Fluorescence Quenching by Benzoic Acid

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Summary Fluorescence quenching by benzoic acid proceeds by a hydrogen-bonding mechanism if the excited molecule is capable of forming a hydrogen bond and by an electron-transfer mechanism if it is not.

MIWA and KOIZUMI[1] reported the quenching of the fluorescence of 2-naphthol, 2-naphthylamine, 2-methoxynaphthalene, and 2-dimethylaminonaphthalene by benzoic acid. They suggested that the quenching occurs by an electron-transfer mechanism with the benzoic acid dimer acting as the electron acceptor and the excited naphthalene derivative as the electron donor. This suggestion was based on the results of the quenching experiments (the slopes of the Stern–Volmer plots for the quenching of each of the naphthalene derivatives have similar magnitudes), the fact that benzoic acid is largely dimerized in solution, and the results of some solvent studies. The above arguments do not eliminate the possibility of a hydrogen-bonding mechanism. We have studied the fluorescence quenching by benzoic acid in an attempt to elucidate the quenching mechanism.

If the quenching occurs by an electron-transfer mechanism, the quenching constant should correlate with ${}^1\Delta E_A + \epsilon(A_s^-/A_s)$ if the excited molecule acts as the electron acceptor or with $\epsilon(D_s^+/D_s) - {}^1\Delta E_D$ if the excited molecule acts as the electron donor.[2-4] The singlet excitation energies of the acceptor and donor are represented by ${}^1\Delta E_A$ and ${}^1\Delta E_D$, respectively, and the polarographic redox potentials of acceptor and donor are given by $\epsilon(A_s^-/A_s)$ and $\epsilon(D_s^+/D_s)$, respectively. The possibility that benzoic acid quenches by acting as an electron donor was tested first by attempting to quench the fluorescence of 1-cyanonaphthalene, an excellent electron acceptor in the excited state.[4] The addition of benzoic acid had no effect upon the fluorescence of 1-cyanonaphthalene. It is therefore, concluded that benzoic acid does not quench by acting as an electron donor.

As a test of benzoic acid as an electron acceptor quencher, the quenching constants were obtained for a series of compounds including some which could and some which could not form a hydrogen bond with the benzoic acid monomer (Table). For naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene, where there is no possibility of hydrogen bond formation, a correlation between k_q and ${}^1\Delta E_D - \epsilon(D_s^+/D_s)$ is apparent. By contrast, the quenching constants for 1-methoxynaphthalene and 2-methoxynaphthalene are an order of magnitude greater than would be expected from their ${}^1\Delta E_D - \epsilon(D_s^+/D_s)$ values.

The fluorescence spectra of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene in cyclohexane show, in the presence of benzoic acid very weak, broad, structureless emissions at lower energy than the emissions of the hydrocarbons. As the benzoic acid concentration is increased the intensity of this emission increases while the intensity of the hydrocarbon emission decreases. The broad bands are attributed to the fluorescence of charge-transfer complexes as found by Weller,[5,6] in similar systems. The fluorescence spectra of 1-methoxynaphthalene and 2-methoxynaphthalene in the presence of benzoic acid show no broad structureless emissions, only decreases in emission intensity with increasing benzoic acid concentration.

Fluorescence quenching by benzoic acid in cyclohexane

Compound	τ^a (ns)	${}^1\Delta E_A$ (ev)	$\epsilon(D_s^+/D_s)$ *vs.* S.C.E. (ev)	${}^1\Delta E_D - \epsilon(D_s^+/D_s)$	$k_q\tau$ (M^{-1})	$k_q \times 10^{-8}$ ($M^{-1}\,s^{-1}$)
Naphthalene	96	3·95	1·72	2·23	11	1·1
2-Methylnaphthalene	59	3·87	1·55	2·32	14	2·4
1-Methylnaphthalene	67	3·91	1·53	2·38	24	3·5
2-Methoxynaphthalene	13	3·76	1·52	2·24	34	26
1-Methoxynaphthalene	49	3·82	1·38	2·44	338	69

[a] Obtained from "Handbook of Fluorescence Spectra of Aromatic Molecules," I. B. Berlman, Academic Press, New York, 1965, or determined by the oxygen quenching technique, p. 35 above.

The data suggest that the fluorescence quenching in these two groups of compounds occurs by two different mechanisms. In the first case, where there is no possibility of hydrogen bonding, the quenching occurs by an electron-transfer mechanism with the benzoic acid acting as an electron acceptor. In the second case the quenching mechanism appears to involve the formation of a hydrogen bond between the excited molecule and benzoic acid. There may be a small amount of quenching *via* an electron-transfer mechanism but this is not the predominant pathway. Thus our results indicate that in the systems studied by Miwa and Koizumi[1] the predominant quenching mechanism involves hydrogen-bond formation and not electron transfer.

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