Formation of Exciplexes between Aromatic Hydrocarbons and Halogen Anions

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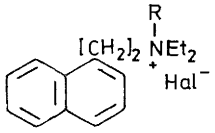
Summary Salts of *NN*-diethyl-2-(1-naphthyl)ethylamine with hydrogen halides and alkyl halides exhibit exciplex formation in aprotic, but not in protic solvents.

SEVERAL examples of intramolecular exciplex[1] and excited charge-transfer complex[2] formation have been reported. We report that the salts (**1a**—**c**) and (**2a**,**b**) exhibit exciplex formation.



	R	Hal
(1a)	H	Cl^-
(1b)	H	Br^-
(1c)	H	I^-
(2a)	Et	Br^-
(2b)	Et	I^-

In acetonitrile and ethanol solution the salts (**1a**—**c**) and (**2a**,**b**) have absorption spectra very similar to that for 1-methylnaphthalene. The salts in aprotic solvents show two fluorescence bands. There is a band having a maximum at 350 nm, which corresponds to the unquenched fluorescence derived from the excited naphthalene nucleus. From the quantum yield of this fluorescence (Table) it can be seen that the efficiency of quenching by the anions is $I^- > Br^- > Cl^-$. The longer wavelength fluorescence band is structureless and its position is dependent upon the polarity of the solvent used [*e.g.* for (**1b**); benzene, 425, 1,2-dimethoxyethane 460, acetonitrile 500 nm]. When the solutions of these salts are frozen, the observed emission is that of fluorescence and phosphorescence from the naphthalene nucleus. The intensity of these emissions is similar to the corresponding emissions of 1-methylnaphthalene. In ethanolic solution, all the salts exhibited fluorescence typical of that of the naphthalene nucleus. The quantum yield of fluorescence was comparable to that for the fluorescence of 1-methylnaphthalene.

From these observations we conclude that in aprotic solvents, the anions are responsible for quenching the first excited singlet state of the naphthalene nucleus.[†] Furthermore, from the relative efficiency of quenching by the iodide, bromide, and chloride ions and from the formation of the new fluorescence band to the red of the naphthalene fluorescence, we conclude that quenching occurs *via* a charge-transfer process, *i.e.* electron transfer from the halide anion to the excited hydrocarbon. The observed solvent dependence of this new band parallels the solvent dependence of many other examples of exciplex and charge-transfer fluorescence.[1–3] That the new band is not due to impurities is attested by the fact that the normal fluorescence and phosphorescence is exhibited by the salts in frozen solution. This observation also shows that most of the quenching in solution is by a dynamic and not a static process.

TABLE. *Quantum yields*[a] *of fluorescence for* 1-*methylnaphthalene and the salts* (**1a—c**) *and* (**2a,b**)[b] *in acetonitrile solution*

Compound	Quantum yield of fluorescence from naphthalene nucleus	Quantum yield of fluorescence of exciplex (λ_{max} emiss./nm)
1-Methylnaphthalene	0·10	
(**1a**)	0·051	0·020 (490)
(**1b**)	0·041	0·023 (490)
(**1c**)	0·037	0·041 (490)
(**2a**)	0·09	0·006 (495)
(**2b**)	0·08	0·013 (495)

[a] Quinine sulphate used as standard, W. H. Melhuish, *J. Phys. Chem.*, 1960, **64**, 762; 1961, **65**, 229. [b] In all cases the solutions had an O.D. of 0·10 at 300 nm. This corresponds to a concentration of *ca.* 1 × 10^{-4}M.

The lack of quenching by the anions in ethanol, compared with relatively high efficiency in aprotic solvents, is thought to be due to the salts existing mainly as ion pairs[‡] in aprotic solvents and being extensively dissociated in protic solvents.[4] Quenching in the ion pairs is efficient because of the proximity of the anion to the hydrocarbon nucleus. When dissociation into free anions occurs, the concentration of the anions is too low for efficient quenching by a bimolecular process.

The reported results unequivocally demonstrate that halide ions quench the fluorescence of polycyclic aromatic hydrocarbons by a charge-transfer process. Such a mechanism has been previously suggested but no concrete evidence for the formation of exciplexes was presented.[5] These results also suggest that formation of triplet hydrocarbons by quenching excited singlet states with anions,[6] occurs *via* exciplex intermediates. Such a mechanism has been accepted for the formation of triplets in other systems in which excited charge-transfer complexes[7] and exciplexes are intermediates.[8]

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[†] A referee has suggested that the quenching in aprotic solvents may be due to the formation of hydrogen-bonded complexes of the type $R_3N\cdots HX$. If this did occur, fluorescence of the type observed would be expected since the free amino-compounds exhibit intramolecular exciplex formation. Evidence against participation of the hydrogen-bonded complexes includes (a) the n.m.r. spectra of the salts in aprotic solvents clearly show resonances due to $CH_2\overset{+}{N}R_3$ and (b) salts derived from amines which do not show intramolecular exciplex formation exhibit fluorescence similar to (**1a—c**) and (**2a,b**).

[‡] There are other explanations for this solvent effect, *e.g.*, quenching is more efficient in aprotic solvents because the ions are less solvated and hence more reactive. Experiments are in progress which, it is hoped, will identify the species in which quenching occurs.

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