FLUORESCENCE QUENCHING OF SUBSTITUTED ANTHRACENES BY TRIS(PENTAFLUOROPHENYL)PHOSPHINE[†]

MARIA EUNICE R. MARCONDES and VICENTE G. TOSCANO

Instituto de Química, Universidade de São Paulo, São Paulo (Brazil)

RICHARD G. WEISS

Department of Chemistry, Georgetown University, Washington, D.C. 20057 (U.S.A.)

(Received July 7, 1978; in revised form August 30, 1978)

Summary

Rate constants k_q for fluorescence quenching of eleven 9 and 9,10 substituted anthracenes (A_i) by tris(pentafluorophenyl)phosphine (FP) are reported. Correlations of k_q with the electronic properties of A_i and FP reveal that $A^+ FP^-$ charge-transfer interactions are important in the quenching process for several of the A_i. No one quenching mechanism is able to explain all of the data. The quenching mechanism of anthracene, 9-methylanthracene and 9,10-dimethylanthracene in benzene appears to lack a pathway available to anthracenes whose substituents contain a lone pair of electrons.
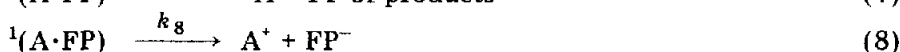
1. Introduction

We have previously [1, 2] described the fluorescence quenching of eleven 9 or 9,10 substituted anthracenes (A_i) by triphenylphosphine (P) and N,N-dimethylaniline (DMA) which proceeds via formation of exciplexes. Correlations between the observed quenching rate constants k_q and electronic properties of the A_i and quencher led to a number of conclusions concerning the mechanisms which are operative. It was shown that the degree of $A^- X^+$ (X=P or DMA) charge-transfer character in the quenching steps increases with solvent dielectric and with the electron-withdrawing ability of the substituents on the anthracene rings. In some experiments, especially those conducted in benzene and with A_i containing electron-donating sub-

stituents, the quenching mechanism appeared to involve exciplexes in which charge transfer is less important than excitation-resonance stabilization. However, in no case was it necessary to include A^+X^- charge-transfer contributions in order to describe the exciplexes adequately.

To determine whether further electronic modification of either A_i or quencher, without grossly altering the structure of either, can yield exciplexes in which the A^+X^- stabilization is evident, we have extended our study to include tris(pentafluorophenyl)phosphine (FP) as quencher. The choice of FP represents a logical extension of our previous work with P: FP and P contain a lone pair of electrons on their phosphorus heteroatoms (potential electron donors) and are similar in structure. However, the substitution of fluorines for the ring hydrogens of P should make FP a potent electron acceptor[†].

Assuming a standard exciplex kinetic scheme like the following,

$$A \xrightarrow{h\nu} {}^1A \tag{1}$$

$${}^1A \xrightarrow{k_2} A \text{ or } {}^3A \tag{2}$$

$${}^1A \xrightarrow{k_3} A + h\nu' \tag{3}$$

$${}^1A + FP \xrightarrow{k_4} {}^1(A \cdot FP) \tag{4}$$

$${}^1(A \cdot FP) \xrightarrow{k_5} {}^1A + FP \tag{5}$$

$${}^1(A \cdot FP) \xrightarrow{k_6} A + FP + h\nu'' \tag{6}$$

$${}^1(A \cdot FP) \xrightarrow{k_7} {}^3A + FP \text{ or products} \tag{7}$$

$${}^1(A \cdot FP) \xrightarrow{k_8} A^+ + FP^- \tag{8}$$

$$\frac{I_0}{I} = 1 + \frac{k_4(k_6 + k_7 + k_8)[FP]}{(k_5 + k_6 + k_7 + k_8)(k_2 + k_3)} = 1 + k_q\tau[FP] \tag{9}$$

k_q can be determined conveniently via Stern–Volmer treatment of the fluorescence intensities in the absence (I_0) and presence (I) of FP (see eqn. (9)).

Since k_q is really a composite of several rate constants, determination of the dependence of each component rate constant on the solvent and the nature of the substituents on A_i would offer the maximum information. This type of analysis, although possible, is difficult, tedious and has been performed in only a limited number of cases (*e.g.* ref. 4 and references cited therein). Alternatively, conclusions can be drawn from the dependence of k_q on the electronic properties of A_i and FP. In this work we have followed the latter course in order to develop a structure–reactivity relation for the quenching mechanism. Our results demonstrate clearly that the trends of k_q

---

[†]The electronegativities of H and F on the electrostatic scale are 2.1 and 4.1 respectively [3].

observed in the A_i–P or A_i–DMA systems [1, 2] are reversed when FP is the quencher.

R₁ structure (anthracene with R₁ top, R₂ bottom)

$$R_1$$

$$R_2$$
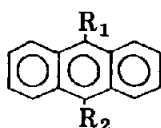
$$A_i$$

i	R_1	R_2
1	CN	CN
2	H	CN
3	Br	Br
4	H	Br
5	Cl	Cl
6	H	Cl
7	H	H
8	H	Me
9	Me	Me
10	H	OMe
11	OMe	OMe

2. Experimental

The methods, chemicals and apparatus are, for the most part, as described previously [1].

FP was synthesized by the method of Wall *et al.* [5]. The product, with melting point 109 - 114 °C (literature value [5], 116 - 117 °C), was obtained in 30% yield after sublimation at 3 Torr. Resublimation resulted in a white solid, with melting point 113 - 114 °C, whose UV spectrum (methanol) displayed λ_{max} = 253 nm (ϵ = 10 600) and λ_{min} = 240 nm (ϵ = 8960) (literature values [5], λ_{max} = 253 nm (ϵ = 10 400) and λ_{min} = 241 nm (ϵ = 8900)).

Half-wave oxidation potentials of the A_i were measured with Sargent Model III and Model XV polarographs. Internal resistances in the solutions were less than 300 Ω in all cases. Acetonitrile solutions, containing 10^{-2} - 10^{-3} M A_i and 0.5 M dry sodium perchlorate as electrolyte, were thermostatted at 26 °C and were deoxygenated by bubbling dry nitrogen through the liquid. All measurements were performed in duplicate. The reference electrode was an Ag/AgNO₃ (0.1 M) couple and the working electrode was a platinum wire spun at 1800 rev min⁻¹. The half-wave reduction potential of FP at 26 °C in a deoxygenated acetonitrile solution (0.1 M dry tetraethylammonium iodide as electrolyte) was found to be − 1.15 V *versus* a mercury pool.

No new UV absorptions were observed when the A_i were mixed in benzene with the largest concentration of FP employed in the Stern–Volmer

TABLE 1

Data related to the quenching of A_i singlets by FP

A_i	$k_q \times 10^{-8}$ $(M^{-1} s^{-1})$		$E(A^+/A)$ (V vs. Ag/Ag$^+$ in acetonitrile)	$\dfrac{k_q^i (\text{acetonitrile})}{k_q^i (\text{benzene})}$
	Observed[a]	Calculated[b]		
A_1	< 0.1		1.43	
A_2	0.42 (0.32)	17	1.14	0.8
A_3	2.5		1.08	
A_4	9.3		0.98	
A_5	1.1 (2.7)	46	1.04	2.5
A_6	7.0		0.97	
A_7	3.7 (49)	130	0.85	13
A_8	2.8		0.75	
A_9	4.0 (93)	130	0.69	23
A_{10}	14		0.65	
A_{11}	17 (43)	130	0.59	2.5

[a] Numbers in parentheses are from experiments performed in acetonitrile; all other rate constants were determined in benzene.
[b] According to the method of Weller [14] (eqn. (10)).

experiments. These same samples were irradiated in the sample chamber of our spectrophotofluorometer (Hg–Xe lamp) for 15 min at the excitation wavelengths corresponding to the 0,0 bands of the A_i employed in the Stern–Volmer experiments. The decreases in fluorescence intensities ranged from about 1% for A_7 to about 5% for A_{10}.

All A_i excitations were at $\lambda > 350$ nm, where FP absorption is almost zero. No emissions other than those from A_i were observed when degassed sealed benzene or acetonitrile solutions of A_i and FP were irradiated. Direct excitation of FP in degassed cyclohexane at ambient temperatures and in the absence of A_i resulted in no discernible emissions.

Correlation coefficients for slopes of Stern–Volmer plots constructed from the fluorescence quenching data were not less than 0.98 except for A_2 in acetonitrile ($r = 0.94$). Each plot comprised at least six data points.

3. Results and discussion

Rate constants k_q for the supression of A_i fluorescence, half-wave oxidation potentials for A_i and other pertinent data not reported elsewhere [1, 2] are summarized in Table 1. The estimated errors in k_q near $k_{\text{diffusion}}$ and much less than $k_{\text{diffusion}}$ are ± 20% and ± 40% respectively. The fluorescence quenching of A_1 by FP was insufficient to allow a k_q to be calculated. An upper limit of 10^7 M^{-1} s^{-1} was estimated based upon the sensitivity of our spectrophotofluorometer.

The trend of k_q to increase as the substituents on A_i become more electropositive as defined by Ingold [6] is incompatible with exciplex formation
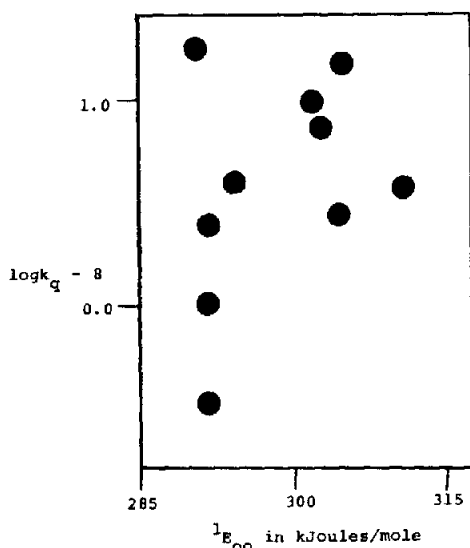
Fig. 1. Plot of log k_q vs. $^1E_{00}$ for A_i singlet quenching by FP in benzene.

in which A^- FP^+ charge-transfer interactions are important: the k_q increase as the electron-donating ability of the A_i increases. Our previous studies with P and DMA as quenchers showed a completely different trend which indicated the lack of importance of A^+ P^- and A^+ DMA^- exciplex interactions.

Similar reversals in the charge-transfer character of quenching mechanisms have been observed by others when singlets of naphthalene derivatives are supressed by carbon tetrachloride and diethylamine [7], when singlets of anthracene derivatives are intercepted by benzonitrile and anisole [8] or by 4,4'-dimethoxy-1,1-diphenylethylene and 4,4'-dinitro-1,1-diphenylethylene [9], and when triplets of benzophenone derivatives are quenched by substituted benzenes [10].

We have reported that the Hammett plot of log (k_q^i/k_q^7) versus σ for A_i fluorescence quenching by P has two positive ρ slopes [11][†]. A Hammett correlation, employing FP as quencher, yields a reasonable fit to a single straight line whose slope is unmistakably negative: $\rho = -1.15$ ($r = 0.937$); $\rho^+ = -0.78$ ($r = 0.939$). While these results are of qualitative interest, especially with regard to the change of sign of the ρ slopes, we are reluctant to discuss them quantitatively since it is unclear whether or not ground state σs can be applied directly to excited states[††].

As has been noted by Hammond and coworkers [13], a correlation between log k_q and the A_i singlet excitation energies $^1E_{00}$ should exist for a series of exciplexes which are primarily excitation-resonance stabilized. The resonance contribution from excitation resonance will be a maximum when

---

[†]Two positive ρ slopes, similar in magnitude to those reported for P, are found when DMA is the quencher.

[††]This question is being investigated [12].

2.0

1.0

$\log k_q - 8$

0.0

-2.50 -2.00
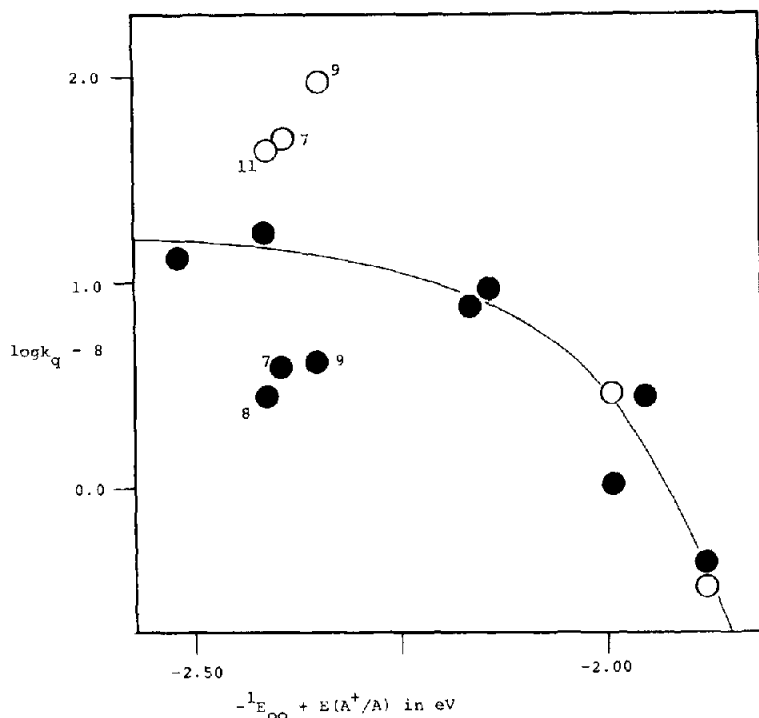
$-{}^1E_{00} + E(A^+/A)$ in eV

Fig. 2. Plot of log k_q *vs.* $-{}^1E_{00} + E(A^+/A)$ for A_i singlet quenching in benzene (●) and in acetonitrile (○). An approximate best fit curve is drawn for the benzene points from A_i with substituents containing lone pairs of electrons.

charge-transfer resonance is minimized (*i.e.* in non-polar solvents). Figure 1 shows a plot of log k_q *versus* ${}^1E_{00}$ for the A_i being quenched by FP. As can be seen, no clear trend exists, although log k_q appears to increase as ${}^1E_{00}$ increases.

Weller's semi-empirical theory of fluorescence quenching via exciplex formation applies when A^+ FP^- charge-transfer interactions dominate [14]. The theory predicts that two limiting slopes should be observed when k_q (as log k_q), which varies from near $k_{\text{diffusion}}$ to much less than $k_{\text{diffusion}}$, is plotted against $-{}^1E_{00} + E(A^+/A)$. Figure 2 shows such a plot for k_q obtained in benzene, a non-polar solvent ($\epsilon = 2.28$), and in acetonitrile, a polar solvent ($\epsilon = 38.8$). Since only five points in acetonitrile were obtained, no best fit line was attempted. At first glance the data in benzene do not appear to allow a reasonable best fit line. However, a curve whose shape is near that predicted [14] can be drawn for the seven points for which the substituents contain an unshared pair or electrons. The A_i ($i = 7$ - 9) for which no unshared electrons are on the substituents fall far below the curve. That A_7 - A_9 do exhibit k_q lower than "normal" is supported by the ratio of the k_q in acetonitrile and benzene (Table 1). Of the five ratios measured, only those of A_7 and A_9 are much larger than the value of 2.2 obtained for the self-diffu-

sion ratio of the solvents[†]. In addition, a plot of log k_q (benzene) *versus* $-{}^1E_{00} + IP_A$ (where IP_A is the ionization potential of the A_i (obtained from ref. 15)) for A_2 - A_{10} is similar in appearance to Fig. 2. The points for A_7 - A_9 fall below the curve described by the other data. Thus, it appears that an important quenching pathway available to the other A_i in benzene is not operative in A_7 - A_9. Considering the differences between A_7 - A_9 and the other A_i and the electrophilic nature of the quencher FP, it seems plausible that the unavailable pathway involves a substantial charge-transfer interaction between A_i and FP.

The data in acetonitrile indicate that the more polar solvent allows the charge-transfer quenching pathway (or another of equal efficiency) to occur with A_7 - A_9. The Weller theory [14] has predictive value in that k_q in acetonitrile can be calculated for an A^+ FP^- charge-transfer-dominated quenching process as follows:

$$k_q = \frac{20 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}}{1 + 0.25 \{\exp(\Delta H^{\ddagger}/RT) + \exp(\Delta H/RT)\}} \tag{10}$$

$$\Delta H = E(A^+/A) - E(FP^-/FP) - {}^1E_{00} - e^2/\epsilon r \tag{11}$$

where $\Delta H^{\ddagger}$ is the enthalpy of activation for step (8) in which the exciplex $(A \cdot FP)$ is depicted as an encounter complex and ΔH, given in eqn. (11), is the thermodynamic ethalpy difference for the same step. $\Delta H^{\ddagger}$ is approximated by a best fit equation in which ΔH is the only variable. The coulombic term $e^2/\epsilon r$ in eqn. (11) is approximated also since the distance r between A_i and FP at which electron transfer occurs is unknown. Previous work indicates that $r \approx 6$ Å (and $e^2/\epsilon r \approx 0.05$ eV) is appropriate [2, 16]. The calculated k_q (Table 1) do not agree well with the observed values when $k_q \ll k_{\text{diffusion}}$. The observed and calculated values do approach Weller's self-imposed difference limit of $\pm$ 100% when k_q is near $k_{\text{diffusion}}$.

Interestingly, A_7, A_9 and A_{11} seem to behave similarly in acetonitrile, both on the basis of Fig. 2 and of the proximity of their observed and calculated k_q. It would appear, then, that at least the singlets of A_i with electron-donating substituents are quenched by FP in acetonitrile by a predominantly charge-transfer mechanism. In benzene only those A_i whose substituents are electron donating and which contain lone pairs of electrons undergo quenching via a similar pathway.

While it is tempting to discuss further why A_7 - A_9 do not react like the other A_i in benzene, the paucity of data makes a detailed analysis inappropriate and any further conclusions speculative at best. The results obtained thus far clearly demonstrate that neither excitation-resonance nor charge-transfer models alone can account for the quenching of all of the A_i by FP. The trend in the k_qs, to increase as the electron richness of the sub-

---

[†]The error in these ratios, especially for A_2, is potentially large. The trends, however, are unmistakable and beyond possible error.

stituents on A_i increases, is opposite that found when either P or DMA was quencher. The results discussed here, combined with those reported previously, clearly show that the electronic nature of a series of exciplexes comprising structurally similar quenchers and quenchees can be altered completely by altering the electronic properties of either component: a complete spectrum of exciplex types, varying from A^+X^- to A^-X^+, has been found.

Acknowledgments

References

1 M. E. R. Marcondes, V. G. Toscano and R. G. Weiss, J. Am. Chem. Soc., 97 (1975) 4485.
2 M. E. R. Marcondes, V. G. Toscano and R. G. Weiss, J. Photochem., 10 (1979) 315.
3 E. G. Rochow and A. L. Allred, J. Inorg. Nucl. Chem., 5 (1958) 264, 269.
4 M.-H. Hui and W. R. Ware, J. Am. Chem. Soc., 98 (1976) 4718.
5 K. A. Wall, R. E. Donadio and W. J. Pummer, J. Am. Chem. Soc., 82 (1960) 4846.
6 C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell Univ. Press, New York, 1953, p. 10.
7 S. Ander, H. Blume, G. Heinrich and D. Schulte-Frohlinde, Chem. Commun., (1968) 745.
8 D. Schulte-Frohlinde and H. Hermann, Ber. Bunsenges. Phys. Chem., 81 (1977) 562.
9 W. R. Ware, J. D. Holmes and D. R. Arnold, J. Am. Chem. Soc., 96 (1974) 7861.
10 M. W. Wolf, R. E. Brown and L. A. Singer, J. Am. Chem. Soc., 99 (1977) 526.
11 M. E. R. Marcondes, V. G. Toscano and R. G. Weiss, Tetrahedron Lett., (1974) 4053.
12 L. A. King, J. Chem. Soc. Perkin Trans. 2, (1976) 1725; (1977) 919.
13 D. A. Labianca, G. N. Taylor and G. S. Hammond, J. Am. Chem. Soc., 94 (1972) 3679.
    G. N. Taylor and G. S. Hammond, J. Am. Chem. Soc., 94 (1972) 3684, 3687.
14 D. Rehm and A. Weller, Isr. J. Chem., 8 (1970) 259.
    A. Weller, in S. Clausson (ed.), Fast Reactions and Primary Processes in Chemical Kinetics, Proc. Fifth Nobel Symp., Interscience, New York, 1967, p. 413.
15 L. Klasinc, B. Kovac, S. Schoof and H. Güsten, Croat. Chem. Acta, submitted for publication.
16 T. J. Chuang and K. B. Eisenthal, J. Chem. Phys., 62 (1975) 2213.