THE QUENCHING OF THE FLUORESCENCE OF AROMATIC HYDROCARBONS BY TERTIARY DERIVATIVES OF GROUP V ELEMENTS

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Summary

A study is made of the quenching of fluorescence of a number of aromatic compounds by triphenyl derivatives of group V elements and by triethylamine in both non-polar and polar solvents. Whilst quenching is observed in many cases, the lack of correlation of the quenching rate with the ionization potential of the quencher suggests that this does not simply involve electron or charge transfer. Evidence is presented that a heavy atom effect involving the group V element is also important. Further, a search has been made for evidence of exciplex formation in the quenching of azulene S_2 fluorescence by a variety of compounds. However, no new emissions attributable to such a species are observed under the conditions studied. In addition, in polar solvents there is no evidence for an overall electron-transfer reaction in the quenching suggesting that if an intermediate charge-transfer or ion pair state is formed this may be of higher energy than the lowest singlet or triplet state, and may decay to yield one of these levels.

Introduction

Excited singlet states of a variety of aromatic compounds have been shown to interact with amines [1], inorganic anions [2], organo-derivatives of lead, tin and mercury [3], and various other inorganic, organic and organic and organometallic derivatives, as indicated by the quenching of the hydrocarbon fluorescence. The quenching is generally attributed to charge-transfer

or electron-transfer from the quencher to the hydrocarbon. In suitable cases the presence of quencher is replaced by a new structureless emission band at longer wavelengths [4], assigned to an exciplex formed between the quencher and the hydrocarbon. Nanosecond flash photolysis studies have allowed observation of absorption spectra of these exciplexes [5], and have confirmed their charge transfer character. Exciplex formation is only rarely observed in polar solvents, where normally complete electron-transfer occurs from the quencher to the hydrocarbon [6].

In the present study we have had two main objectives. Whilst there have been many studies on the quenching of excited states by amines, there have only been very few reports of fluorescence quenching by phosphines [7 - 9], and the only examples we have been able to find of quenching by organic derivatives of other group V elements are two recent notes [10, 11] on quenching of carbonyl triplet and singlet states by the triphenyl derivatives. However, ionization potentials of trialkyl [12], and triphenyl [13 - 15] derivatives of P, As, Sb and Bi are not very much higher than those of the corresponding amines, and a study of their efficiencies as fluorescence quenchers is expected to be valuable. Secondly, an interest in potential photochemistry in upper excited states has led us to look at the quenching of azulene fluorescence, which is known to occur predominantly from the second excited state [16], in a search for evidence of exciplex formation in upper excited states.

Experimental

Fluorescence spectra were recorded on Perkin-Elmer MPF 3 and Farrand MK-1 instruments. Solutions commonly contained $10^{-4} - 10^{-5}$ mol/dm^3 hydrocarbon, to avoid any excimer formation, and were purged with oxygen-free nitrogen immediately before running spectra. Problems of quencher solubility and of overlapping of the absorptions of quencher with those of the hydrocarbon limited the range of aromatics which could be studied. Hydrocarbon fluorescences were normally excited at a wavelength where the quencher did not absorb. Where this was not possible a correction [17] was made to the data allow for the quencher absorption. For flash photolysis experiments the system described previously [18] was used.

Spectroscopic grade cyclohexane was purified immediately prior to use by passing through an alumina column impregnated with silver nitrate followed by a column of calcium carbonate. Acetonitrile was either spectroscopic grade, or was purified by the method of Walter and Ramaley [19]. Triethylamine was purified as described previously [18]. Other compounds were of the purest grade commercially available and were normally recrystallized prior to use. The sample of acenaphthene used was found by gas chromatography to contain some acenaphthylene. However, this did not affect the fluorescence spectrum of the acenaphthene. Whilst the lowest excited singlet

state of acenaphthylene lies below that of acenaphthene, at the concentrations employed in this study singlet–singlet energy transfer is not expected to be significant and there was no evidence for any emission from acenaphthylene when the acenaphthene was excited.

Results and Discussion

The quenching was studied of the fluorescence of degassed acetonitrile and cyclohexane solutions of various hydrocarbons by triphenylamine, triphenylphosphine, triphenylamine, triphenylstibene and triethylamine. With the triphenyl derivatives the range of quenching studies was restricted by both low quencher solubilities, and by the overlapping of quencher and hydrocarbon absorptions. Over the quencher concentration range studied (typically up to 0.1 mol/dm^3 with triethylamine and up to 2×10^{-3} M with the other quenchers) no new fluorescence bands attributable to exciplex emissions were observed, even in cyclohexane. Exciplex emissions have been observed [20] from solutions of naphthalene, benzene, or p-terphenyl with triethylamine. However, it is thought that the presence of such an emission depends very markedly on the electron affinity of the excited state of the acceptor.

Absorption spectra of all solutions showed the absence of any new bands attributable to ground state charge-transfer complexes, and the quenching in all of the cases is thought to be predominantly via a bimolecular reaction between the quencher and the excited singlet state of the hydrocarbon. Stern–Volmer constants and bimolecular quenching rates calculated from these are presented in Tables 1 and 2. The range of quenchers studied in acetonitrile was rather less than that in cyclohexane. Whilst all of the triphenyl derivatives studied showed some kind of quenching, the mechanism for this did not appear to involve just exciplex formation or electron-transfer. Thus, whilst Weller and Rehm [6] have shown that for fluorescence quenching by an electron-transfer mechanism the free energy change is a linear function of the oxidation potential of the donor, the reduction potential of the acceptor, and the electronic excitation energy, for each of the hydrocarbons which had been studied with all of the quenchers in cyclohexane, there was no obvious correlation between the logarithm of the quenching rate and the adiabatic ionization potentials of Ph$_3$N(6.75 eV), Ph$_3$P(7.37 eV), Ph$_3$As(7.60 eV) and Ph$_3$Sb(7.80 eV) from Debies and Rabalais [15] (Fig. 1). Similarly no correlation was observed when graphs were drawn of the logarithm of the quenching rate against the vertical ionization potential in either solvent. Thus, while the quenching rate is expected to decrease with increasing ionization potential in the series Ph$_3$N < Ph$_3$P < Ph$_3$As < Ph$_3$Sb, in some cases the quenching is actually more efficient with triphenylstibene than with triphenylamine. However, another factor which is expected to become important with these compounds is quenching by an external heavy-atom effect involving enhanced intersystem crossing [21].

TABLE 1

Stern–Volmer data for the quenching of fluorescence in cyclohexane solution

Hydrocarbon	τ/ns	Quencher[a]	K_{sv}/dm^3/mol	k_Q/dm^{3}mol^{-1}s^{-1}
Acenaphthene	46[b]	Et$_3$N	1.54($\pm$0.13)	3.35 $\times$ 10^7
		Ph$_3$P	263($\pm$27)[g]	5.72 $\times$ 10^9
		Ph$_3$Sb	104($\pm$3)[g]	2.26 $\times$ 10^9
Anthracene	4.9[c]	Et$_3$N	1.74($\pm$0.13)	3.55 $\times$ 10^8
		Ph$_3$P	35($\pm$9)[g]	7.14 $\times$ 10^9
Anthanthrene	5.0[b]	Et$_3$N	1.23($\pm$0.14)	2.46 $\times$ 10^8
		Ph$_3$N	3($\pm$0.5)	6.00 $\times$ 10^8
		Ph$_3$P	8($\pm$1)	1.60 $\times$ 10^9
		Ph$_3$As	15($\pm$4)	3.00 $\times$ 10^9
		Ph$_3$Sb	13($\pm$1)	2.60 $\times$ 10^9
Azulene[d]	1.4[c]	Et$_3$N	14.3($\pm$0.8)	1.02 $\times$ 10^{10}
		Ph$_3$N	10($\pm$1.2)	7.14 $\times$ 10^9
		Ph$_3$P	19($\pm$2)[g]	1.36 $\times$ 10^{10}
		Ph$_3$As	5.2($\pm$0.5)[g]	3.71 $\times$ 10^9
		Ph$_3$Sb	21.4($\pm$1)[g]	1.53 $\times$ 10^{10}
1, 2, 3, 4-Dibenzan-thracene	53.5[e]	Et$_3$N	1.54($\pm$0.2)	2.88 $\times$ 10^7
1, 2, 3, 4-Dibenz-pyrene		Et$_3$N	17.3($\pm$0.3)	—
		Ph$_3$N	11($\pm$1)	—
		Ph$_3$P	<0.1	—
		Ph$_3$As	<0.1	—
		Ph$_3$Sb	11($\pm$1.5)	—
Fluoranthene	53[c]	Et$_3$N	40($\pm$5)	7.55 $\times$ 10^8
		Ph$_3$N	10($\pm$1)	1.89 $\times$ 10^8
		Ph$_3$P	32($\pm$9)[g]	6.04 $\times$ 10^8
		Ph$_3$As	10($\pm$0.5)	1.89 $\times$ 10^8
		Ph$_3$Sb	47($\pm$6)	8.87 $\times$ 10^8
Phenanthrene	56[f]	Et$_3$N	1.11($\pm$0.11)	1.98 $\times$ 10^7
		Ph$_3$As	11($\pm$1.8)	1.96 $\times$ 10^8
		Ph$_3$Sb	18.4($\pm$4)[g]	3.29 $\times$ 10^8

[a] Et = C$_2$H$_5$, Ph = C$_6$H$_5$. [b] From I. B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic, New York, 2nd Edn, 1971. [c] From J. B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, London, 1970. [d] Fluorescence from S$_2$. [e] From G. Porter and M. R. Topp, Proc. R. Soc. (A), 315 (1970) 163. [f] From ref. [b] corrected for change in solvent. [g] Corrected for quencher absorption in excitation region.

TABLE 2

Stern–Volmer data for the quenching of fluorescence in acetonitrile solution

Hydrocarbon	τ/ns	Quencher	K_{sv}/dm^3/mol	k_Q/dm^{3}mol^{-1}s^{-1}
Acenaphthene	54[a]	Et$_3$N	25.9($\pm$0.8)	4.80×10^8
		Ph$_3$As	<0.1	—
Anthracene	5.7[a]	Et$_3$N	32.4($\pm$1.0)	5.68×10^9
Anthanthrene	5.8[a]	Et$_3$N	26.6($\pm$0.9)	4.59×10^9
		Ph$_3$As	5($\pm$0.1)	8.62×10^8
Azulene	1.6[a]	Et$_3$N	29.7($\pm$1.5)	1.86×10^{10}
		Ph$_3$P	105($\pm$9)[c]	6.56×10^{10}
		Ph$_3$As	28.1($\pm$6)[c]	1.76×10^{10}
		(CH$_3$)$_2$NPh	103($\pm$7)	6.44×10^{10}
1, 2, 3, 4-Dibenzanthracene	62[a]	Et$_3$N	56.1($\pm$2.1)	9.05×10^8
		Ph$_3$As	9.8($\pm$1)	1.58×10^8
1, 2, 3, 4-Dibenzpyrene		Et$_3$N	32.8($\pm$1.05)	—
		Ph$_3$P	11($\pm$1)	—
		Ph$_3$As	1($\pm$0.2)	—
Fluoranthene	62[a]	Et$_3$N	201($\pm$9)	3.24×10^9
		Ph$_3$P	113($\pm$1)	1.82×10^9
		Ph$_3$As	27($\pm$2)	4.35×10^8
Naphthalene	118[b]	Et$_3$N	141	1.19×10^9
Phenanthrene	64[a]	Et$_3$N	16.4($\pm$1.0)	2.56×10^8
		Ph$_3$As	<0.1	—

[a] From Table 1, corrected for change in solvent. [b] From J. B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, London, 1970. [c] Corrected for quencher absorption in excitation region.

The presence of heavy atoms in the system increases spin-orbit coupling, thus relaxing the spin selection rules. The extent of heavy atom quenching should be directly proportional to some power of the atomic number, Z, of the perturbing atom. With group II atoms the intensity of the ^{3}P, ^{3}P$_1 \leftarrow$ ^{1}S$_0$ forbidden transition increases as a function of Z^5, although theoretical considerations suggest that the probability of this transition should be proportional to approximately Z^8 [22]. If a similar effect is operative in the present case we might expect a dependence of the heavy atom quenching on Z^n, where n is a constant, and if we can treat the heavy atom and change-transfer (or electron-transfer) quenchings as separable effects we can write the overall quenching rate constant, k, in the form:
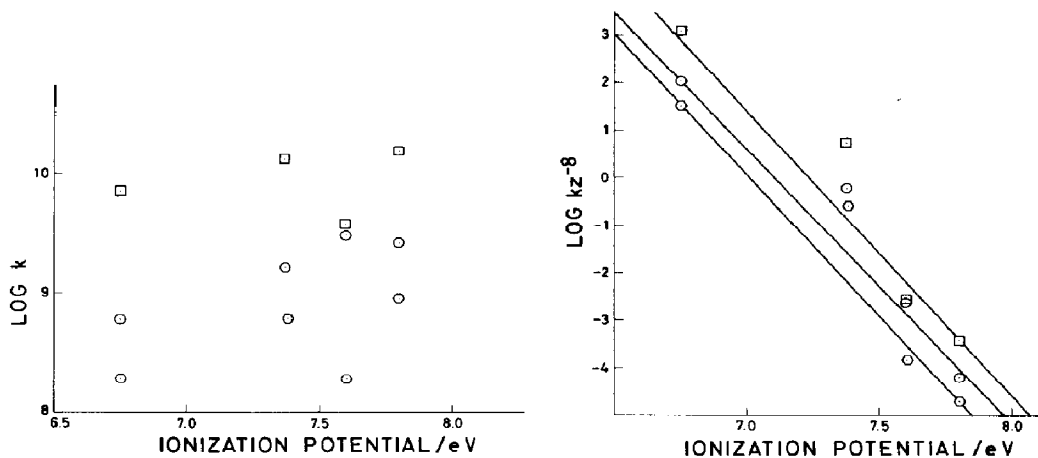
Fig. 1. Plot of log k against ionization potential for the quenching of the fluorescence of cyclohexane solutions of anthanthrene (⊙), azulene (▣), and fluoranthene (◎) by triphenyl derivatives of group V elements.

Fig. 2. Plot of log kZ^{-8} against ionization potential for the quenching of the fluorescence of cyclohexane solutions of anthanthrene (⊙), azulene (▣), and fluoranthene (◎) by triphenyl derivatives of group V elements.

$$k = aZ^n e^{-bI}$$

where, for a particular hydrocarbon at constant temperature, a and b are constants involving electron affinities, excitation energies, etc. and I is the ionization potential of the quencher. For a particular hydrocarbon a plot of log kZ^{-n} against I should be linear with slope $-b$ and intercept a. We have tried fitting this function for the results for anthracene, azulene and fluoranthracene in cyclohexane solution, and find the best correlation with $n = 8$ (Fig. 2), in agreement with the theoretically predicted dependence of the heavy atom effect on Z^8. The lines for the three hydrocarbons are roughly parallel. Further, the values of a for the three hydrocarbons appear to be a function of both the electron affinity and the electronic excitation energy of the aromatic hydrocarbon* (Table 3), as might be expected for charge transfer quenching [6]. Thus we feel that we have evidence for the contribution of both mechanisms to the quenching process. A similar conclusion has been reached in a study by Lema and Scaiano [11] of the quenching of excited singlet and triplet states of various carbonyl compounds by derivatives of group V atoms. The fluorescence quenching by triphenylphosphine do not appear to fit Fig. 2 very well. We feel that two factors might be important here. First, whilst the literature ionization potential for this compound was obtained from the same source as for the other compounds [15], this value might not be appropriate for liquid solutions**. Secondly, as

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*Note, however, that, as the lines are not exactly parallel in the region of ionization potentials displayed on the graph the line for anthanthrene lies above that for fluoranthene. It is possible that both a and b have a complex dependence on both electron affinities and electronic excitation energy.

**If an ionization potential of 7.12 is assumed, a good fit is obtained for all three hydrocarbons.

TABLE 3

Reduction potentials, excitation energies, and values of a for anthanthrene, azulene and fluoranthene.

Hydrocarbon	$\epsilon_{1/2}(A/A^{'-})/V$	$\Delta E_{0-0}/cm^{-1}$ [c]	$\epsilon_{1/2}(A^{'-}/A) + \Delta E_{0-0}/kJ/mol$	a [d]
Anthanthrene	1.71 [a]	23,090	111.2	40.85
Fluoranthene	1.77 [b]	25,300	132.0	41.65
Azulene	1.61 [b]	28,300 (S_2)	181.4	42.99

[a] In ethyleneglycol monomethylether from I. Bergman, Trans. Faraday Soc., 50 (1954) 829, corrected to b by adding 0.52 V. [b] In 75% dioxane—water from ref. [30].
[c] From J. B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, London, 1970. [d] From Fig. 2.

Lema and Scaiano have pointed out [11], the availability of lone pairs may well be an important factor in the quenching.

With azulene it is well known that this violates Kasha's rule [23] and fluoresces from the S_2 level [16]. We have accordingly looked at the quenching of this state to see if we could find any new emission attributable to an S_2 exciplex. However, in none of these systems was any new emission observed. We have also looked at the quenching of the fluorescence of n-hexane solutions of azulene by N,N-dimethylaniline (K_{sv} 91.9 ± 11.1), carbon tetrabromide (K_{sv} 77.8 ± 13.6) and triethylamine (K_{sv} 51.6 ± 5.9), and whilst the quenching followed good Stern—Volmer kinetics in all cases, no new emissions were observed. Since in polar solvents such as acetonitrile quenching is normally thought to involve complete electron transfer, we have designed experiments to try and find evidence for such an electron transfer to excited azulene. Aerated acetonitrile solutions of azulene and N,N-dimethylaniline were flash photolyzed. Under these conditions if quenching is by electron transfer it is anticipated that any azulene radical anion formed will react with oxygen, leaving the N, N-dimethylaniline radical cation (λ_{max} 460 nm[24]). However, under the conditions of our experiment no transient absorptions were observed in the region 350 - 490 nm. Further, whilst photolysis of degassed acetonitrile solutions of naphthalene and a number of other aromatic compounds in the presence of triethylamine and water has been shown [25] to lead to reduction of the aromatic compounds, no photoreduction was observed following photolysis for one hour of a degassed acetonitrile solution of azulene (5 × 10^{-4} mol/dm^3), water (1 mol/dm^3) and triethylamine (1 mol/dm^3), as demonstrated by the absence of any change in the ultra-violet spectrum. Thus it seems likely that in these cases complete electron transfer followed by diffusion of radical cations and anions does not occur. Possibly it is better to consider that the quenching in these cases involves either intersystem crossing, or internal conversion to S_1 induced by some charge-transfer or ion-pair state. With azulene both the lowest singlet

$(14,200 \text{ cm}^{-1}$ [26]$)$ and triplet $(13,650 \text{ cm}^{-1}$ [27]$)$ states lie at low energies, and it seems not unreasonable that these lie at lower energies than any charge transfer or ion pair state [28], thus favouring such a mechanism.

Acknowledgement

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