point, therefore, that the model appears both to be selfconsistent and to conform to experiment.

As a further and independent test of the derived value of $K_{\rm AC}$, proton NMR measurements⁴⁷ (description of the method is given in ref 48) were performed for chloroform with solutions of HD with DBEHA; the results gave K_{AC} of 2.32 dm³ mol⁻¹. Further, the relation first derived by Gil-Av and Herling⁴⁹ and Muhs and Weiss,⁵⁰ eq 20, indi-

$$K^{\circ}_{\mathsf{R}(\mathsf{M})} = K^{\circ}_{\mathsf{R}(\mathsf{B})} + K^{\circ}_{\mathsf{R}(\mathsf{B})} K_{\mathsf{AC}} \phi_{\mathsf{C}} / \bar{V}_{\mathsf{C}}$$
(20)

cates that plots of $K^{\circ}_{\mathrm{R}(\mathrm{M})}$ against ϕ_{C} will be linear and in addition that an apparent K_{AC} can be deduced from the resultant slope/intercept quotient. The linear leastsquares regression correlation coefficient r for the first nine data points ($\phi_{\rm C} = 0-0.508$) of chloroform with HD/DBE-HA at 30 °C (Figure 2b) is 0.9999, the extrapolated $K^{\circ}_{R(B)}$ is 256.5 (258.0 experimental), and the resultant K_{AC} is 2.91 dm³ mol⁻¹. The correlation coefficient across the entire range $\phi_{\rm C} = 0-1$ in fact diminishes only to 0.9989, for which $K_{\rm AC}$ is 2.31 dm³ mol⁻¹. There is hence modest agreement between the complexation constants which arise from application of the more traditional forms of data reduction in NMR and GLC, but considerable disparity between these and that utilized above with eq 15-17. Rationalization of this well-documented and discrepant feature of the study of weak intermolecular complexation has previously been discussed at length,^{1,7} and we hope to pursue this with further appropriate experiment⁴⁷ at a later stage.

(48) R. Foster in "Molecular Complexes", Vol. 2, R. Foster, Ed., Paul Elek (Scientific Books) Ltd., London, 1974, Chapter 3.
(49) E. Gil-Av and J. Herling, J. Phys. Chem., 66, 1208 (1962).
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We must, in any event and in view of the negative equilibrium constants provided in Table VII, regard the conventional approach embodied in eq 11 and 13 with some suspicion, although we of course do not regard its failure in this instance as conclusive evidence of the inappropriateness in general of such models for nonelectrolyte solutions. Further, and in view of the evidence obtained elsewhere for self-association of the amide,²⁶ we recognize that these latter relations should accordingly be extended to include dimerization of one or the other of the solvent components. We assert by way of conclusion, however, that, whatever subsequent forms of eq 8-14 arise, each must, in view of the evidence provided here, yield one or another alternatives of eq 1 and 15 at least by approximation in order to conform with experiment. These must, presumably, and in addition to complexation with concomitant and competitive additive self-association, account for the several hundred solvent systems previously reported²⁻⁷ to conform to eq 1, which at present comprise combinations of alkanes, polysiloxanes, polyfunctional aromatic hydrocarbons, liquid crystals, alcohols, glycols, esters, ethers, and other Lewis acids and bases which purportedly support hydrogen bonding and charge transfer. The matter is one which invites further and comprehensive study and evaluation.

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Supplementary Material Available: Appendix I listing the partition coefficients of all solutes at various temperatures with each pure phase and with 13 blends each of HD and of OD with DBEHA (6 pages). Ordering information is given on any current masthead page.

Nature of the Low-Temperature Emission from 9-Nitroanthracene

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A luminescence study of 9-nitroanthracene indicates that its emission from EPA glasses at 77 K is not molecular phosphorescence but anthraquinone phosphorescence formed via an efficient photochemical reaction. The quantum yield for the reaction at 77 K in ethyl alcohol is estimated to be 0.7. Evidence that 9-nitroanthracene does not phosphoresce was corroborated by forming a 1:1 EDA complex with boron trichloride, which results in a stable complex that inhibits its molecular photodecomposition.

Introduction

In previous studies from this laboratory we have reported on the phosphorescence behavior of nitronaphthalenes¹ and the lack of phosphorescence from nitrobenzene.² In the latter case this was attributed to a short lived $3n\pi^*$ state. In the case of 9-nitroanthracene where the lowest triplet is $\pi\pi^*$, phosphorescence has been reported with a 0-0 band in the vicinity of 20 000 cm⁻¹.^{3,4} In contrast, the $S_0 \rightarrow T_1$ transition of 9-nitroanthracene (9-NA), studied by oxygen perturbation techniques, appears at 14630 cm^{-1,5} which is more compatible with the triplet level of anthracene (14700 cm⁻¹) and its derivatives.^{6,7} We were particularly interested in the fact that the emission and absorption behavior of anthracene and its derivatives are similar, but somewhat inconsistent with the phosphorescence reported for 9-NA. We have undertaken an investigation of the luminescence behavior of this molecule with the additional feature that the formation of an EDA complex was used to assist in elucidating

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Figure 1. Effect of low-temperature (77 K) 366-nm irradiation on the emission from 7.29×10^{-4} M 9-nitroanthracene in ethyl alcohol: (1) initial emission spectrum; (2) after 14-min photolysis; (3) after 30-min photolysis.

the nature of the emission at 77 K. The effect of solvent, e.g., methylcyclohexane vs. ethyl alcohol, on the luminescence was also studied.

Experimental Section

Materials. 9-NA and anthraquinone were recrystallized twice from ethyl alcohol. CP grade boron trichloride, obtained from Matheson Coleman and Bell, was used as received. Spectrograde methylcyclohexane and ethyl alcohol were used as received.

Apparatus and Procedures. Absorption spectra were obtained with a Cary Model 14. The phosphorescence procedures were similar to those employed in an earlier study.⁸ Phosphorescence quantum yield results at 77 K were obtained with reference to benzophenone in methylcyclohexane, for which $\phi_p = 0.50$ with excitation at 366 nm. The photochemical disappearance of 9-NA in ethyl alcohol was followed by its absorbance at 366 nm where its molar extinction coefficient is 4950 M⁻¹ cm⁻¹, and where its optical density is not affected by the absorbance of photoproducts such as anthraquinone ($\epsilon_{366} = 217 \text{ M}^{-1} \text{ cm}^{-1}$) and anthrone ($\epsilon_{366} = 48 \text{ M}^{-1} \text{ cm}^{-1}$).

Results

The 366-nm irradiation of 7.29×10^{-4} M 9-NA in ethvl alcohol at 77 K results in phosphorescence emission, whose intensity increases with irradiation. Figure 1 shows the emission spectrum, which has some vibrational structure. It is evident that this phosphorescence could not originate from 9-NA. In an attempt to further elucidate the nature of this photochemical event we performed the photolysis at 77 K in ethyl alcohol. Curve 1 in Figure 2 shows the emission spectrum from 7.29 \times 10⁻⁴ M 9-NA when photolyzed for 30 min at 77 K with an unfiltered high-pressure mercury lamp. Curve 2 in Figure 2 shows the phosphorescence of 4.89×10^{-4} M anthraquinone when excited at 366 nm. The marked similarity of the emission spectrum from anthraquinone and 9-NA is very striking. In order to provide a comparison to the known photoproducts of 9-NA observed at room temperature,⁹ we give the phosphorescence spectra of 4.89×10^{-4} M anthrone in ethyl alcohol, excited at 366 nm, and an approximately equal weighted mixture of anthrone and anthraquinone as curves 3 and 4 in Figure 2, respectively. These spectra clearly indicate that the phosphorescence emission from 9-NA is primarily due to anthraquinone.



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Figure 2. Phosphorescence spectra in ethyl alcohol (77 K): (1) 7.29 \times 10⁻⁴ M 9-nitroanthracene after 30-min irradiation with unfiltered light; (2) 4.42 \times 10⁻⁴ M anthraquinone (366-nm excitation); (3) 4.89 \times 10⁻⁴ M anthrone (366-nm excitation); (4) approximately equal mixture of anthrone and antrhaquinone (366-nm excitation).



Figure 3. Phosphorescence spectra showing a comparison of room temperature vs. 77 K photolysis (unfiltered lamp) of 7.29×10^{-4} M 9-nitroanthracene in ethyl alcohol: (1) before extended photolysis; (2) after 30-min photolysis at room temperature; (3) after 30-min photolysis at 77 K.

In the course of this investigation it was also observed that the phosphorescence spectrum exhibited more vibrational structure when irradiations were performed at 77 K, rather than at room temperature. An indication of this temperature effect is shown in Figure 3, where spectrum 1 is the weak emission from 9-NA in ethyl alcohol before extended photolysis. Spectrum 2 shows the phosphorescence spectrum after 30 min of photolysis at room temperature while spectrum 3 in Figure 3 shows a distinct vibrational pattern, when photolysis with an unfiltered lamp was performed for 30 min at 77 K. Once again the anthraquinone phosphorescence is clearly evident. It was also noted that the induced photochemistry is more efficient in ethyl alcohol than it is in a nonpolar solvent such as methylcyclohexane. The results in Figure 3 show enhanced photochemical production of anthraquinone at 77 K relative to the room temperature photolysis. Further and more noticeable is that the phosphorescence emission, if it did emanate from 9-NA, would indicate a considerably higher triplet energy than that of anthracene derivatives, which have triplet state energies of approximately 14700 cm⁻¹.^{6,7}

The disappearance of 9-NA with 366-nm excitation was monitored by using UV absorption, which avoids interLow-Temperature Emission from 9-Nitroanthracene



Figure 4. Effect of boron trichloride on the phosphorescence emission from 9-nitroanthracene in methylcyclohexane (366-nm excitation; 77 K): (A) 3.45×10^{-4} M 9-nitroanthracene: (1) no boron trichloride; (2) 3.64×10^{-4} M BCl₃; (3) 1.82×10^{-3} M BCl₃. (B) 6.97×10^{-4} 9-nitroanthracene: (1) no boron trichloride; (2) 4.91×10^{-3} M BCl₃; (3) solution 2 with 1 mL of ethyl alcohol added to destroy the complex.

ference from secondary products. Specifically, the primary photoproduct, anthraquinone, does not absorb strongly, i.e., ϵ_{366} for anthraquinone is 217 M⁻¹ cm⁻¹ while 9-NA has $\epsilon_{366} = 4950$ M⁻¹ cm⁻¹. Anthrone, which also arises as a photoproduct, has $\epsilon_{366} = 48$ and constitutes a negligible contribution to the absorption spectrum of this system at 366 nm during photolysis. In order to determine the quantum yield for the photodecomposition of 9-NA in ethyl alcohol with 366 nm at 77 K, we measured the optical density at room temperature before and after 30 min of irradiation. By determining the number of 9-NA molecules converted and estimating the intensity by using phosphorescence standards we estimated that $\Phi \approx 0.7$; however, it is difficult to exclude the possibility that this value may be near unity.

With the aim of further pursuing and confirming that the low-temperature emission from 9-NA is due to anthraquinone, we have been able to generate the 1:1 EDA complex of 9-NA with boron trichloride in methylcyclohexane. The advantage in forming this complex is that 9-NA is stabilized. When 3.45×10^{-4} M 9-NA in methylcyclohexane is irradiated at 77 K, the weak emission attributed to the formation of anthraquinone can be made to disappear upon addition of boron trichloride. This is clearly seen in Figure 4A, where addition of 1.82×10^{-3} M boron trichloride has complexed 9-NA, thereby removing any evidence of phosphorescence. In Figure 4B we see that the EDA formation is reversed upon addition of ethyl alcohol and that return of free 9-NA leads to increased production of anthraquinone. Spectrum 2 in Figure 4B shows no phosphorescence arising from the complex, while spectrum 3 shows that addition of alcohol destroys the complex leading to growth of anthraquinone.

Discussion

It is evident from the results given above that 9-NA, counter to published reports,^{3,4} does not phosphoresce. Further, the phosphorescence spectrum previously attributed to this molecule is really that of anthraquinone, which arises from a very efficient photochemical process at 77 K with a quantum yield probably approaching unity. Anthraquinone, anthrone, and 10,10'-bianthrone are all known photoproducts from 9-NA.⁹ The photochemical process is significantly faster at 77 K and is enhanced in ethyl alcohol relative to methylcyclohexane. The photoreactivity of anthraquinone in alcohol via hydrogen abstraction is known to be an efficient process.¹⁰ Another effect which is induced by low temperatures is the removal of diffusion, which inhibits bimolecular events such as radical-radical recombinations, i.e., at low-temperature unimolecular products, such as anthraquinone, dominate and this is confirmed in Figure 3, spectrum 3, where the low-temperature photolysis gives a much cleaner anthraquinone phosphorescence spectrum. Room temperature photolysis gives rise to additional photoproducts including bimolecular ones such as 10,10'-bianthrone, which leads to a phosphorescence spectrum that exhibits less vibrational detail.

The 1:1 EDA complex formed between 9-NA and boron trichloride, which is being reported for the first time, provides an interesting situation where a photochemically active molecule has been stabilized by complexation. The UV spectrum of the complex exhibits no new bands, however, it can be isolated as a green solid. The phosphorescence behavior of EDA complexes of some aromatic ketones with boron trichloride has also been described.⁸

In a recent report it was shown that the low-temperature triplet-triplet absorption of 9-NA appears in the region 410-460 nm and that the triplet lifetime at 77 K in EPA is 17.7 ms.¹¹ On the basis of the present study it is tempting to suggest that, in view of the very efficient photodecomposition of 9-NA, what they may have measured is the T-T absorption and lifetime of anthraquinone and not that of 9-NA.

In summary 9-NA does not phosphoresce. The lowtemperature photochemistry of this molecule is much more efficient and specific at 77 K than it is at room temperature when diffusion is prevented.

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