

EXCIPLEX FORMATION BETWEEN AROMATIC AMINES AND 4-DIMETHYLAMINO-2-PYRIDYL 3-PYRIDYL KETONE

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Summary

The fluorescence of 4-dimethylamino-2-pyridyl 3-pyridyl ketone in 2-propanol is quenched by aromatic amines. Exciplex formation appears to be involved in the quenching process. Evaluation of the rate constants for the decay of the exciplex suggests that complete electron transfer from the amine to the ketone may take place.

1. Introduction

The quenching of excited aromatic molecules by amines has been the subject of considerable study since the observation, by Leonhardt and Weller [1], of a fluorescent exciplex formed between excited perylene and *N,N*-dimethylaniline. Many other similar systems have subsequently been discovered and the field has been extensively reviewed [2 - 4].

The interaction between excited aromatic carbonyl compounds and amines has mainly been studied from the viewpoint that the amines are a source of hydrogen for the reduction of the ketone moiety [5]. However, Masuhara *et al.* [6] have recently studied the formation of intermolecular and intramolecular singlet and triplet exciplexes between benzophenone and *N,N*-dimethylaniline. Our recent observation [7] of strong fluorescence from a pyridyl analogue of 4-dimethylaminobenzophenone provides an opportunity to study the interaction between the excited singlet state of an aromatic ketone and various quenchers. We report here the quenching of the fluorescence of 4-dimethylamino-2-pyridyl 3-pyridyl ketone (DMPPK) by aromatic amines in 2-propanol.

2. Experimental details

DMPPK was prepared as described previously [7]. The various amines were purchased from Aldrich or Fluorochem and were purified by repeated

vacuum distillation before use. 2-propanol was BDH spectroscopic or AnalaR grade and contained no detectable fluorescent impurities under the conditions employed here.

Absorption spectra were measured on a Pye–Uvicam SP8-100 spectrophotometer and fluorescence spectra on a modular spectrofluorometer designed and built by Applied Photophysics Ltd. [8]. Fluorescence decays were determined by the method of time-correlated single-photon counting as described by Ware [9] on an Edinburgh Instruments model 199 fluorescence decay time spectrometer incorporating the flash-lamp recently described by Birch and Imhof [10]. The resulting decay profiles were analysed by computer convolution.

3. Results and discussion

Addition of aniline and some of its derivatives to solutions of DMPPK in 2-propanol causes the fluorescence to be quenched. The aliphatic amine butylamine has no effect. For all the quenchers studied there is no evidence for the appearance of a new emission band as the fluorescence of the ketone diminishes. The steady state quenching has been analysed by measuring the intensity of the fluorescence as a function of added quencher Q and plotting the data in the form of the familiar Stern–Volmer relationship

$$\frac{\phi_f^0}{\phi_f} = 1 + k_Q \tau [Q] \quad (1)$$

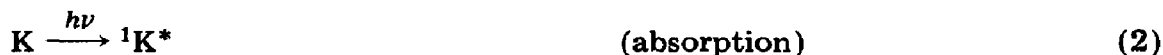
where ϕ_f^0 is the fluorescence intensity in the absence of quencher, ϕ_f is the intensity in the presence of a quencher concentration $[Q]$, τ is the fluorescence decay time for DMPPK and k_Q is the quenching rate constant. The values of k_Q for a range of aniline derivatives are given in Table 1.

TABLE 1

Quencher	k_Q ($\times 10^{-8} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	Ionization potential (eV)	Reference
Aniline	5.95	7.70	[11]
<i>N</i> -methylaniline	7.81	7.39	[11]
<i>N,N</i> -dimethylaniline	8.33	7.18 ^a	[12]
<i>N,N</i> -diethylaniline	16.05	7.18 ^a	[12]
2-fluoroaniline	3.40	7.95	[11]
3-fluoroaniline	4.66	7.90	[11]
4-fluoroaniline	5.87	7.82	[11]
2-chloroaniline	4.38	7.86 ^a	[13]
3-chloroaniline	4.68	7.98	[11]
4-chloroaniline	8.19	7.72 ^a	[13]

^aValues corrected to an ionization potential for aniline of 7.70 eV.

It can be seen from Table 1 that there is a correlation between the measured quenching rate constant and the ionization potential of the amine. The rate constants vary by an order of magnitude and appear to increase with the ease with which the amine can lose an electron. We therefore postulate the possibility of exciplex formation as given by the following mechanism:



We have neglected the formation of an encounter complex prior to exciplex formation.

The steady state rate constants k_Q are related to the above rate constants by

$$k_Q = \frac{k_+ k_q}{k_- + k_q} \quad (6)$$

and, with the postulate that the exciplex is stabilized by charge transfer from the amine to the ketone, $\log_{10} k_Q$ would be expected to vary linearly with the ionization potential of the amine. This is shown in Fig. 1 where there is seen to be a reasonable correlation between $\log_{10} k_Q$ and the ionization potential.

Some of the more efficient quenchers exhibit a slight positive deviation from linearity. The absorption spectra of DMPPK in the presence and absence of these amines appear to be identical so this non-linearity is not attributable to ground state complexation. The probable cause is therefore quenching of the exciplex itself by a second amine molecule.

Analysis of the quenching mechanism reveals that the fluorescence decay of the ketone will exhibit a dual-exponential behaviour [14 - 16]:

$$I_f = C_1 \exp(-\lambda_1 t) + C_2 \exp(-\lambda_2 t) \quad (7)$$

where

$$\lambda_{1,2} = \frac{1}{2} [(k_f + k_{NR} + k_+[Q] + k_- + k_q) \mp \{(k_- + k_q - k_f - k_{NR} - k_+[Q])^2 + 4k_+k_-[Q]\}^{1/2}] \quad (8)$$

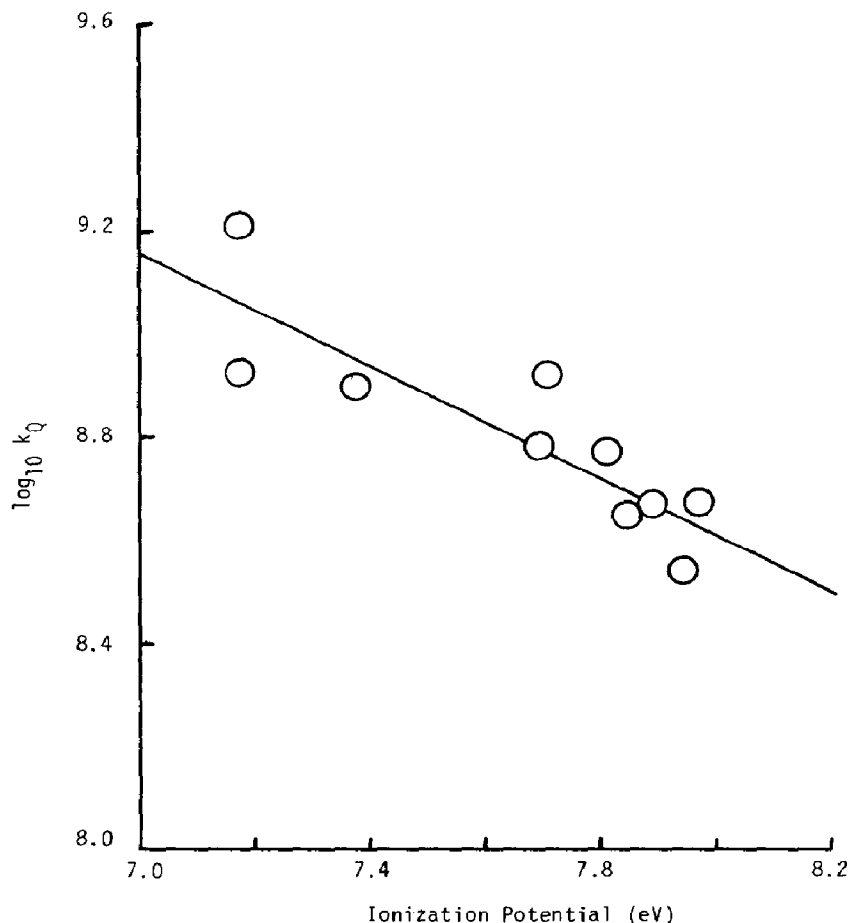


Fig. 1. The variation in $\log_{10} k_Q$ with the ionization potential of the amine. (The straight line is the best fit to the data calculated by the method of least squares.)

$$C_1 = \frac{\lambda_2 - x}{\lambda_2 - \lambda_1} \quad (9)$$

$$C_2 = \frac{x - \lambda_1}{\lambda_2 - \lambda_1} \quad (10)$$

$$x = k_f + k_{NR} + k_+[Q] \quad (11)$$

The dual-exponential nature of the decay has been confirmed for aniline, *N*-methylaniline and *N,N*-dimethylaniline on the basis of χ^2 and a random distribution of residuals. The rate constants in the kinetic scheme may be evaluated by considering the variation in $\lambda_1 + \lambda_2$ and $\lambda_1\lambda_2$ with $[Q]$ [16] and by evaluating x in eqn. (11) and also plotting it against $[Q]$. The resulting rate constants are given in Table 2.

The first point which must be made about the results reported in Table 2 is that the reported lifetime of DMPPK [7] is in error by an order of

TABLE 2

Rate constant	Rate constants for the following quenchers		
	Aniline	N-methylaniline	N,N-dimethylaniline
$k_f + k_{NR}$ (s^{-1})	5.7×10^8	5.2×10^8	5.5×10^8
k_+ ($dm^3 mol^{-1} s^{-1}$)	3.5×10^9	4.0×10^9	3.4×10^9
k_- (s^{-1})	8.2×10^7	4.6×10^7	1.7×10^8
k_q (s^{-1})	7.9×10^6	1.1×10^7	8.6×10^7

magnitude. This value was measured for us in another laboratory, but remeasurement on our fluorescence decay time system shows that the decay time is 1.6 ± 0.2 ns in aerated solution. The values of $k_f + k_{NR}$ from the quenching studies are, as expected, in good agreement with these values. The size of k_+ for the three quenchers indicates that the formation of the exciplex is diffusion controlled, but that once formed it has a lifetime of the order of 10 ns. There is no obvious pattern in the values of k_- which vary by a factor of 3 over the three quenchers, but k_q increases steadily with the electron-donating ability of the amine and suggests that the products of the quenching may involve complete electron transfer from the amine to the ketone.

We are at present investigating the product(s) of this quenching reaction and the effect of temperature on the various rate constants in the kinetic scheme. These results will be reported at a later date.

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References

- 1 H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67** (1963) 791.
- 2 M. Gordon and W. R. Ware (eds.), *The Exciplex*, Academic Press, New York, 1975.
- 3 N. Mataga and M. Ottolenghi, in R. Foster (ed.), *Molecular Association*, Vol. II, Academic Press, London, 1979.
- 4 H. Beens and A. Weller, in J. B. Birks (ed.), *Organic Molecular Photophysics*, Vol. II, Wiley-Interscience, New York, 1975, p. 159.
- 5 S. Inbar, H. Linschitz and S. G. Cohen, *J. Am. Chem. Soc.*, **103** (1981) 1048, and references cited therein.
- 6 H. Masuhara, Y. Maeda, H. Nakajo, N. Mataga, K. Tomita, H. Tatemitsu, Y. Sakata and S. Misumi, *J. Am. Chem. Soc.*, **103** (1981) 634.

- 7 R. G. Brown, P. J. Haslam, J. D. Hepworth, G. E. Scott and P. Wearden, *Chem. Ind. (London)*, (1980) 572.
- 8 C. A. Pullin, R. G. Brown and E. H. Evans, *FEBS Lett.*, 101 (1979) 110.
- 9 W. R. Ware, in A. Lamola (ed.), *Creation and Detection of the Excited State*, Vol. 1B, Dekker, New York, 1971.
- 10 D. J. S. Birch and R. E. Imhof, *Rev. Sci. Instrum.*, 52 (1981) 1206.
- 11 R. Bralsford, P. V. Harris and W. C. Price, *Proc. R. Soc. London, Ser. A*, 258 (1960) 459.
- 12 A. D. Baker, D. P. May and D. W. Turner, *J. Chem. Soc., B* (1968) 22.
- 13 S. Tajima, N. Wasada and T. Tsuchiya, *Tetrahedron Lett.*, (1970) 139.
- 14 C. Lewis and W. R. Ware, *Mol. Photochem.*, 5 (1973) 261.
- 15 D. V. O'Connor and W. R. Ware, *NBS Spec. Publ. 526*, 1978, p. 193 (National Bureau of Standards, U.S. Department of Commerce).
- 16 W. R. Ware, D. Watt and J. D. Holmes, *J. Am. Chem. Soc.*, 96 (1974) 7853.