THE QUENCHING OF EXCITED AROMATIC ESTERS BY TRIETHYLAMINE

SILVIA M. de B. COSTA, A. L. MAÇANITA, E. C. C. MELO and M. J. PRIETO

Centro de Quimica Estrutural, Complexo I, Instituto Superior Tecnico, Av. Rovisco Pais, Lisboa-1 (Portugal)

Summary

The interaction of excited aromatic esters with tertiary aliphatic amines, triethylamine (TEA) and diazobicyclo [2.2.2] octane has been investigated. In non-polar solvents the fluorescence quenching that is observed is accompanied in most cases by an exciplex emission when TEA is the quencher, whereas the radical anions of the esters are detected in polar solvents.

The large dipole moments found for the exciplexes (9—16 debye) and the correlation of the bimolecular rate constant k_q with the half-wave potential of the excited esters and the ionization potentials of the amines show that a charge transfer mechanism is operative in these systems.

1. Introduction

The quenching of the singlet excited state of N,N-dimethyl-2-naphthylamine by benzoates and phthalates has been assigned to a charge transfer interaction [1] which has been further confirmed by the detection of the radical cation of the aromatic amine [2].

In contrast, aliphatic amines can act as effective reductants of benzylic and allylic benzoates [3]. However, we have found that, while the photochemical reaction was much less efficient with benzyl aromatic esters that have higher electron affinities than benzyl benzoate, their fluorescence was strongly quenched in the presence of tertiary aliphatic amines.

We now report some preliminary quenching studies using as acceptors aromatic esters (Fig. 1) which possess low lying (π,π^*) states [4] and triethylamine (TEA) and diazobicyclo [2.2.2] octane (DABCO) as donors.

2. Experimental

All compounds were synthesized using methods described in a previous paper [4]. TEA was freshly distilled under nitrogen whenever used. DABCO was purchased from Aldrich Chemicals and recrystallized with ligroin.
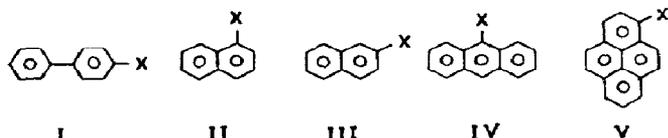
Fig. 1. The structures of compounds I - V: X - CO_2CH_2Ph.

Fluorescence spectra were recorded in a Hitachi Perkin–Elmer spectro-fluorimeter, model MPF-3, equipped with a correction unit. The flash photolysis studies were carried out on a conventional apparatus from Applied Photophysics. Unless otherwise stated, the flash lamps were filtered with an aqueous solution of copper (II) sulphate to remove light of wavelength less than 375 nm. The absorption spectra were determined using the method described by Porter [5].

Polarographic half-wave potentials for reduction of the aromatic esters in dimethylformamide (0.1 M tetrabutylammonium iodide) were determined with a Radiometer Polarograph PO4 equipped with a dropping mercury electrode separated from a standard calomel electrode (SCE) by a KCl salt bridge.

The concentration of the esters used was in all cases 10^{-4} M and no self-quenching was observed.

3. Results and discussion

The fluorescence of the compounds studied [4] is strongly quenched in the presence of TEA in polar and non-polar solvents. In non-polar solvents the monomer emission of all compounds except IV is accompanied by a new long wavelength broad emission, which was attributed to an exciplex, as shown in Fig. 2.

The increase of solvent polarity shifts the long wavelength emission to the red and its intensity is decreased, as would be expected for charge transfer complexes. The maximum wavenumber of the exciplex emissions correlates linearly with that of the anthracene–diethylaniline system used as reference (μ_R = 10 debye and a_R = 5Å) [6]. The dipole moments of the exciplexes were estimated from the equation

$$\widetilde{\nu}_E = \frac{\mu_E^2 a_R^3}{\mu_R^2 a_E^3} \widetilde{\nu}_R - \left\{ \frac{\mu_E^2 a_R^3}{\mu_R^2 a_E^3} \widetilde{\nu}_R(0) - \widetilde{\nu}_E(0) \right\} \tag{1}$$

where the indexes E and R refer to the unknown exciplex and to that of the reference system respectively, and $\widetilde{\nu}$, μ and a have the usual meanings.

The dipole moments presented in Table 1 are of the order of magnitude of the naphthalene–TEA exciplex [7]; this clearly indicates the charge transfer nature of the exciplexes observed.

The lack of exciplex emission in the system IV–TEA may be related to the photochemistry observed in this system [8], the dissipation of energy
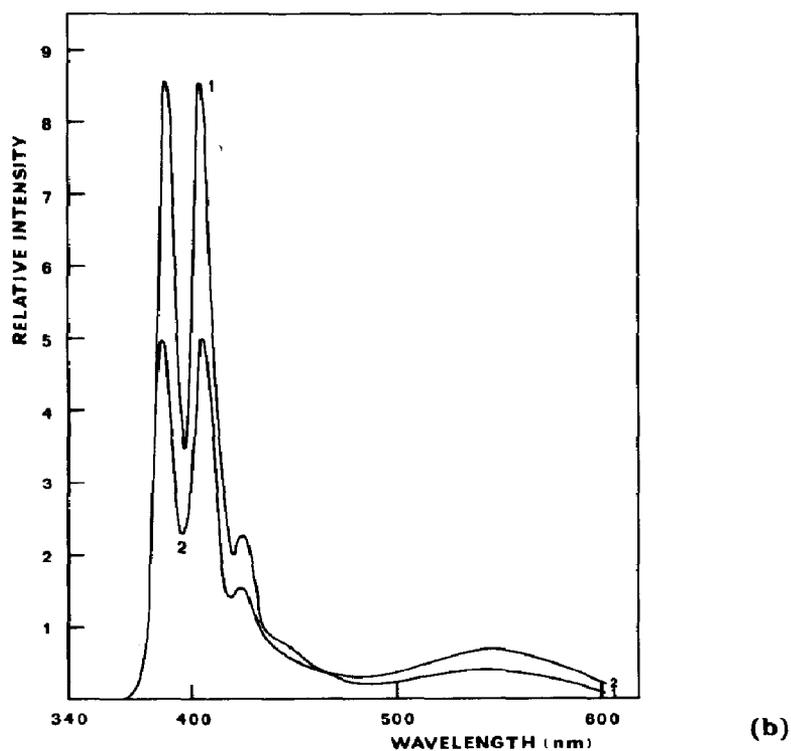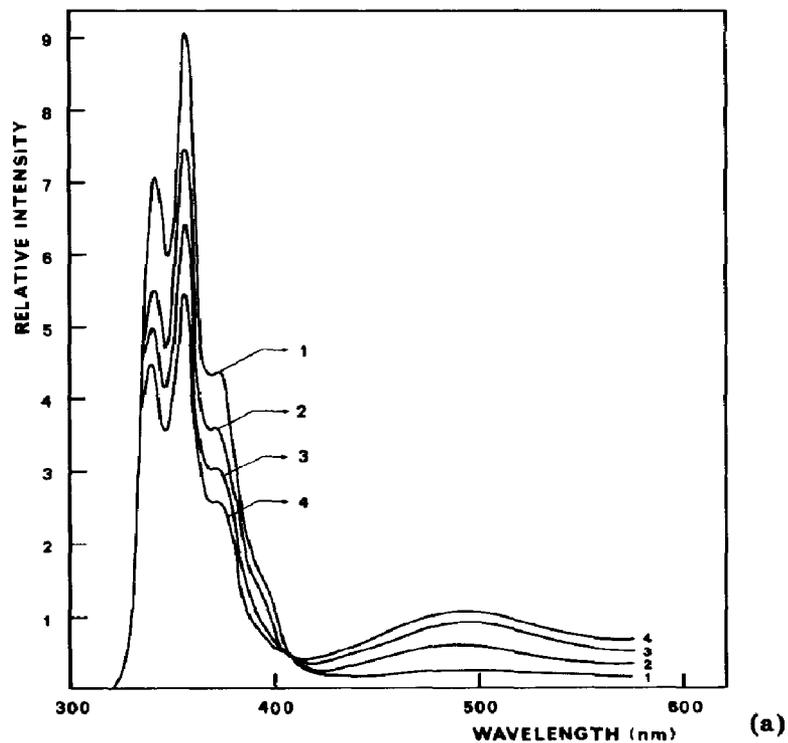
Fig. 2. Monomer and exciplex fluorescence of: (a) III–TEA in benzene ([TEA] = 0.4 M
(1), 0.6 M (2), 0.8 M (3) and 1.0 M (4)); (b) V–TEA in hexane ([TEA] = 0.5 M (1) and
1.0 M (2)).

TABLE 1

Dipole moments μ_E and maximum wavenumber emissions $\bar{\nu}_E^{max}$ of aromatic ester–TEA exciplexes

System	$\bar{\nu}_E^{max} \times 10^{-3}$ [a] (cm^{-1})	μ_E (debye)	a (Å)
I–TEA	19.8	12	5.5
II–TEA	19.2	10	5
III–TEA	21.7	16	5
IV–TEA	no emission	—	
V–TEA	18.4	9	5.5

[a]In hexane.

through non-radiative modes of decay competing favourably with radiative emission from the exciplex.

The quenching of the fluorescence of III by DABCO was also observed but no exciplex emission was detected in agreement with previous results obtained using different acceptors and this quencher [9].

The flash photolysis of solutions of III, IV and V with TEA in aceto-nitrile led to the appearance of new transients (Fig. 3), which have been assigned to the radical anions of the esters since their disappearance follows second order decay kinetics. The radical anion of IV was also observed in the presence of DABCO in dimethylformamide; this gives support to these assignments.

The experimental evidence obtained from the interaction of the singlet excited states of these esters with TEA or DABCO is consistent with the charge transfer mechanism described by Leonhardt and Weller [10].
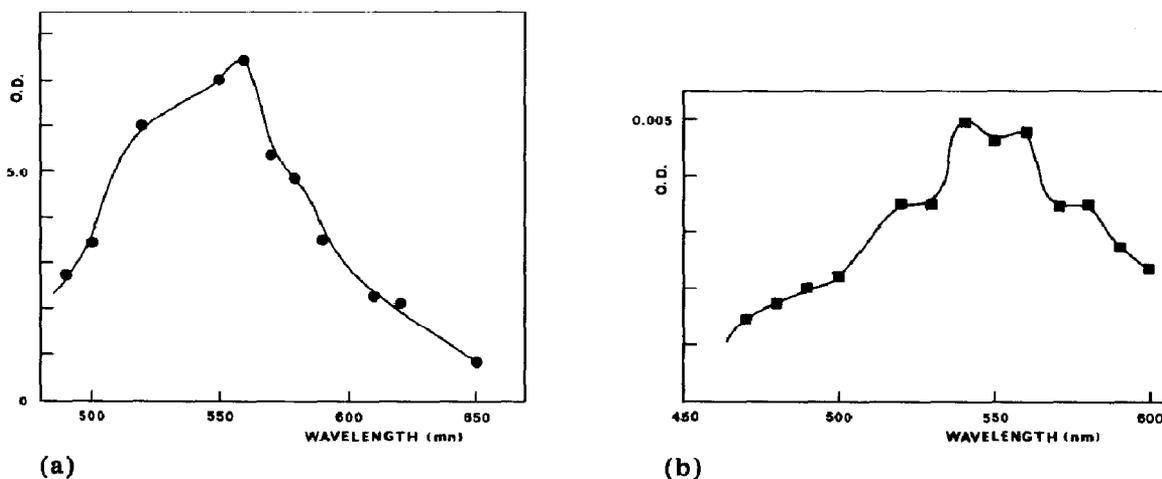

(a)   (b)

Fig. 3. Absorption spectra of radical anions in acetonitrile of: (a) IV and (b) V in the presence of 0.24 M of TEA.

TABLE 2

Quenching rate constants of aromatic ester–TEA systems in different solvents

Solvent	k_{diff}[a] $\times 10^{-10}$ (dm^3 mol^{-1} s^{-1})	k_q[b] $\times 10^{-10}$ (dm^3 mol^{-1} s^{-1})					
		I–TEA	II–TEA	III–TEA	III–DABCO	IV–TEA	V–TEA
Hexane	3.08	10[c]	3.33[c]	1.51	2.57	1.67	1.13
Cyclohexane	1.06	9[c]	1.50[c]	1.01	1.15	0.88	0.73
Acetonitrile	2.78	0.82	2.20	1.78	2.30	1.83	1.22
Dimethylformamide	1.07	0.58	0.87	0.98	1.19	0.95	0.77

[a] Calculated from $k_{diff} = 8RT/2000\eta$ at $T = 295$ K.
[b] From $k_q = K_{SV}/\tau_0$ [4].
[c] Upper limit values.

Table 2 gives the data obtained from the linear Stern–Volmer relationship and fluorescence lifetimes determined for each system.

The quenching rate constants are of the order of the diffusion rate constants calculated using the Stokes–Einstein relation; this suggests a diffusion-controlled process. However, the fact that the bimolecular rate constants obtained with DABCO are higher than those obtained using the same acceptor and TEA suggests that the process might be near diffusion controlled.

Indeed, the increase in the rate constant when the quencher is changed from TEA to DABCO may be attributed to the lower ionization potential of DABCO, although this factor is not the only one affecting the quenching rate constants [11]. The charge transfer contribution contained in k_q is shown by the relationship found between the ln k_q and the half-wave potentials $E_{1/2}^*$ in the excited state of the esters [12] listed in Table 3 and the ionization potentials IP of the amines (Fig. 4).

TABLE 3

Half-wave potentials in the ground and excited state
of esters I, II, III, IV and V

Compound	$-E_{1/2}$ (eV) (vs. SCE)	$E_{1/2}^*$ [a] (eV) (vs. SCE)
I	1.93	2.32
II	1.80	2.02
III	1.85	1.85
IV	1.47	1.67
V	1.48	1.74

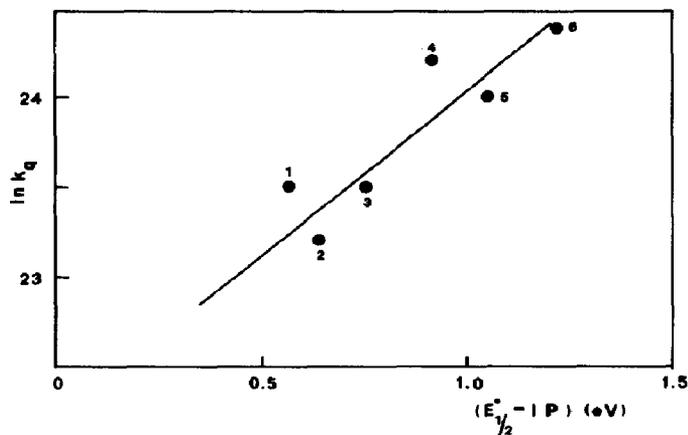[a] $E_{1/2}^* = E_{1/2} + \Delta E_{0-0}$ (hexane).

Fig. 4. Plot of the logarithm of the quenching rate constants in hexane for the systems IV–TEA (1), V–TEA (2), III–TEA (3), II–TEA (4), III–DABCO (5) and I–TEA (6) vs. the difference between the half-wave potential of the excited ester and the amine ionization potential.

However, the failure to observe a clear correlation between the quenching rate constants and the solvent polarity points to the need of an assessment of the charge transfer contribution to the bimolecular rate constant. A detailed kinetic treatment of these systems will be presented in a separate publication.

Acknowledgment

References

1 K. Kaneta and M. Koizumi, *Bull. Chem. Soc. Jpn*, *40* (1967) 2254.
2 M. Koizumi and H. Yamashita, *Z. Phys. Chem. (Frankfurt am Main)*, *57* (1968) 103.
3 R. C. Cookson, J. Hudec and N. A. Mirza, *Chem. Commun.*, (1967) 824.
4 S. M. B. Costa, A. L. Maçanita and M. J. Prieto, *J. Photochem.*, *11* (1979) 109.
5 G. Porter, in A. Weissberger (ed.), *Rates and Mechanisms of Reactions*, Vol. VIII, Part II, Interscience, New York, 1963, p. 1055.
6 H. Knibbe, A. Weller, *J. Chem. Phys.*, *47* (1967) 1183.
7 M. G. Kuzmin and L. W. Guseva, *Chem. Phys. Lett.*, *3* (1969) 71.
8 S. M. B. Costa and E. C. C. Melo, *Proc. VII IUPAC Symp. on Photochemistry*, *Leuven, 1978*, Katholike Univ. Leuven, Louvain, 1978, p. 95.
9 A. Zweig and J. B. Gallivan, *Mol. Photochem.*, *6* (1974) 397.
   S.-P. Van and G. S. Hammond, *J. Am. Chem. Soc.*, *100* (1978) 3895.
10 H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, *67* (1963) 791.
11 H. J. Heller and H. R. Blattmann, *Pure Appl. Chem.*, *36* (1973) 141.
12 A. Weller, in S. Claesson (ed.), *Fast Reactions and Primary Process in Chemical Kinetics*, Wiley, New York, 1967, p. 413.