

Short Communication

Quenching of the fluorescence of aromatic hydrocarbons by amino alcohols

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It has been previously established by Weller¹ and others²⁻⁴ that tertiary amines interact with the first excited singlet states of aromatic hydrocarbons to give exciplexes. This interaction involves quite a considerable degree of electron transfer (as judged by the dipole moments of the complexes^{4,5}) from the amine to the excited hydrocarbon. The efficiency of exciplex formation is governed by four factors; (a) the energy of the first excited singlet state of the aromatic hydrocarbon; (b) the reduction potential of the excited state of the hydrocarbon^{1,6}; (c) the oxidation potential of the amine; and (d) the ability of the solvent to stabilize the exciplex^{2,7-9}. It has been shown that increasing the polarity of the solvent favours the electron transfer process leading to exciplex formation and also favours dissociation of the latter into radical ions. The electron transfer process leads to:



ArH = aromatic hydrocarbon Am = amine

quenching of the fluorescence of the hydrocarbon. From the Stern Volmer equation (1) the bimolecular rate constant for quenching (k_q) can be determined.

$$\frac{\Phi_F}{\Phi_{Fq}} = 1 + k_q \bar{\tau}_0 [Q] \quad (1)$$

where

- Φ_F = quantum yield of fluorescence,
- Φ_{Fq} = quantum yield of fluorescence in presence of quencher,
- $[Q]$ = quencher concentration,
- τ_0 = lifetime of excited singlet state in absence of quencher.

Generally, the values of k_q increase as the polarity of the solvent is increased and this may be understood by reference to Fig. 1a. In this figure, the solvent is shown as affecting the reaction by stabilizing the exciplex and not as affecting the energy

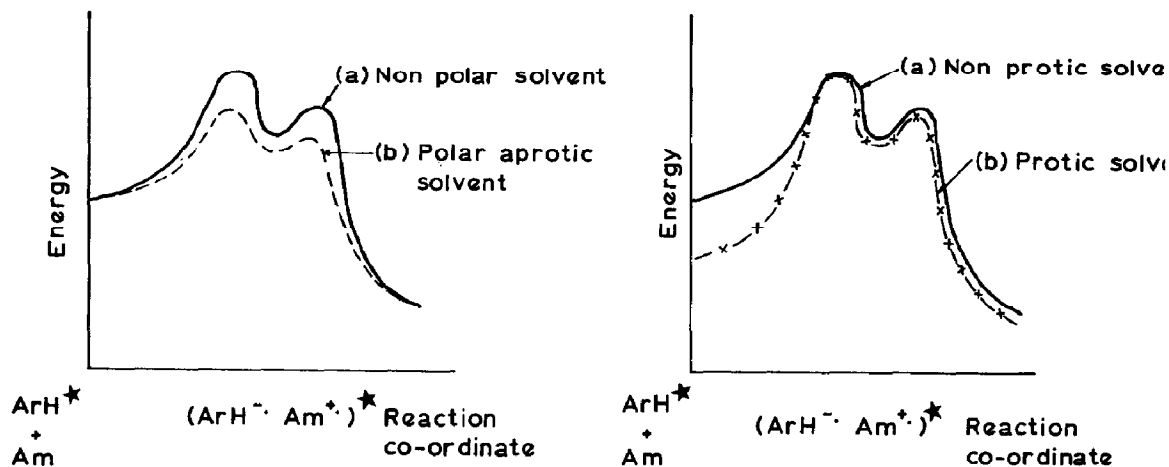


Fig. 1. The effect of solvent upon the quenching of aromatic hydrocarbon fluorescence by tertiary amines. (a) Interactions in non-polar and polar aprotic solvents; (b) interactions in non-polar and polar protic solvents.

of the reactants. Protic solvents behave in an anomalous way in that the rate constants for quenching in these solvents are much lower than those expected on the basis of their polarity^{7,8}. It has been suggested⁸ that this is due to the long dielectric relaxation times of the alcohols, *i.e.* the formation and decay of exciplexes occurs before the alcohols can undergo solvent re-orientation. This may be interpreted, by reference to the Figure, as the alcohols being unable to reduce the energy of the exciplex. An alternative suggestion is that alcohols stabilize the ground state amine through hydrogen bond formation (Fig. 1b) and thereby increase the energy of activation for exciplex formation. The true reason may be a compromise between these two suggestions, *i.e.* alcohols ineffectively solvate exciplexes and also decrease the availability of the nitrogen lone-pair electrons for exciplex formation.

In order to assess the importance of hydrogen bond formation upon electron transfer processes we have studied the quenching of the fluorescence of some

TABLE I

RATE CONSTANTS FOR THE QUENCHING OF THE FLUORESCENCE OF SOME AROMATIC HYDROCARBONS BY AMINO-ALCOHOLS IN ACETONITRILE

Hydrocarbon	Rate constants for quenching ($M^{-1}sec^{-1}$) ^a		
	$Me_2NCH_2CH(Me)OH$	Tropine	$PhN(Me)CH_2CH_2OH$
Anthracene	6.0×10^8	2.5×10^9	1.9×10^{10}
Perylene	4.3×10^8	8.8×10^8	1.2×10^{10}
Naphthalene	2.3×10^8	4.3×10^8	^b

^a Lifetimes of the first excited singlet states of anthracene, perylene and naphthalene were taken as 4.9×10^{-9} s, 6.4×10^{-9} s and 96×10^{-9} s respectively (I. Beriman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, London, 1965).

^b Value not determined due to overlap of the absorption spectrum of the amine and the hydrocarbon.

TABLE II

RATE CONSTANTS FOR THE QUENCHING OF THE FLUORESCENCE OF SOME AROMATIC HYDROCARBONS BY AMINES IN VARIOUS SOLVENTS

Amine	Solvent	Rate constants ($M^{-1}\text{sec}^{-1}$)		
		Anthracene	Perylene	Naphthalene
$\text{Me}_2\text{NCH}_2\text{CH}_2\text{OEt}$	MeCN	4.6×10^9	2.0×10^9	1.1×10^9
Et_3N	MeCN	6.3×10^9	2.1×10^9	1.3×10^9
Et_3N	iPrOH	9.7×10^8	6.5×10^8	2.5×10^8
PhNEt_2	MeCN	1.9×10^{10}	1.9×10^{10}	—
PhNEt_2	iPrOH	4.91×10^9 ^a	4.92×10^9 ^a	—

^a Values from ref. 8.

aromatic hydrocarbons by amino alcohols in acetonitrile solution. The intensity of fluorescence of the hydrocarbons in acetonitrile solution containing varying amounts of the amino alcohols, was determined with a Baird Atomic SF 800E spectrofluorimeter. Since the intensity of fluorescence is directly related to the quantum yield of fluorescence, the values of the intensity of fluorescence were substituted directly into the Stern Volmer equation (1). The results so obtained are shown in Table I and some other relevant results we have obtained are shown in Table II. From these Tables it will be seen that the rate constants for quenching by the alkylamino alcohols, 1-dimethylaminopropan-2-ol and tropine (I) are much lower than those for triethylamine.



That the inefficiency is due to the hydroxyl group is attested by the fact that the rate constants for quenching by 2-dimethylaminoethyl ether approach the values for quenching by triethylamine. In contrast to the alkylamino alcohols, the quenching rate constants for the *N*-arylamino alcohol 2-(*N*-methylanilino) ethanol, are very similar to those for quenching by *N,N*-diethylaniline, *i.e.* the hydroxyl group in the *N*-arylamino alcohol has little effect upon the quenching process. These results may be understood by a consideration of the ability of the amines in question to form hydrogen bonds in which the nitrogen atom participates. The relative basicity of *N,N*-diethylaniline and triethylamine (pK_a 6.56 and 10.65 respectively) may be taken as an indication of the greater favourability for hydrogen bond formation with the alkylamine compared with the arylamine. This is no doubt due to necessity for disruption of the $p\pi$ -bonding in arylamines for hydrogen bond formation to take place. At the concentration used in the quenching experiments in acetonitrile, it is unlikely that extensive hydrogen bonding to the nitrogen atom of the 2(*N*-methylanilino) ethanol occurs. It is more likely that hydrogen bonding occurs between the hydroxyl groups. Thus the arylamino alcohol behaves like a

'free amine' in acetonitrile solution and therefore the quenching process is not affected. Furthermore, at the concentrations used, it is likely that the species, formed by the electron transfer process, are solvated by acetonitrile rather than by the hydroxyl groups of the amino alcohol and hence dielectric relaxation of the alcohol is likely to be unimportant.

The inefficiency of quenching by the alkylamino alcohols may be attributed to involvement of the nitrogen atom in hydrogen bond formation. The strong basic character of the nitrogen atoms in these compounds indicates the readiness with which they will form hydrogen bonds. At the concentrations used in the quenching experiments, it is unlikely that the species produced by electron transfer will be solely solvated by the hydroxyl groups but rather they will be solvated by acetonitrile. Thus under these circumstances, it is unlikely that the inefficiency of quenching can be attributed to lack of stabilization of the charge transfer species and is more likely to be due to stabilization of the reactants. The finding that tropine is a more efficient quencher than 1-dimethylamino propan-2-ol probably reflects the decreased favourability for hydrogen bond formation with tropine because of steric interactions in the hydrogen bonded species.

It is interesting to note that the quenching of the fluorescence of biacetyl by triethylamine is also much less efficient in polar protic solvents than in polar aprotic solvents¹⁰. In contrast, the quenching of triplet carbonyl compounds by amines is insensitive to the nature of the solvent^{11,12}. This leads one to question the claim that aliphatic amines interact with triplet carbonyl compounds by an electron transfer process¹⁰⁻¹².

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