of proton to give the enolate radical. An electron-transfer mechanism has been proposed in the oxidation of phenol by $Ir^{IV}Cl_6{}^{2-}$ [26] and the presence of cation radical in the oxidation of phenol by Lewis acids was reported.[27]

Finally one other difference between the present work and Littler's study is the effect of oxygen on the rate. We found no rate enhancement in the presence of oxygen, suggesting the scheme given in eq 4-7 is not operative.

Experimental Section

Materials. 2,2′-Bipyridyl, 1,10-phenanthroline, the substituted phenanthrolines, and tris(2,2′-bipyridyl)ruthenium(II) chloride were purchased from G. Frederick Smith Co.

Tris(1,10-phenanthroline)iron(II), ferroin, the substituted ferroin complexes, and tris(2,2′-bipyridyl)iron(II) were prepared by a published procedure[3a] which consisted of adding an equivalent amount of appropriate ligand to a solution of $FeSO_4{\cdot}7H_2O$ in 3:1 molar ratio. The perchlorate and chloride salts of tris(1,10-phenanthroline)-ruthenium(II) were prepared according to a literature method.[28]

The Fe(III) complexes were obtained by oxidation of the Fe(II) complexes with PbO_2 in ~1 M H_2SO_4. The Fe(III) complexes were precipitated as perchlorate salts. Stock solutions of the Fe(III) complexes were made up in concentrated H_2SO_4 or concentrated $HClO_4$ medium. Such solutions were diluted with water to appropriate acid strength immediately before each kinetic run. The Ru(III) complexes were made in situ by oxidizing the Ru(II) solutions with PbO_2 and then filtering off the precipitate of PbO_2 or $PbSO_4$.

Baker analyzed reagent grade cyclohexanone was obtained from J.T. Baker Chemical Co. and was used without further purification.

Kinetic Studies. Tris(polypyridyl)iron(II) and -ruthenium(II) complexes have extinction coefficients of the order of 10^4 in the region of 510 and 450 nm, respectively, while the corresponding Fe(III) and Ru(III) complexes were practically transparent at these wavelengths. Thus the rate of oxidation of cyclohexanone could be conveniently monitored by following the increase in optical density with time at ~510 and 450 nm.

Kinetic studies for the oxidation were carried out on a Durrum stopped-flow spectrophotometer, Unicam SP 800, Unicam SP 1700, and Cary 118 spectrophotometers. The reaction was carried out under pseudo-first-order conditions with excess cyclohexanone and reasonably good pseudo-first-order kinetics were obtained. The psuedo-first-order rate constants were obtained by plotting log ($OD_\infty - OD_t$) against time.

Acknowledgment. We wish to thank the Defence Research Board of Canada, Environment Canada, and the National Research Council of Canada for financial support.

References and Notes

(1) Presented in part at the Electron Transfer Symposium at the 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, Abstracts INOR-101.

(2) J. S. Littler, *J. Chem. Soc.*, 827, 832 (1962).

(3) (a) H. J. der Hertog, Jr., and E. C. Kooyman, *J. Catal.*, **6**, 357 (1966); (b) E. I. Heiba and R. M. Dessau, *J. Am. Chem. Soc.*, **93**, 524 (1971).

(4) J. S. Littler and I. G. Sayce, *J. Chem. Soc.*, 2545 (1964).

(5) For recent reviews, see (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2d ed, Wiley, New York, N.Y., 1967, pp 454–525; (b) A. G. Sykes, *Adv. Inorg. Chem. Radiochem.*, **10**, 153 (1967); (c) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, N.Y., 1970; (d) J. E. Earley, *Prog. Inorg. Chem.*, **13**, 243 (1970); (e) R. G. Linck, *MTP Int. Rev. Sci., Inorg. Chem., Ser. One*, **9**, 1 (1971); (f) N. Sutin, *Chem. Brit.*, **8**, 148 (1972).

(6) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963), *Annu. Rev. Phys. Chem.*, **15**, 155 (1964), *J. Chem. Phys.*, **43**, 679 (1965).

(7) (a) M. H. Ford-Smith and N. Sutin, *J. Am. Chem. Soc.*, **83**, 1830 (1961); (b) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963); (c) H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964). (d) R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, **3**, 1091 (1964).

(8) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968); A. O. Cohen and R. A. Marcus, *ibid.*, **72**, 4249 (1968).

(9) R. Cecil, J. S. Littler, and G. Easton, *J. Chem. Soc. B*, 626 (1970).

(10) G. St. Nickolov, *Inorg. Chim. Acta*, **5**, 559 (1971).

(11) K. Reinschmiedt, J. C. Sullivan, and M. Woods, *Inorg. Chem.*, **12**, 1639 (1973).

(12) A. A. Schilt, "Analytical Applications of 1,10-Phenanthroline and Related Compounds", Pergamon Press, London, 1969, p 113.

(13) "Handbook of Chemistry and Physics", 49th ed, The Chemical Rubber Co., Cleveland, Ohio, 1968, p D-91.

(14) T. S. Lee, I. M. Kolthoff, and D. L. Leussing, *J. Am. Chem. Soc.*, **70**, 2348 (1948); **72**, 2173 (1950).

(15) H. Irving and D. H. Mellor, *J. Chem. Soc.*, 3457 (1955).

(16) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2d ed, Wiley, New York, N.Y., 1967, p 143.

(17) J. K. Yandell, D. P. Fay, and N. Sutin, *J. Am. Chem. Soc.*, **95**, 1131 (1973).

(18) P. Hambright and E. B. Fleisher, *Inorg. Chem.*, **4**, 912 (1965).

(19) C. E. Castro and H. F. Davis, *J. Am. Chem. Soc.*, **91**, 3505 (1969).

(20) A. J. Green, T. J. Kemp, J. S. Littler, and W. A. Waters, *J. Chem. Soc.*, 2722 (1964).

(21) R. P. Bell and K. Yates, *J. Chem. Soc.*, 1927 (1962).

(22) J. E. Dubois and J. Toullec, *Chem. Commun.*, 478 (1969).

(23) R. P. Bell and P. W. Smith, *J. Chem. Soc. B*, 241 (1966).

(24) P. A. Best, J. S. Littler, and W. A. Waters, *J. Chem. Soc.*, 822 (1962).

(25) R. P. Bell, "The Proton in Chemistry", 2d ed, Cornell University Press, Ithaca, N.Y., 1973, p 227.

(26) R. Cecil and J. S. Littler, *J. Chem. Soc. B*, 1420 (1968).

(27) V. D. Pokhodenko, V. A. Khizhnyi, V. G. Koshechko, and O. I. Shkrebtii, *Dokl. Akad. Nauk SSSR*, **210**, 640 (1973).

(28) C. F. Liu, N. C. Liu, and J. C. Bailer, Jr., *Inorg. Chem.*, **3**, 1086 (1964).

Studies of Intramolecular Excimer Formation in Dibenzyl Ether, Dibenzylamine, and Its Derivatives

Yung-Chyung Wang[1] and Herbert Morawetz*

Contribution from the Department of Chemistry, Polytechnic Institute of New York, Brooklyn, New York 11201. *Received October 25, 1975*

Abstract: Dibenzyl ether exhibits a normal fluorescence with a peak at 285 nm and an excimer band at 335 nm. The ratio of the emission intensities of monomer and dimer (I_M/I_D) is linear in the solution viscosity η. This is consistent with the assumption that the rate constant for conformational transitions is of the form $(A + B\eta)^{-1}$ where A characterizes the height of the energy barrier. I_M/I_D was used as a measure of the microscopic viscosity impeding excimer fluorescence of dibenzyl ether incorporated into a glassy or a rubbery polymer. Dibenzylamine exhibits both normal and excimer fluorescence when associated with Lewis acids. Poly(*N,N*-dibenzylacrylamide) exhibits only excimer emission, but monomer emission is also observed in solutions of a methyl methacrylate copolymer containing a small proportion of *N,N*-dibenzylacrylamide. Films cast from this copolymer exhibit no excimer fluorescence.

Ten years after the discovery of excimer fluorescence by Förster and Kasper,[2] it was observed by Hirayama[3] that 1,3-diphenylpropane exhibits, in addition to the fluorescence band analogous to that of toluene (with a peak at 285 nm), a broad excimer band with an emission maximum at 335 nm. The emission spectrum was found to be independent of dilution, so that the excimer must form by an intramolecular process. None of the other α,ω-diphenylalkanes behaved in this way.

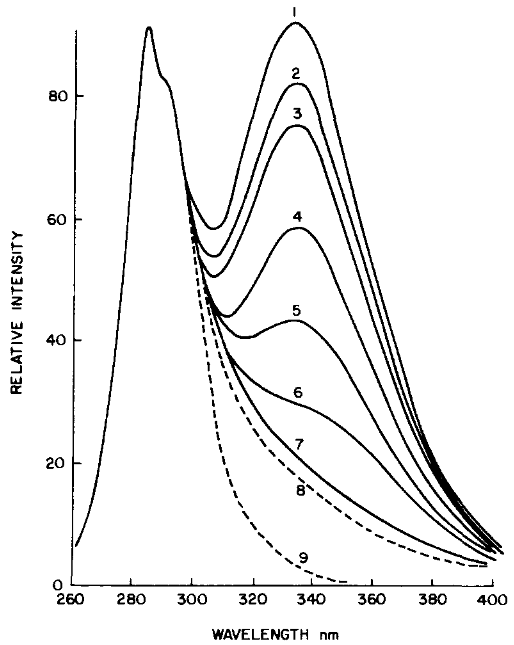


Figure 1. Fluorescence spectra of dibenzyl ether in (1) EtOH; (2) 80:20 EtOH/ethylene glycol (EG); (3) 60:40 EtOH/EG; (4) 20:80 EtOH/EG; (5) 10:80:10 EtOH/EG/glycerol (G); (6) 80:20 EG/G; (7) 60:40 EG/G; (8) poly(methyl methacrylate) film; (9) normal emission band of phenyl group (toluene).

It was concluded that the molecule in which the phenyl residues are separated by three carbon atoms can exist in a conformation in which the aromatic rings lie approximately parallel to one another at a distance close enough for excimer formation. In 1,2-diphenylethane the angle between the planes of the two rings is too large, while for $C_6H_5(CH_2)_nC_6H_5$ with $n > 3$, the necessary conformation has apparently a too low statistical probability. Excimer formation from condensed aromatic structures is more highly exothermic and in this case intramolecular excimer formation is less critically dependent on the number of methylenes separating the aromatic residues. For instance, Chandross and Dempster[4] found that both 1,3-di(α-naphthyl)propane and 1,4-di(α-naphthyl)butane exhibit excimer emission and Zachariasse[5] has observed that with $Py(CH_2)_nPy$ (Py = pyrene) excimer emission is observed over a broad range of n.

The intramolecular process which follows the excitation of one of the chromophores leading to the formation of the excimer[6,7] involves undoubtedly a conformational transition which is required to bring the two aromatic residues into proper juxtaposition. Thus, excimer formation is related to the height of the energy barrier separating the ground-state conformation and the conformation in which the aromatic residues are in their proper steric relationship. Up to now, no studies have been reported on substances in which the linkage separating the two chromophores contains heteroatoms, and it was one of the aims of the present study to obtain data on such molecules.

Rates of conformational transitions would be expected to depend on the viscosity of the medium, but the nature of this dependence is poorly understood. The current study was, therefore, also designed to illuminate this problem.

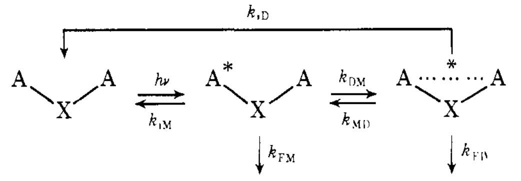
Results and Discussion

Dibenzyl Ether. Figure 1 shows the emission spectrum of dibenzyl ether in ethanol and in mixtures of ethanol, ethylene glycol, and glycerol. It may be seen that the spectrum contains an excimer band with a maximum at about 330 nm in addition to the normal emission at 285 nm. The excimer band becomes weaker as the viscosity of the medium increases. This would be expected, since a viscous medium should slow down the conformational transition required for excimer formation, and a qualitatively similar effect has been reported by Avouris et al.[7] for 1,3-di(α-naphthyl)propane in ethanol-glycerol mixtures.

The rate of conformational transition is related to the concept of the "internal viscosity" η_i of polymer chains. This was initially defined[8] as the ratio of a force applied to the ends of a molecular chain to the rate of their separation, when the chains are suspended in a medium of negligible viscosity. Originally, it was believed that η_i arises from the need to overcome potential barriers for the conformational transitions needed to expand the chain, and η_i was, therefore, believed to be an intrinsic property of the chain, independent of the nature of the solvent. More recently, experimental evidence has been obtained which indicates that η_i depends on the viscosity of the medium in which the chain molecule is dissolved, and Peterlin has suggested[9] that the internal viscosity is the sum of two terms, a viscosity-independent term arising from the height of the potential barriers to be surmounted in conformational transitions and a term proportional to the viscosity of the medium η which is due to the frictional dissipation of energy when a conformational transition takes place. Since η_i must be inversely proportional to the rate of conformational transitions, the dependence of this rate on η should be of the form $(A + B\eta)^{-1}$.

The processes occurring in a substance which may emit normal fluorescence of intensity I_M and excimer fluorescence of intensity I_D can be represented, in analogy to the scheme characterizing systems in which intermolecular excimers are formed, by[7] Scheme I. Here k_{iM} and k_{iD} are rate constants for internal quenching, k_{FM} and k_{FD} are rate constants for fluorescence from monomer and excimer, while k_{DM} and k_{MD} characterize the rates of intramolecular excimer formation and the excimer dissociation. The ratio of monomer and excimer fluorescence intensity is

Scheme I



$$\frac{I_M}{I_D} = \frac{k_{FM}(k_{FD} + k_{iD} + k_{MD})}{k_{FD}k_{DM}}$$

Of the terms in the numerator, only k_{MD} can be viscosity dependent. Thus, provided $k_{MD} \ll k_{FD} + k_{iD}$, I_M/I_D should be proportional to k_{DM}^{-1}, and since k_{DM} represents the rate constant of a conformational transition, I_M/I_D should be *linear* in the viscosity of the medium. (We found I_D/I_M in ethanol solution to be 1.8 at 0 °C and 3.1 at 40 °C. Since this ratio increases with rising temperature, we are in the region in which k_{DM} governs the excimer yield and k_{MD} can be neglected).

Our analysis differs from the assumption of Avouris et al.[7] that k_{DM} depends on viscosity in the same way as a diffusion coefficient, i.e., that it is *proportional* to $1/\eta$. If this were the case, a plot of I_M/I_D against η should pass through the origin, while our assumptions predict a finite positive intercept.

In Figure 2 we have plotted I_M/I_D against η for dibenzyl ether in ethanol-glycerol or ethylene glycol-glycerol mixtures. It may be seen that the expected linear relation is obeyed and that I_M/I_D tends to a limiting value as $\eta \rightarrow 0$. This is clearly due to the fact that in media of low viscosity the rate of conformational transition becomes insensitive to the medium,

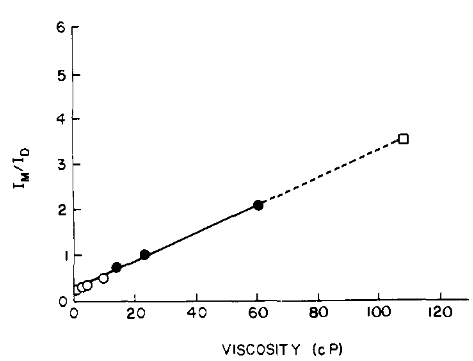


Figure 2. The ratio of intensities of the normal and excimer emission bands (I_M/I_D) of dibenzyl ether as a function of the solvent viscosity: ○, ethanol-ethylene glycol mixtures; ●, ethylene glycol-glycerol mixtures; □, I_M/I_D of dibenzyl ether in poly(methyl methacrylate) film.

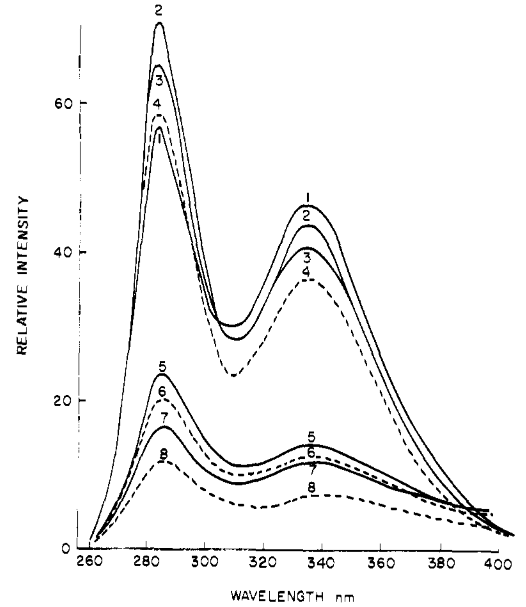


Figure 3. Fluorescence spectra of ethanol solutions containing equimolar mixtures of 1.7×10^{-3} M dibenzylamine and various Lewis acids: (1) HCl, (2) $Cl_2CHCOOH$, (3) $ClCH_2COOH$, (4) CF_3COOH, (5) CH_3COOH, (6) CH_3CH_2COOH, (7) $ZnCl_2$, (8) $MgCl_2$.

being governed by the height of the potential energy barrier. (Avouris et al.[7] reported a similar plot which was concave toward the abscissa at low η values but in their case, also, the data did not extrapolate to $I_M/I_D = 0$ for zero viscosity.)

We recorded also the fluorescence spectrum from dibenzyl ether incorporated in a poly(methyl methacrylate) film, shown as curve no. 8 on Figure 1. It may be seen that excimer fluorescence is not entirely suppressed even in this rigid medium. Plasticization of the film with 20% of glycerol triacetate produced no significant change in the emission spectrum. Assuming that I_M/I_D is here governed by a "microscopic viscosity",[11] we have estimated its value, by extrapolation of the linear plot in Figure 2, as being about 110 cP. It is well known that the mobility of small molecular species, inversely proportional to the microscopic viscosity of the medium, may be quite high even in polymeric systems with extremely high macroscopic viscosities. Nevertheless, it is remarkable that the microscopic viscosity governing the excimer formation of dibenzyl ether in a glassy polymer has this relatively low value and that it remains apparently unchanged when the film becomes rubbery on plasticization.

Intermolecular excimer fluorescence has previously been used to characterize the viscosity of biological membranes.[12] In this case, relatively large concentrations of the fluorescing substance have to be used to obtain an adequate intensity of excimer emission. The use of reagents in which excimers are formed by an intramolecular process would have the advantage that I_D/I_M is concentration independent, so that minute concentrations of the probe could be employed.

Table I. Relative Fluorescence Quantum Yield (Q) and Ratios of the Intensities of Excimer and Monomer Emission Bands (I_D/I_M) from Solutions of Equimolar Mixtures (1.7×10^{-3} M) of Dibenzylamine and Lewis Acids in Ethanol

Acid	Q	I_D/I_M
HCl	3.26	1.68
$Cl_2CHCOOH$	3.36	1.54
$ClCH_2COOH$	3.21	1.58
CF_3COOH	2.84	1.75
CH_3COOH	1.14	1.56
C_2H_5COOH	1.00	1.56
$ZnCl_2$	0.90	2.27
$MgCl_2$	0.63	2.06

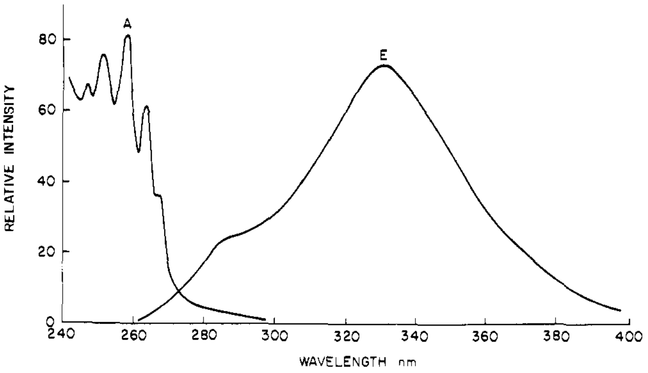


Figure 4. Absorption (A) and emission (E) spectra of N,N-dibenzyl formamide in ethanol solution.

Dibenzylamine. Solutions of dibenzylamine in ethanol exhibited no detectable fluorescence. However, a solution in a pH 7 buffer showed emission bands with peaks at 285 and 335 nm. Benzylmethylamine, used as an analogue of dibenzylamine, did not fluoresce in its basic form but had an emission with a maximum at 283 nm in its protonated form. We see then, that the emission of the dibenzylammonium ion at 285 nm is due to the monomer, while the 335-nm band may be assigned to the excimer. Tribenzylamine was found to behave in a similar way, being nonfluorescent in its basic form and emitting at 285 and 340 nm when protonated.

We carried out a study of the fluorescence behavior of dibenzylamine adducts with various Lewis acids in ethanol solution. All these adducts showed the same emission bands as shown in Figure 3, but both the relative fluorescence quantum yields and the I_D/I_M ratios varied significantly from species to species (Table I). For the carboxylic acids (except CF_3COOH), I_D/I_M had values of 1.56 ± 0.02; significantly higher ratios were observed for the dibenzylammonium chloride, trifluoroacetic acid, and particularly for dibenzylamine adducts with $MgCl_2$ and $ZnCl_2$.

Acylated Dibenzylamine. N,N-Dibenzylformamide in ethanol solution exhibited a very strong excimer band with a maximum at 330 nm, while the monomer emission at 285 nm appeared merely as a shoulder on the fluorescence spectrum (Figure 4). This behavior of an acylated dibenzylamine led us to the preparation of polymers in which excimers can be formed in individual side chains. Figure 5 shows the emission spectra of poly(N,N-dibenzylacrylamide) and of a copolymer containing only 0.9 mol % of N,N-dibenzylacrylamide residues. In the homopolymer, only the excimer emission may be seen,

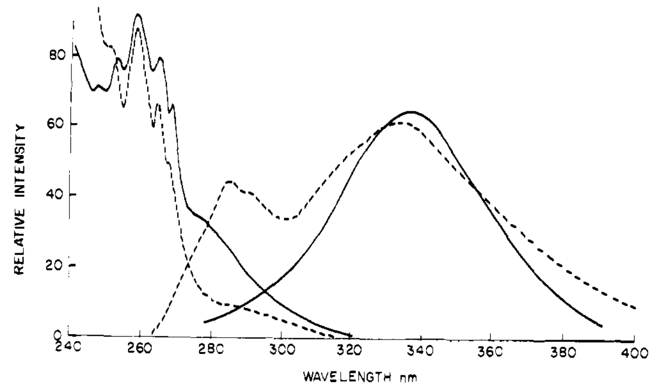


Figure 5. Absorption and emission spectra of *N*,*N*-dibenzylacrylamide homopolymer (——) and a copolymer of *N*,*N*-dibenzylacrylamide (0.9 mol %) with methyl methacrylate (- - - -) in dioxane solution. Concentration of aromatic monomer residues 1.67×10^{-3} M.

while the monomer emission is observed in the polymer in which the acylated dibenzylamine residues are well separated from one another. This indicates that excimers form in the homopolymer also by interaction of chromophores in different monomer residues. The result is remarkable because of the relatively long spacing of the aromatic rings from the backbone of the polymer chain. Also shown on Figure 5 are the absorption spectra of the homopolymer and copolymer. A component of these spectra extending beyond 280 nm is much more intense in the homopolymer than in the copolymer. We have no convincing interpretation for this hyperchromic effect.

Availability of a copolymer with widely separated sites capable of forming excimers makes it possible to utilize excimer emission for the characterization of the conformational mobility of these chain substituents in bulk samples of the polymer. A film of a methyl methacrylate copolymer containing 0.9 mol % of *N*,*N*-dibenzylacrylamide was found to exhibit only normal emission, even when plasticized with 20% of glycerol triacetate. The contrast between this result and the result obtained with dibenzyl ether in a poly(methyl methacrylate) matrix shows that conformational transitions are more severely hindered in polymer side chains than in small molecules unattached to the polymer.

Harrah[13] has observed excimer emission from polyvinylnaphthalene to be similar in dilute solution and when the polymer was dissolved in styrene which was then polymerized. He assumed that in this case the polyvinylnaphthalene was molecularly dispersed in the polystyrene matrix, so that his result would imply that the rigidity of the medium is without influence on excimer formation. However, the interpretation of Harrah's results is uncertain, since phase separation probably occurs during the polymerization of the styrene because of the well-known incompatibility of polymers with one another.[14] Such a phase separation would be difficult to observe with a low concentration of polyvinylnaphthalene in the original solution, but the fluorescence behavior would, in this case, reflect the properties of a separate polyvinylnaphthalene phase, in which excimers may form also by intermolecular chromophore interactions. It is with a view to overcoming this difficulty that we chose to study a copolymer with widely separated excimer-forming sites.

Miscellaneous Observations. A number of other diphenyl derivatives in which the chromophores are separated by three atoms were investigated in ethanol solution. Diphenylurea and dibenzoylmethane did not fluoresce. Diphenyl carbonate, diphenylacetone, and dianilinomethane exhibited only a single emission band with a maximum at 285, 390, and 345 nm, respectively. The emission from diphenyl carbonate is the typical monomer emission from phenyl residues, and the absence of excimers is believed to be due to a high energy barrier for rotation around the C–O bond of the ester group.[15] The diphenylacetone emission reported earlier by Engel[16] is believed to involve a single aromatic ring. The shift of the emission band to longer wavelength is related to an analogous shift of the absorption spectrum, which contains a peak at 285 nm. Such peaks in α-phenyl ketones have been interpreted[17] as due to an overlap of the phenyl and carbonyl orbitals. This overlap would also be expected to raise the barrier for rotation around the bond joining the benzyl and carbonyl groups and would, thus, account for the absence of excimer emission. Finally, the emission peak in dianilinomethane has a location similar to that of aniline (345 nm) and may, therefore, be assigned to the monomer. The absence of evidence for excimer fluorescence in this case may be due to facilitation of intersystem crossing by the attachment of a heteroatom to the aromatic ring, as observed by Castro and Hochstrasser[18] in the luminescence of crystals of halogenated benzene. We have recently observed that poly(*p*-aminostyrene) exhibits no excimer fluorescence, in contrast to polystyrene. This shows that nitrogens attached to the benzene residues prevent excimer formation even when they do not form part of the linkage between the chromophores.

Experimental Section

Materials. Dibenzyl ether and dibenzylamine (Pfaltz and Bauer, Inc.) were redistilled collecting the middle fraction. *sym*-Diphenylurea (mp 234–6 °C), dibenzyl ketone (mp 34–5 °C), diphenyl carbonate (mp 80–1 °C), dibenzoylmethane (mp 70–1 °C), and dianilinomethane (mp 92–92.5 °C) were obtained from Pfaltz and Bauer, Inc. and recrystallized from ethanol. Tribenzylamine (93–94 °C) was obtained from the Eastman Kodak Co. *N*,*N*-Dibenzylformamide (mp 49.5–50 °C) was a gift from Professor A. H. Lewin. *N*,*N*-Dibenzylacrylamide was prepared under Schotten–Baumann conditions (bp >200 °C at 10 Torr). The NMR spectrum showed a single aromatic peak at δ 7.17, a broad methylene group centered at δ 4.45, and quartet and triplet peaks of the vinyl group between δ 5.4 and 6.6. The ir spectrum had peaks at 1440 (tertiary amide), 1650 (carbonyl), and 1615 cm^{-1} (vinyl conjugated with carbonyl). The polymerization and copolymerization of *N*,*N*-dibenzylacrylamide was carried out in dioxane solution at 65 °C using azobis(isobutyronitrile) initiator. In preparing the copolymer, 1 g of dibenzylacrylamide and 20 g of methyl methacrylate were used, and the copolymer, obtained at 9% conversion, was found to contain 0.9 mol % of dibenzylacrylamide by uv spectral analysis. Poly(*p*-aminostyrene) was prepared from the monomer (Polysciences Inc.) using the same polymerization conditions as given above.

Preparation of Films. Thin films were prepared by casting polymer solutions in tetrahydrofuran on a quartz plate. The films were dried at room temperature for 24 h and in an oven at 50 °C for another day. Films of *N*,*N*-dibenzylacrylamide and methyl methacrylate copolymer containing 0.9 mol % of the aromatic monomer residues were prepared with or without 20 weight % glycerol triacetate plasticizer. Similarly, plasticized or unplasticized films containing 0.01 g of dibenzyl ether in 1.0 g of poly(methyl methacrylate) were prepared.

Fluorescence Measurement. A Hitachi Perkin-Elmer MPF-2A spectrophotometer was used to record emission spectra of solutions and films. No attempt was made to eliminate atmospheric oxygen during fluorescence measurements. The ratios of the quantum yields of monomer and excimer fluorescence were estimated from the integrated emission spectra.

Acknowledgment. We are grateful for financial support of this study by Grant GM-05811 of the National Institutes of Health and Grants GH-33134 and DMR 7505234 of the National Science Foundation.

References and Notes

(1) Abstracted from a Ph.D. dissertation to be submitted by Y.-C.W. to the Graduate School of the Polytechnic Institute of New York, June 1976.
(2) T. Förster and K. Kasper, *Z. Elektochem.*, **59**, 976 (1955).
(3) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).
(4) E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 3586 (1970).
(5) K. Zachariasse, private communication.

(6) W. Klöpffer, *Ber. Bunsenges. Phys. Chem.*, **74**, 693 (1970).
(7) P. Avouris, J. Kordas, and M. A. El-Bayoumi, *Chem. Phys. Lett.*, **26**, 373 (1974).
(8) W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **29**, 609 (1946).
(9) A. Peterlin, *J. Polym. Sci., Polym. Lett. Ed.*, **10**, 101 (1972).
(10) J. B. Birks, M. D. Lumb, and I. H. Munro, *Proc. R. Soc. London, Ser. A*, **280**, 289 (1964).
(11) H. Morawetz, "Macromoleculars in Solution", 2nd ed, Wiley-Interscience, 1975, pp 305-306.
(12) H. J. Pownall and L. C. Smith, *J. Am. Chem. Soc.*, **95**, 3136 (1973).
(13) L. A. Harrah, *J. Chem. Phys.*, **56**, 385 (1972).
(14) S. Krause, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C7**, 251 (1972).
(15) T. L. Brown, *Spectrochim. Acta*, **18**, 1655 (1962).
(16) P. S. Engel, *J. Am. Chem. Soc.*, **92**, 6074 (1970).
(17) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).
(18) G. Castro and R. N. Hochstrasser, *J. Chem. Phys.*, **45**, 4352 (1966).

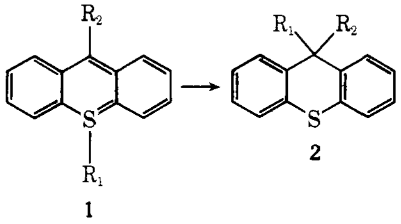
Rearrangement Kinetics of 10-Aryl-10-thiaanthracenes

Fumio Ogura, W. Douglas Hounshell, Cynthia A. Maryanoff, W. Jürgen Richter, and Kurt Mislow*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received October 2, 1975*

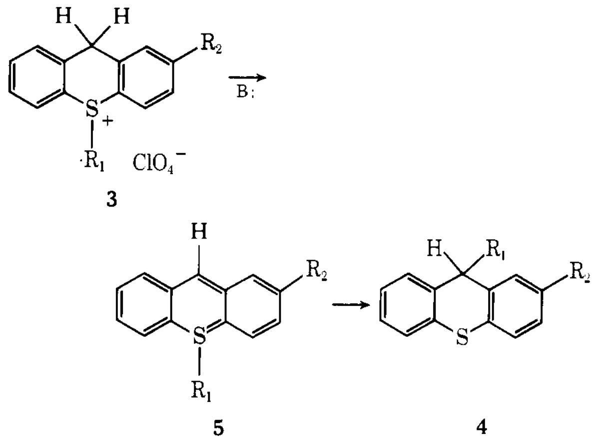
Abstract: A variety of 10-arylthioxanthenium salts have been deprotonated to yield 10-aryl-10-thiaanthracenes, whose rates of rearrangement to the corresponding 9-substituted thioxanthenes have been studied. The ylidic character of the intermediate thiaanthracenes is manifested by the upfield shift of the 9-proton, by solvent and substituent effects on the rates of rearrangement, and by generation of a stable thiaanthracene, the anion of 10-*p*-hydroxyphenyl-10-thiaanthracene. The small $\Delta S^{\ddagger}$ for the rearrangements of 2-chloro-10-(2,5-xylyl)-10-thiaanthracene and 10-(*p*-anisyl)-10-thiaanthracene is consistent with the intramolecularity of the reaction.

All previously known thiaanthracenes [**1**] have been shown to be "notably unstable compounds which readily undergo rearrangement to thioxanthenes[**2**] and which can only be observed as transient reaction intermediates." [1] The present study was initiated with the principal aim of determining the effects of substitution pattern in **1** on the rate of rearrangement to **2**.



Results and Discussion

Rearrangement Reactions. Deprotonation of thioxanthenium salts (type **3**) had previously been found to yield the corresponding 9-substituted thioxanthenes (type **4**),[1,2] and it had been shown[1] that this reaction proceeds by the rearrangement of an intermediate thiaanthracene (type **5**) (eq 1). 10-Arylthioxanthenium salts **3a–i** were prepared by standard methods[1,3] and were deprotonated using dimsyl anion[4] in dimethyl sulfoxide (Me$_2$SO). The rearrangement reaction of the deprotonated species was monitored using ^{1}H NMR and visible spectroscopy (see below). All the reactions initially produced an intense red color, due to a transition near 500 nm which is characteristic of thiabenzenes in general.[1] The ^{1}H NMR spectra of these red solutions exhibited a resonance attributable to the 9-proton of **5**, typically at δ 5.7.[5] The upfield shift of this proton relative to an aromatic system is in agreement with that observed for other thiabenzenes and thus with the ylidic character of this ring system.[1] The red color was discharged in synchrony with the disappearance of this resonance, and a resonance attributable to the 9-proton of **4** (δ ~5.3-5.7) simultaneously became more intense. Yields in the rearrangement reaction are listed in Table I.



(1)

a, R$_1$ = phenyl; R$_2$ = H
b, R$_1$ = 2,5-xylyl; R$_2$ = H
c, R$_1$ = phenyl; R$_2$ = Cl
d, R$_1$ = 2,5-xylyl; R$_2$ = Cl
e, R$_1$ = *p*-anisyl; R$_2$ = H
f, R$_1$ = 2,4,6-trimethoxyphenyl; R$_2$ = H
g, R$_1$ = 2,4-dimethoxyphenyl; R$_2$ = H
h, R$_1$ = 2,4-dimethoxyphenyl; R$_2$ = methoxy
i, R$_1$ = 2,4-dimethoxyphenyl; R$_2$ = Cl

Rate Determinations. The visible spectra of thiaanthracenes (**5**) all feature absorptions near 500 and 385 nm. In order to put the stability of thiaanthracenes on a quantitative basis, the rate of decomposition (rearrangement) in Me$_2$SO was measured by monitoring the absorbance (A) at the long wavelength peak as a function of time, with the implicit assumption that the rate of deprotonation is much greater than the rate of rearrangement. Plots of $-\ln A$ vs. time were linear over at least 2 half-lives ($\tau_{1/2}$)[6] and there appeared to be no dependence of the rate constant on initial concentration, in harmony with first-order kinetics. Rate constants (k) were determined by least-squares analysis of the data. Results are listed in Table II.

For one particular run, monitoring the maximum at 385 nm for **5d** yielded the same rate constant over the first half-life

Mislow et al. / Rearrangement Kinetics of 10-Aryl-10-thiaanthracenes