Tetrahedron Letters,Vol.25,No.5,pp 475-478,1984	0040-4039/84 $3.00 + .00
Printed in Great Britain

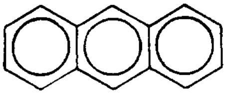
QUENCHING OF ANTHRACENE FLUORESCENCE BY DIALKYLANILINES IN SATURATED HYDROCARBONS

Nien-chu C. Yang* and Zhong-he Lu[1]

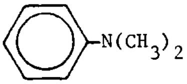
Department of Chemistry, University of Chicago, Chicago, Illinois 60637

Abstract: The bimolecular quenching constants of anthracene fluorescence by dialkylanilines in saturated hydrocarbons depend on the solvent viscosity and may exceed theoretical diffusion controlled limit in viscous hydrocarbons.

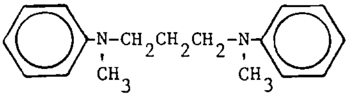
Dialkylanilines interact with photoexcited anthracene in benzene at a rate slightly less than the diffusion controlled limit to form a luminescent exciplex.[2-4] At high aniline concentrations, the exciplex formed may undergo further reactions with another molecule of dialkylaniline.[3-5] In order to investigate the mechanism of this interaction between an exciplex and another donor molecule, we investigated the interaction of photoexcited anthracene with a bichromophoric dialkylaniline, 1,3-bis-(N-phenyl-N-methylamino)propane (DMA-AMD), in several saturated hydrocarbons and compared the results with those from dimethylaniline (DMA) and N-methyl-N-ethylaniline (MEA). The concentration range of anilines used varies from 0.00 to 0.03 M within which linear Stern-Volmer plots were obtained indicating that bimolecular processes involving exciplexes were unimportant. The experimental methods used have been described previously.[3] The results on the stern-Volmer quenching constants in degassed solutions and various properties of exciplexes formed are tabulated in the Table.



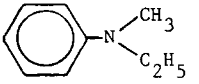
Anthracene, An



Dimethylaniline, DMA



1,3-bis-(N-Phenyl-N-methylamino)propane, DMA-AMD



N-Methyl-N-ethylaniline
MEA

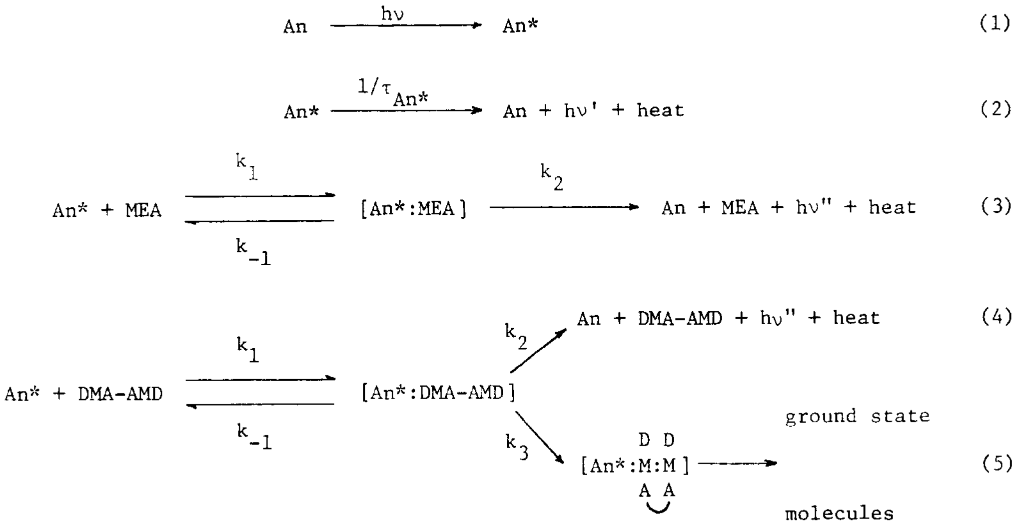
Table[a]

	n-pentane	methylcyclohexane	$\underline{n}$-hexadecane
η, CP	0.22	0.73	3.34
ε	1.84	2.02	2.06
$\lambda_{An}*(0\rightarrow 0)$	397±1	398±1	400±1
$\tau_{An}*$ (nsec)[b]	5.81	5.18	5.30
K_{sv}(An*:DMA-AMD), M^{-1}, (0-0.03M)[c]	140.5±1.5	66.5±1.5	32.8±0.8
K_{sv}(An*:MEA), M^{-1}, (0-0.03M)[c]	77.5±1.5	49.3±0.7	30.3±0.7
K_{sv}(An*:DMA), M^{-1}, (0-0.03M)[c]	69.6±0.6	45.2±1.2	29.9±1.2
k_{diff} ($10^9 M^{-1} sec^{-1}$)	30	9.0	2.0
$k_{diff}\tau_{An}*$, M^{-1}	174	46.6	10.6
λ_{max}(An*:DMA-AMD) nm[c]	476±2	478±2	480±2
λ_{max}(An*:MEA), nm[c]	475±2	477±2	478±2
λ_{max}(An*:DMA), nm[c]	475±2	476±2	477±2
ϕ_f(An*:DMA-AMD)[c,d]	0.20	0.21	0.21
ϕ_f(An*:MEA)[c,d]	0.43	0.39	0.37
ϕ_f(An*:DMA)[c,d]	0.45	0.41	0.37

[a] Values in this Table are taken from reference 3 unless otherwise noted. [b] J. Rice, D. B. McDonald, L-K. Ng, and N. C. Yang, J. Chem. Phys., 73, 4144 (1980). [c] This work. [d] Experimental uncertainty, ±10%.

We found that DMA-AMD is in general a more efficient quencher of anthracene fluorescence than the monochromophoric analogs and yields an exciplex which emits at the same wavelength as that of MEA but with a lower quantum yield. No new emission was detected. The results are consistent with a mechanistic Scheme that photoexcited anthracene forms an exciplex reversibly with a dialkylaniline, $K = k_1/k_{-1}$. In the absence of another quencher molecule, the exciplex formed undergoes a unimolecular decay with a rate of k_2 (equation 3). The observed quenching rate will then be $[k_1][k_2]/(k_{-1}+k_2)$ and the quantum yield of exciplex emission will be a function of this expression depending on the absolute rate of exciplex emission.[3,4] Since [An*:dialkylaniline] is known to react with a second molecule of dialkylaniline to undergo a bimolecular non-radiative process,[3] the second dialkylanilino group in DMA-AMD may undergo a similar intramolecular deactivation process (equation 5). The observed quenching rate of An^* by DMA-AMD will then be $[k_1][k_2+k_3]/(k_{-1}+k_2+k_3)$ and the quantum yield of exciplex emission will be a function of $[k_1][k_2]/(k_{-1}+k_2+k_3)$. Since the magnitudes of k_1,k_{-1} and k_2 are expected to be similar for both MEA and DMA-AMD, and k_3 is expected to be a finite number similar in magnitude as $(k_{-1}+k_2)$,[3] k_q observed for DMA-AMD is larger while ϕ_f is smaller than the monochromophoric analogs. Such an explanation would readily account for the experimental results obtained for all three anilines in n-pentane.

Scheme



hν' and hν" denote anthracene fluorescence and exciplex emissions respectively.

However, we also found that the Stern-Volmer constants (K_{sv}), going from n-pentane to n-hexadecane, decrease by a factor of less than five while the viscosity of the medium increases by a factor of 15. Since the lifetime of excited anthracene does not vary appreciably in these solvents, the quenching constants (k_q) in n-hexadecane for all three anilines calculated from their K_{sv}'s exceed the theoretical rate of diffusion in that solvent by a factor of approximately 3.

It has been noted in the literature that a number of bimolecular processes involving excited molecules, excluding energy transfer processes, may proceed with a rate exceeding the theoretical diffusion controlled limit.[6-10] Several explanations had been suggested for these phenomena which include the variation of sliding coefficient between the solute and solvent molecules,[6] the difference in size between the quencher and the fluorescer,[7] the difference in size between the solvent and the solute molecules,[6] and a long range interaction between the fluorescer and the electron donor.[10] However, none of these explanations seems to apply to our experimental data. Hence the variation of the sliding coefficient may increase the diffusion rate by a factor of 1.5;[6] the size of the quencher molecule is not appreciably different from the fluorescer in our case; there is no appreciable effect on k_q when the size of the quencher molecule is doubled (from DMA to DMA-AMD); and the non-polar nature of our media will prevent the electron transfer from the donor to the fluorescer to generate radical ions. A possible explanation which would fit all the experimental data is that excited anthracene will exert a reversible long range interaction on dialkylaniline ($k_1 > k_{diff}$) and the rate of dissociation of the exciplex (k_{-1}) is a function of the solvent viscosity. The mechanism of this phenomenon is being investigated.

The preliminary investigation in our laboratory on the quenching of pyrene fluorescence by these anilines in _n_-hexadecane indicated that k_q's also exceed that of the theoretical diffusion controlled limit.

Acknowledgment. The authors wish to thank the National Science Foundation for the support of this work, and one of us (Z-HL) wishes to thank the Academia Sinica for a fellowship in order to carry out this investigation.

References and Notes

1. Visiting Scholar from the Academia Sinica; current address: Guangzhou Institute of Chemistry, Guangzhou, Guandong, PRC.
2. For original reviews on anthracene:dialkylaniline exciplexes, see A. Weller, "Nobel Symposium 5, Fast Reactions and Primary Process in Chemical Kinetics," S. Claesson, Editor, John Wiley & Sons, New York, N.Y., 1967, p. 413; _Pure Appl. Chem._, _16_, 115 (1968).
3. N. C. Yang, D. M. Shold, and B. Kim, _J. Am. Chem. Soc._, _98_, 6587 (1976).
4. J. Saltiel, D. E. Townsend, B. D. Watson, P. Shannon, and S. L. Finson, _J. Am. Chem. Soc._, _99_, 884 (1977).
5. For the quenching of exciplexes or excimers by ground state molecules, see also, H. Beens and A. Weller, _Chem. Phys. Lett._, _2_, 140 (1968); E. A. Chandross and H. T. Thomas, _ibid._, _9_, 397 (1971); R. A. Caldwell, D. Creed, D. C. DeMarco, L. A. Melton, H. Ohta, and P. H. Wing, _J. Am. Chem. Soc._, _102_, 2369 (1982) and references therein; S. G. Cohen and S. Ojanpera, _ibid._, _97_, 5633 (1975); T. Mimura and M. Itoh, _ibid._, _98_, 1095 (1976); _Bull. Chem. Soc. Japan_, _50_, 1739 (1977); K. H. Grellman and U. Suckow, _Chem. Phys. Lett._, _32_, 250 (1975): R. A. Beecroft, R. S. Davidson and T. D. Whelan, _J. Chem. Soc. Chem. Commun._, 911 (1978); F. D. Lewis and D. E. Johnson, _J. Am. Chem. Soc._, _100_, 983 (1978); J. R. Larson, J. W. Petrich and N. C. Yang, _J. Am. Chem. Soc._, 104, 5000 (1982) and references therein.
6. For a review on diffusion controlled rate processes, see A. H. Alwattar, M. D. Lamb, and J. B. Birks, in J. B. Birks, Editor, "Organic Molecular Physics," John Wiley & Sons, New York, N.Y. Volume 1, 1973, pages 403-456.
7. W. R. Ware, _J. Phys. Chem._, _66_, 455 (1962).
8. B. Stevens and B. E. Algar, _J. Phys. Chem._, _72_, 2582 (1968).
9. E. Döller and Th. Föster, _Z. Phys. Chem. (N. F.)_, 34, 132 (1962).
10. J. R. Miller, J. A. Peeples, M. J. Schmitt, and G. L, Closs, _J. Am. Chem. Soc._, _104_, 6488 (1982).

(Received in USA 11 November 1983)