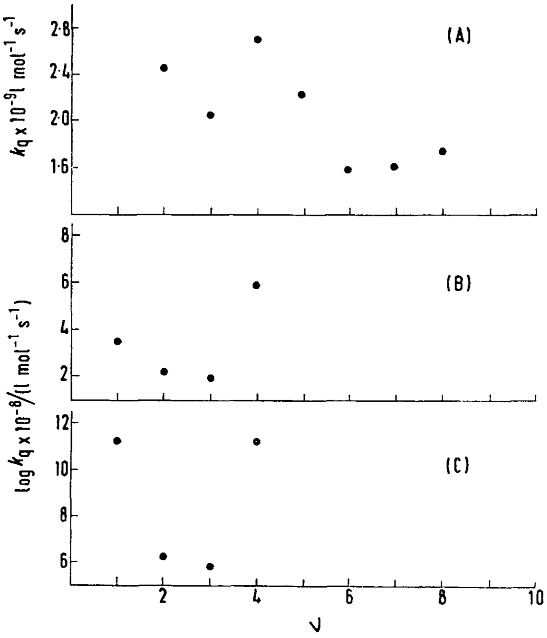

Figure. (A) Rate constants for the quenching of Rose Bengal fluorescence by $NNN'N'$-tetraethyl-α,ω-diaminoalkanes in methanol solution (k_q for triethylamine = $4{\cdot}1 \times 10^8$ l mol^{-1} s^{-1}). (B) Rate constants for the quenching of Rose Bengal fluorescence by α,ω-(di-2-naphthyl)-alkanes in pyridine solution (k_q for 2-methylnaphthalene = $6{\cdot}1 \times 10^7$ l mol^{-1} s^{-1}). (C) Rate constants for the quenching of Rose Bengal fluorescence by 1-(diethylaminoalkyl)-naphthalenes in methanol (k_q for 1-methylnaphthalene = $1{\cdot}56 \times 10^8$ l mol^{-1} s^{-1}). (N = length of polymethylene chain.)

The results with the α,ω-diaminoalkanes suggest that the quenching process involves encounter complexes since the quenching efficiency is far greater than the statistical factor of 2. The particularly efficient quenching by the diamino-ethanes, -propanes, and -butanes can be understood in terms of quenching resulting from an encounter complex which involves the excited state of the dye and both amino groups, *i.e.* a ternary complex. The favourability of fluorescence quenching occurring from complexes having three interacting groups has been commented upon in the preceding communication.[3] The efficiency of quenching by diamines having five or more methylene groups on the linking chain is attributed to the multi-collisional quenching process described there.[3]

The observation that the quenching efficiency by α,ω-dinaphthylalkanes and naphthylalkylamines is the least efficient when the structure of the bifunctional compound should favour a ternary encounter complex formation is, at first sight, rather surprising. In the case of the diamines, the ternary complexes produced should be of the type D,D,A (D = electron donor, A = electron acceptor). Previously described systems in which ternary complex formation has been observed involve complexes of the DDA type. This type of complex is unlikely to be formed by the α,ω-dinaphthylalkanes and naphthylalkylamines. For the dinaphthylalkanes to form such complexes the second naphthyl group would have to act as a donor to the naphthyl group initially involved in encounter complex formation. This is unlikely to occur because naphthalene is a relatively poor electron donor (particularly when compared with a tertiary amine). Usually when two naphthalene groups are involved in complex formation, the interaction between them is of an exciton nature rather than of a charge transfer type. Formation of the initial encounter complex between the naphthylalkylamines and the excited dye is more likely to involve the amino rather than the naphthalene group. For the reasons outlined, this naphthalene group is unlikely to participate in ternary complex formation. It is worth pointing out that in the systems described the very short lifetime of the initially formed encounter complexes will disfavour ternary complex formation. In those cases where exterplex (ternary complex) formation has been observed,[4] the systems favour the formation of relatively long lived exciplexes which give the intervention by a third group a very good chance.

Both the α,ω-dinaphthylalkanes and naphthylalkylamines quench the fluorescence of Rose Bengal very efficiently and we suggest that this is due to a multi-collisional process. The effect of change in rate constant with change in chain length reflects flexibility and conformational preferences of the quenchers in the solvent used. Thus the trimethylene compounds will have a greater proportion of molecules in an 'elongated' conformation (A) than say a hexamethylene chain where some degree of coiling is possible. Such coiling will favour the multi-collisional process.

(A)

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[1] There have been very few reports of fluorescence quenching by bifunctional compounds: A. Zweig and J. B. Gallivan, *Mol. Photochem.*, 1974, **6**, 397; E. Van der Donckt, M. R. Barthels, N. Anthewrus, and M. Swinner, *ibid.*, 1977, **8**, 121; R. S. Atkinson, D. R. G. Brimage, R. S. Davidson, and E. Gray, *J.C.S. Perkin I*, 1973, 960.

[2] R. S. Davidson and K. R. Trethewey, *J. Amer. Chem. Soc.*, 1976, **98**, 4008.

[3] R. A. Beecroft, R. S. Davidson, and T. D. Whelan, *J.C.S. Chem. Comm.*, 1978, 911 (preceding communication).

[4] Examples of quenching fluorescent exciplexes to give fluorescent exterplexes include: H. Been and A. Weller, *Chem. Phys. Letters* 1968, **12**, 140; K. H. Grellmann and W. Suckow, *ibid.*, 1975, **32**, 250; T. Mimura and M. Itoh, *J. Amer. Chem. Soc.*, 1976, **98**, 1095. Examples of quenching fluorescent exciplexes by a ground state species resulting in non-fluorescent complexes (S_{EX} reactions) include: R. A. Caldwell, D. Creed, and H. Ohta, *J. Amer. Chem. Soc.*, 1975, **97**, 3246; D. Creed, R. A. Caldwell, H. Ohta, and D. C. DeMarco, *ibid.*, 1977, **99**, 277.