

# Photochemistry of Aza Aromatics. Identification of the Reactive Intermediate in the Photoreduction of Acridine

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**Abstract:** The photoreduction of acridine in the presence of several hydrogen atom donors has been investigated. A study of the effect of hydrogen donor concentration on fluorescence and reduction efficiencies indicates that the fluorescent singlet of acridine is not the reactive state. Flash spectroscopic studies and sensitization experiments together with consideration of previous findings indicate that the acridine triplet is not the major reactant; on the basis of kinetic evidence it is suggested that the primary reactant is a low-lying  $n,\pi^*$  singlet. Evidently the  $n,\pi^*$  singlet lies lower in energy than the fluorescent  $\pi,\pi^*$  singlet; population of the  $n,\pi^*$  singlet may be reversible in certain cases but equilibrium is not attained. The lifetime of the  $^1n,\pi^*$  state of acridine in 2-propanol is estimated to be *ca.*  $5 \times 10^{-9}$  sec. Experiments with deuterated toluene and *p*-methylanisole show small isotope effects for reaction with excited acridine.

Several nitrogen heteroaromatic compounds undergo addition, reduction, and substitution reactions upon photolysis in the presence of suitable hydrogen-atom donors.<sup>2-6</sup> Although attractive mechanistic analogies can be drawn between these reactions and reactions of excited carbonyl compounds, the identity of the reactive intermediate has not been firmly established for most of the reactions involving the nitrogen compounds. Similarities to the carbonyl photoreactions suggest an initial hydrogen abstraction by an electron-deficient nitrogen with considerable radical character;  $n,\pi^*$  excited states are obvious candidates for such reactions. However, for most nitrogen compounds  $n,\pi^*$  states are not spectroscopically detectable and there is considerable evidence that phosphorescence and fluorescence originate from  $\pi,\pi^*$  states similar to those of the parent hydrocarbon.<sup>7</sup>

A nitrogen compound whose photochemistry has been particularly well studied is acridine.<sup>8-16</sup> The photochemical behavior of acridine is in many ways typical of the larger aza aromatics. Irradiation of acridine in the presence of hydrocarbons, alcohols, or other hydrogen atom donors leads to reduction of acridine to diacridan, various 9-substituted acridans, and 9,10-dihydroacridine. The acridanyl radical,

formed by initial hydrogen-atom abstraction, has been identified as the key intermediate in the reaction,<sup>17</sup> although there is some evidence that a "molecular mechanism" (involving formation of an acridan by a process in which the acridanyl radical cannot be detected) may account for a small portion of the reaction.<sup>18</sup> In contrast to photoreductions with carbonyl compounds in which the triplet state is considerably more reactive than the singlet,<sup>19</sup> for acridine a singlet state is the reactive species toward most hydrogen donors.<sup>12,14-16,18</sup> However, minor involvement of a higher triplet has been indicated in certain cases.<sup>18,20</sup>

As with other nitrogen heterocycles, there is strong evidence that the fluorescent singlet is a  $\pi,\pi^*$  singlet.<sup>15,21</sup> Absorption and fluorescence spectra of acridine are similar to those of anthracene. Excited-state  $pK_A$  measurements indicate that both the fluorescent singlet and the triplet of acridine are stronger bases than the ground state;<sup>22,23</sup> in the fluorescent singlet in particular, a large increase in electron density on nitrogen is indicated. Although acridine fluorescence is similar to that of anthracene and calculated rates of fluorescence are nearly the same for the two compounds,<sup>24</sup> acridine's fluorescence shows a solvent dependence not observed for the hydrocarbon. Acridine is nonfluorescent in benzene, hexane, and other hydrocarbons;<sup>25</sup> however it fluoresces strongly in alcohols. Addition of a small amount of alcohol or water to hydrocarbon solutions of acridine facilitates the appearance of fluorescence. A variety of explanations have been suggested for the hydroxylic solvent enhancement of fluorescence of N heterocycles including diminished rates of singlet-

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- (19) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2503 (1967).
- (20) Earlier experiments suggesting involvement of the triplet in photoreduction of acridine in 2-propanol<sup>13</sup> have been shown to involve chemical sensitization processes.<sup>14-16</sup>
- (21) S. J. Ladner and R. S. Becker, *J. Phys. Chem.*, **67**, 2481 (1963).
- (22) A. Weller, *Z. Electrochem.*, **61**, 956 (1957); *Progr. Reaction Kinet.*, **1**, 189 (1961).
- (23) G. Jackson and G. Porter, *Proc. Roy. Soc., Ser. A*, **260**, 13 (1961).
- (24) I. B. Beriman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, pp 121-123.
- (25) Acridine evidently fluoresces at low temperatures in non-hydroxylic glasses.<sup>21</sup>

triplet intersystem crossing<sup>26,27</sup> as well as inversion of  $^1n,\pi^*$  and  $^1\pi,\pi^*$  levels.<sup>28</sup> While photoreduction from a singlet state is observed for acridine in solvents where acridine fluoresces strongly as well as in hydrocarbons where it is nonfluorescent, it has been found that quenching of fluorescence by biacetyl<sup>18</sup> or iodide<sup>15</sup> causes concurrent quenching of photoreduction.

In the present paper we report results of a study of the effects of several reductants on the fluorescence and photoreduction of acridine. Our experiments demonstrate that the fluorescent  $\pi,\pi^*$  singlet of acridine is *not* the reactive species; our results suggest that a lower lying  $n,\pi^*$  singlet is the likely reactant in the photoreduction.

### Experimental Section

**Materials.** Benzene (James Hinton, 99.99%, zone refined) and 2-propanol (Matheson Coleman and Bell, chromatogquality) were used as received. *p*-Methylanisole (Eastman) and anisole (Eastman) were passed through alumina columns, dried over magnesium sulfate, and vacuum distilled. *tert*-Butyl alcohol (Eastman) was purified by crystallization, followed by treatment with metallic sodium and distillation. Toluene (B and A Reagent Grade) was stirred over concentrated sulfuric acid for 2 hr at 25–30°, washed with water and sodium carbonate solution, dried over magnesium sulfate, and then distilled from  $P_2O_5$ . Perdeuteriotoluene was purchased from Stohler Isotope Chemicals and used as received. Lithium aluminum deuteride was purchased from Alfa Inorganic Chemicals. Triphenylene (Aldrich) was crystallized twice from ethanol; its purity was determined by vpc to be greater than 99%. Michler's ketone (4,4'-bis(dimethylamino)benzophenone) (K and K) was recrystallized from ethanol, decolorized with carbon, chromatographed over alumina, and recrystallized several times from ethanol until colorless crystals were obtained. Acridine (Aldrich) was crystallized several times from ethanol after decolorizing with carbon. The semipurified acridine was zone refined through 78 cycles; *ca.* 1 g from the total of 15 g of zone-refined material was retained. Vpc analysis indicated purity of the selected acridine to be greater than 99.9%.

***p*-Methylanisole- $d_3$ .** Anisic acid (Eastman) was dissolved in 1:1 ether-ethanol and treated with an ethereal solution of diazomethane<sup>29</sup> to yield methyl (*p*-methoxy) benzoate. Reduction of the ester with lithium aluminum deuteride<sup>30</sup> gave the corresponding deuterated benzyl alcohol in greater than 90% yield. The deuterated *p*-methoxybenzyl alcohol was converted to the chloride by gentle reflux with thionyl chloride. Treatment of the chloride with lithium aluminum deuteride<sup>30</sup> led to the product in greater than 90% yield. Structures of the intermediates and product were confirmed by melting point and by nmr and ir spectra. Vpc analysis indicated the *p*-methylanisole- $d_3$  to be *ca.* 99% pure.

**Photolysis Studies.** Solutions of acridine (*ca.*  $1\text{--}1.5 \times 10^{-3}$  M) in various solvents for direct irradiation were degassed by 3–4 cycles of the freeze-pump-thaw method and sealed in Pyrex ampoules. The samples were irradiated in a merry-go-round apparatus<sup>31</sup> with the 366-nm band of a medium-pressure mercury lamp. Ferrioxalate actinometry was used to monitor light intensity. As the photoproducts of acridine do not absorb near the long-wavelength  $\lambda_{\text{max}}$  of acridine, the reaction was easily followed by monitoring decrease of acridine absorption at 358 nm.

Samples for sensitized reaction were prepared with Michler's ketone ( $4 \times 10^{-2}$  M) and acridine ( $1 \times 10^{-3}$  M) such that more than 99% of the light at 366 nm was absorbed by the ketone. These were degassed and sealed as described above. Analysis was by vpc. Degassed samples of acridine ( $4.9 \times 10^{-4}$  M) and triphenylene ( $3.9 \times 10^{-3}$  M) in toluene were irradiated with a super-high-pressure mercury lamp, selecting the 300-nm region through a high-intensity Bausch and Lomb monochromator. Under these condi-

tions the triphenylene absorbed *ca.* 96% of the light. These solutions could be analyzed by monitoring change in acridine absorption at 358 nm.

**Spectra.** Uv absorption spectra were recorded using either a Unicam or a Cary Model 14 spectrophotometer. Fluorescence spectra were recorded on either an Aminco-Bowman spectrophotometer or a Hitachi Perkin-Elmer MPF-2A fluorescence spectrophotometer. Quantum yields were determined from relative intensities and comparison with the known quantum yield of acridine fluorescence in ethanol of 0.03.<sup>32</sup> Optical densities of the samples for fluorescence were less than 1 at  $\lambda_{\text{max}}$ . Similar results were obtained for degassed samples and nondegassed samples. Samples for flash photolysis were degassed by several cycles of the freeze-pump-thaw method and sealed in cylindrical quartz cells (25-mm path).

### Results

**Direct Irradiation.** The photoreduction of acridine was investigated by spectrophotometrically measuring the decrease of acridine absorption at its  $\lambda_{\text{max}}$ . Table I

**Table I.** Quantum Efficiencies for Acridine Photoreduction in Various Solvents<sup>a</sup>

| Solvent                    | $\phi_{-A}$       |
|----------------------------|-------------------|
| Benzene                    | 0.00              |
| Toluene                    | 0.05 <sup>b</sup> |
| <i>p</i> -Methylanisole    | 0.12              |
| Anisole                    | <0.01             |
| 2-Propanol                 | 0.10 <sup>b</sup> |
| <i>tert</i> -Butyl alcohol | <0.01             |

<sup>a</sup> Degassed solutions, (acridine)  $\approx 1.5 \times 10^{-3}$  M, wavelength = 366 nm. <sup>b</sup> These values are slightly lower than those previously reported: A. Kellman, *Bull. Soc. Chim. Belg.*, 71, 811 (1962).

compares quantum efficiencies for disappearance of acridine in several different solvents. As the data indicate, acridine is not readily reduced in benzene, *tert*-butyl alcohol, or anisole, solvents which lack readily donatable hydrogen atoms. Therefore the solvents listed in Table I can be considered as three pairs, each pair comprising one reactive hydrogen donor and one unreactive, but having otherwise similar properties. The general procedure followed in these studies was to investigate the effect of varying the concentration of reactive hydrogen donor while keeping other solvent properties the same. Both fluorescence and reduction efficiencies were measured for the various systems studied.

Although acridine is very nearly nonfluorescent in benzene, addition of a small amount of *tert*-butyl alcohol causes the appearance of strong fluorescence. It was found convenient to use 4–20% *tert*-butyl alcohol solutions for monitoring both fluorescence and reduction. As Table I indicates, *p*-methylanisole (PMA) was found to be a good reducing agent for excited acridine. Figure 1 shows a plot of the reciprocal of the reduction quantum yield,  $(\phi_{-A})^{-1}$ , *vs.*  $(\text{PMA})^{-1}$  in a 20% *tert*-butyl alcohol-benzene-PMA solution. The plot is linear (correlation coefficient 0.99), as anticipated, for the high concentration range. Fluorescence efficiencies for acridine in the same system were also investigated as a function of (PMA). Figure 2 compares the fluorescence spectrum of acridine in the absence of PMA with that obtained at very high concentration. Although the shape of the spectrum is changed (perhaps indicating a new fluorescing species,

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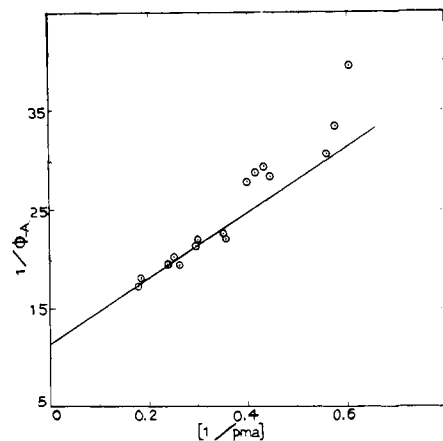


Figure 1. Photoreduction of acridine in 20% (volume) *tert*-butyl alcohol-benzene as a function of *p*-methylanisole concentration.

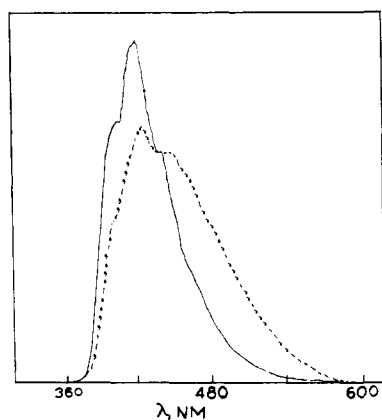


Figure 2. Fluorescence spectra of acridine in 20% (volume) *tert*-butyl alcohol in benzene (solid line) and in 20% (volume) *tert*-butyl alcohol in *p*-methylanisole (dashed line).

*vide infra*), very little quenching was observed. The small, but real quenching occurred at low (PMA) and leveled off so that increase in (PMA) at higher concentrations produced little decrease in fluorescence. Figure 3 shows a plot of  $(\varphi_t^0/\varphi_t)$  vs. (PMA). The maximum value of  $\varphi_t^0/\varphi_t$  was 1.5 obtained in 80% PMA-20% *tert*-butyl alcohol. In contrast to the results obtained with PMA, anisole neither quenched acridine fluorescence nor altered its fluorescence spectrum.

Reduction of excited acridine by PMA occurred readily in the absence of *tert*-butyl alcohol where no fluorescence could be detected. Figure 4 gives a plot of  $(\varphi_{-A})^{-1}$  vs.  $(\text{PMA})^{-1}$  for PMA-benzene solutions. Reduction of acridine by *p*-methylanisole-*d*<sub>3</sub> was also investigated. As data in Table II indicate, there was

Table II. Isotope Effect on Acridine Photoreduction

| H (D) donor                     | $\varphi_{-A}$ | $\varphi_{-A(\text{H})}/\varphi_{-A(\text{D})}$ |
|---------------------------------|----------------|---|
| PMA <sup>a</sup>                | 0.042          | 1.17  |
| PMA- <i>d</i> <sup>a</sup>      | 0.036          |   |
| Toluene <sup>b</sup>            | 0.049          | 1.92  |
| Perdeuteriotoluene <sup>b</sup> | 0.025          |   |

<sup>a</sup> 3 M PMA (or PMA-*d*) in 20% *tert*-butyl alcohol (vol) benzene.  
<sup>b</sup>  $1.5 \times 10^{-3}$  M acridine dissolved in pure toluene (perdeuteriotoluene).

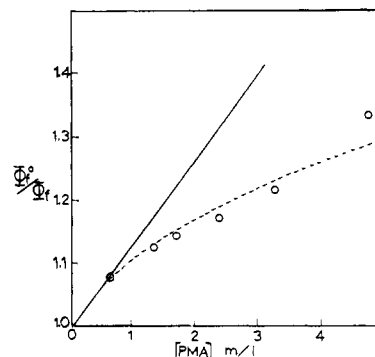


Figure 3. Acridine fluorescence yield as a function of *p*-methylanisole concentration in 20% *tert*-butyl alcohol-benzene solution.

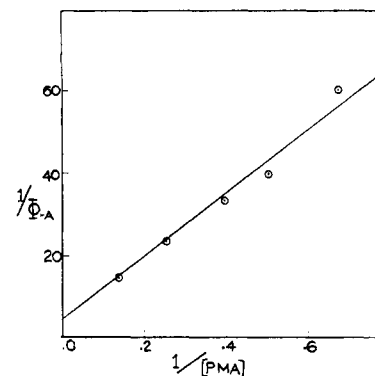


Figure 4. Photoreduction of acridine in benzene-*p*-methylanisole solutions as a function of *p*-methylanisole concentration.

a very small isotope effect under the conditions used in a limited number of investigations.

The system toluene-benzene-4% *tert*-butyl alcohol was also investigated. Gradual replacement of benzene with toluene led to an increase in the efficiency of photoreduction of acridine. The intercept/slope ratio is given in Table III along with summarized data for other

Table III. Effect of Hydrogen Donor Concentration on  $\varphi_{-A}$

| Hydrogen donor          | % <i>tert</i> -butyl alcohol <sup>a</sup> | Data from high-concentration region of plot of $(\varphi_{-A})^{-1}$ vs. (hydrogen donor) <sup>-1</sup> |           |                 |
|-------------------------|---|---|-----------|-----------------|
|                         |   | Slope   | Intercept | Intercept/slope |
| PMA <sup>b</sup>        | 20  | 30  | 12        | 0.40            |
| PMA <sup>c</sup>        | 20  | 43.5  | 11.6      | 0.27            |
| PMA <sup>c</sup>        |   | 67  | 4         | 0.06            |
| Toluene <sup>d</sup>    | 4   | 290   | 4         | 0.013           |
| Toluene <sup>d</sup>    |   | 190   | 2         | 0.01            |
| 2-Propanol <sup>c</sup> | Variable                                  | 70.9  | 9.6       | 0.135           |

<sup>a</sup> For toluene and PMA the remainder of the solvent was benzene.  
<sup>b</sup> Values obtained graphically using only data from (PMA) > 2.8 M.  
<sup>c</sup> Values obtained from a least-squares determination using high-concentration data. <sup>d</sup> Limited confidence should be placed in these intercept/slope values due to the sensitivity of the low values of the intercept.

systems. Replacement of benzene with toluene did not change the shape of the fluorescence spectrum of acridine; in fact toluene produced virtually no quenching of acridine fluorescence ( $\varphi_t^0/\varphi_t = 1.04$  for 5.7 M toluene). There is a modest isotope effect

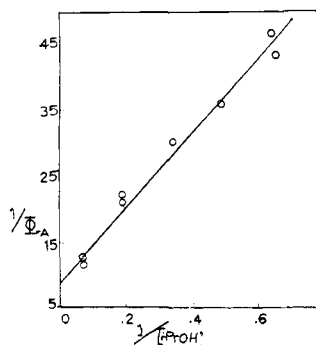


Figure 5. Photoreduction of acridine in 2-propanol-*tert*-butyl alcohol solutions as a function of 2-propanol concentration.

observed on the reduction efficiency upon replacing toluene with perdeuteriotoluene (Table II).

Photoreduction of acridine in 2-propanol has been investigated previously by several groups. The value obtained in this study ( $\varphi_{-A} = 0.10$ ) agrees well with reported values. Figure 5 gives a plot of  $(\varphi_{-A})^{-1}$  vs.  $(2\text{-propanol})^{-1}$ . Table III summarizes slopes, intercepts, and the intercept/slope ratio for a number of systems. While simultaneous increase of 2-propanol and decrease of *tert*-butyl alcohol caused a steady increase in  $\varphi_{-A}$ , the change in alcohol composition caused no change whatsoever in the intensity or dispersion of acridine fluorescence.

**Sensitized Reactions.** Solutions of triphenylene and acridine in toluene were irradiated under conditions where 96% of the light was absorbed by the triphenylene. Solutions of Michler's ketone and acridine in PMA were also irradiated under conditions where essentially all the light was absorbed by the ketone. Results of these experiments are given in Table IV.

Table IV. Sensitized Reactions of Acridine with Toluene and PMA

| Hydrogen donor <sup>a</sup> | Sensitizer       | $\varphi_{-A}$ |
|-----------------------------|------------------|----------------|
| PMA <sup>b</sup>            | Michler's ketone | 0.002          |
| PMA <sup>c</sup>            | Michler's ketone | 0.0016         |
| Toluene                     | Triphenylene     | 0.006          |

<sup>a</sup> See Experimental Section for details as to concentrations, wavelength of irradiating light, etc. <sup>b</sup> Acridine and sensitizer in pure PMA. <sup>c</sup> Acridine and sensitizer in 20% *tert*-butyl alcohol-PMA by volume.

Very little disappearance of acridine was observed in these experiments.

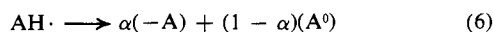
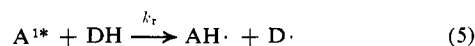
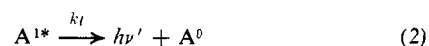
**Flash Studies.** The acridine triplet, which has been identified previously in flash spectroscopic studies,<sup>17,18</sup> absorbs at 440 nm. The triplet-triplet absorption and its decay were observed following flash excitation of acridine in degassed benzene, toluene, 2-propanol, and *tert*-butyl alcohol solutions. The triplet lifetimes in benzene and toluene were the same within experimental error, 57 and 56  $\mu\text{sec}$ , respectively. However, the relative intensity of the initial triplet-triplet transition was lower (75% as intense) in toluene. The initial intensity of the acridine triplet-triplet transition in 2-propanol was 69% of the value in *tert*-butyl alcohol. The triplet lifetime was shorter in 2-propanol than in

*tert*-butyl alcohol; values for 2-propanol and *tert*-butyl alcohol are 53 and 385  $\mu\text{sec}$ , respectively.

## Discussion

Previous investigations<sup>14,15,17,18</sup> have established that the acridine triplet is unreactive toward reduction in 2-propanol. This has been shown both by the failure of substances with low-lying triplets to quench the reduction as well as by the inability of triplet sensitizers to promote reaction. It has been suggested<sup>18</sup> that a higher triplet of acridine is reactive in certain alcohols. The fact that sensitizers with triplet energies as high as triphenylene ( $E_T = 67$  kcal/mol)<sup>33</sup> and Michler's ketone ( $E_T = 61$  kcal/mol)<sup>33</sup> fail to promote efficient reduction (Table IV) in toluene and PMA, respectively, suggests that neither an upper nor the lower triplet of acridine is the major reactant toward these donors. It is suspected that the small amount of reaction observed in the triphenylene-toluene system may be due to singlet energy transfer from triphenylene.<sup>34,35</sup>

Studies with iodide<sup>15</sup> and biacetyl<sup>18</sup> as singlet quenchers have demonstrated that quenching of acridine fluorescence in 2-propanol by these substances is concurrent quenching of acridine photoreduction (*vide infra*, however). This, together with the lack of triplet participation in 2-propanol, has led to the conclusion that the fluorescent singlet is the reactive intermediate in photoreduction. If the fluorescent singlet were in fact the reactant, the following kinetic scheme should adequately describe the photochemistry of acridine (eq 1-6).



The fluorescence quantum yield,  $\varphi_f$ , should be given by eq 7. The usual Stern-Volmer relationship is pre-

$$\varphi_f = \frac{k_f}{k_f + k_d + k_{isc} + k_r(DH)} \quad (7)$$

dicted by eq 8, substituting

$$\tau_s = \frac{1}{k_f + k_d + k_{isc}}$$

$$\varphi_f^0/\varphi_f = 1 + k_r\tau_s(DH) \quad (8)$$

Similarly, the quantum yield for disappearance of acridine,  $\varphi_{-A}$ , is given by eq 9, assuming that at a sufficiently high hydrogen donor concentration,  $\alpha$ , the fraction of  $AH\cdot$  radicals going on to product,

(33) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(34) A. B. Smith, III, and W. C. Agosta, *Chem. Commun.*, 466 (1970).

(35) It has been reported recently that second triplets of several anthracene derivatives with energies of ca. 74 kcal/mol have sufficient lifetimes to participate in intermolecular reactions.<sup>36</sup> Attempts to determine if acridine has a triplet in the 66-74 kcal/mol range have been frustrating since we find that "usual" triplet quenchers such as 1,3-pentadiene quench acridine fluorescence.

(36) R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 1492 (1969); **90**, 213 (1968); R. S. H. Liu and D. M. Gale, *ibid.*, **90**, 1897 (1968).

becomes constant.

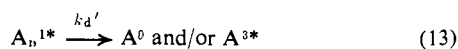
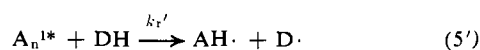
$$\varphi_{-A} = \frac{\alpha k_r(\text{DH})}{k_t + k_d + k_{isc} + k_r(\text{DH})} \quad (9)$$

Equation 10, the reciprocal of eq 9, predicts a linear relationship, such as is observed for high (DH) in Figures 1, 4, and 5, with an intercept/slope ratio equal to  $k_r\tau_s$ .

$$(\varphi_{-A})^{-1} = 1/\alpha + \frac{1}{\alpha k_r\tau_s(\text{DH})} \quad (10)$$

If only the fluorescent singlet were active in photoreduction there should be an equivalence of the fluorescence-quenching Stern-Volmer slopes and the high-concentration intercept/slope ratios for photoreduction listed in Table III. However, for each reductant studied, toluene, 2-propanol, and PMA, there is no such relationship. Fluorescence quenching is either much too small or nonexistent in each case. This indicates that the simple scheme presented in eq 1-6 is inadequate.

In view of previous experimental studies<sup>2-6</sup> as well as theoretical investigations<sup>37,38</sup> on other aza aromatics an attractive possibility is the involvement of an  $n,\pi^*$  singlet in the photoreduction. The lack of significant fluorescence quenching where photoreduction occurs, coupled with the finding that fluorescence quenching is accompanied by quenching of the photoreduction, suggests that the  $n,\pi^*$  singlet lies lower in energy and is reached subsequent to the fluorescent  $\pi,\pi^*$  state. If the  $^1n,\pi^*$  and  $^1\pi,\pi^*$  states reached an equilibrium, the same equivalence of Stern-Volmer slopes and photoreduction intercept/slope ratios should be observed. However, if decay of the initially formed  $^1\pi,\pi^*$  state to a lower  $^1n,\pi^*$  state is irreversible, or reversible, but not to equilibrium, different relationships can be developed. An expanded reaction scheme consists of eq 1-4 plus eq 5' and 11-13 where  $A_n^{1*}$  denotes the  $^1n,\pi^*$  state. An expression, eq 14 (where  $a = k_t +$



$k_d + k_{isc} + k_n$ ), more complicated but similar in form to eq 9, can be developed if the usual steady-state approximations for  $A^{1*}$  and  $A_n^{1*}$  are made. A linear

$$(\varphi_{-A})^{-1} = \frac{a}{\alpha k_n} + \frac{a(k_p + k_d') - k_n k_p}{\alpha k_n k_r'(\text{DH})} \quad (14)$$

relationship between  $(\varphi_{-A})^{-1}$  and  $(\text{DH})^{-1}$  is again predicted. For the effect of (DH) on fluorescence of acridine a complicated expression, eq 15, can be ob-

$$\varphi_t^0/\varphi_t = \left(1 + \frac{ak_r'(\text{DH})}{a(k_p + k_d') - k_p k_n}\right) \times \left(\frac{k_p + k_d'}{k_r'(\text{DH}) + k_p + k_d}\right) \quad (15)$$

tained. The first of the two terms in eq 15 should increase with increasing (DH) while the second term should decrease. At very low concentrations of DH, the second term should be near unity so that the first term would be dominant; consequently eq 15 predicts that an initial Stern-Volmer relationship should level off to yield very little quenching at high (DH). The initial slope of a plot of  $\varphi_t^0/\varphi_t$  vs. (DH) should be equal to the high concentration intercept/slope ratio from a plot of  $(\varphi_{-A})^{-1}$  vs.  $(\text{DH})^{-1}$  (eq 14). Behavior similar to that predicted in the second scheme is observed with acridine-PMA as indicated in Figure 3. These relationships hold providing interconversion of the singlets is reversible.

If interconversion of  $A^{1*}$  to  $A_n^{1*}$  is assumed not to be reversible ( $k_p \approx 0$ ),  $a$  becomes  $\tau_s^\pi$  and  $1/k_d = \tau_s^n$ . Equation 15 under these conditions becomes simply  $\varphi_t^0/\varphi_t = 1$  for all (DH) and eq 14 converts to

$$(\varphi_{-A})^{-1} = \frac{1}{\alpha \tau_s^\pi k_n} + \frac{1}{\alpha \tau_s^\pi \tau_s^n k_n k_r'(\text{DH})} \quad (16)$$

or substituting  $k_n \tau_s^\pi = \varphi_{ic}$ , the quantum efficiency for internal conversion of  $A^{1*}$  to  $A_n^{1*}$ , eq 16 predicts an intercept of  $(\alpha \varphi_{ic})^{-1}$  and an intercept/slope ratio of  $k_r' \tau_s^n$ .

Since the experimental results follow the trends predicted for the modified kinetic scheme, we conclude that different states are responsible for fluorescence and photoreduction. Since fluorescence is nearly unaffected by photoreduction, but photoreduction is quenched when fluorescence is quenched,  $A_n^{1*}$  must be reached following  $A^{1*}$ . Evidently, then, the  $^1n,\pi^*$  state is the lowest excited singlet of acridine in both hydrocarbons and alcohols.<sup>41,42</sup>

A similar conclusion that the fluorescent singlet is not likely the reactive intermediate in photoreduction can be drawn from the data presented in Table III pertaining to possible rates of reaction. According to eq 10, the intercept/slope ratio of plots of  $(\varphi_{-A})^{-1}$  vs.  $(\text{DH})^{-1}$  should equal  $k_r\tau_s$ . Since no fluorescence is observed in benzene-toluene or benzene-PMA solutions and since a yield as low as  $\varphi_f = 0.0001$  could be detected, the lifetime of the fluorescent singlet must be  $1.22 \times 10^{-12}$  sec or less in these solvents. Using this lifetime and the intercept/slope ratio in Table III,  $k_r$  values of  $4.8 \times 10^{10} \text{ l. mol}^{-1} \text{ sec}^{-1}$  and  $8.2 \times 10^9 \text{ l. mol}^{-1}$  are obtained for reaction with PMA and toluene, respectively. The value for PMA exceeds the diffusion-controlled limit by an order of magnitude while the value for toluene is slightly greater than the reported

(41) These results could also be explained by a process involving a "hot ground state" or an unquenchable triplet. However, the fact that a small amount of fluorescence quenching occurs makes these somewhat unattractive alternatives appear unlikely.

(42) As suggested by a referee, we have investigated the absorption spectrum of acridine in glassy solution at low temperature (77°K). In both hydrocarbon (MCIP) and hydroxylic (EPA) solutions a weak long-wavelength shoulder appears on cooling (at 383 and 386 nm, respectively); such behavior is not observed with anthracene in MCIP, although new fine structure appears at shorter wavelengths. Although these may prove to be the "hidden"  $n \rightarrow \pi^*$  transitions, no conclusions can be drawn at present.

(37) L. Pedersen, D. G. Whitten, and M. T. McCall, *Chem. Phys. Lett.*, **3**, 569 (1969).

(38) INDO<sup>39</sup> molecular orbital calculations<sup>40</sup> suggest that the lowest excited states of acridine should be  $n,\pi^*$ ; the  $^3n,\pi^*$  state is estimated to have  $E_T = 46.4$  kcal/mol, surprisingly close to the measured value of 45.3 kcal/mol.<sup>33</sup>

(39) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(40) L. Pedersen, unpublished results.

value for  $k_{\text{diff}}$  in benzene of  $5 \times 10^9$  l. mol<sup>-1</sup> sec<sup>-1</sup>.<sup>43</sup> Since there is an observable isotope effect for toluene (and PMA) it appears unlikely that the reaction is diffusion controlled.

Considering the proposed mechanism involving a  $^1n, \pi^*$  state as the reactive intermediate, some inferences can be drawn regarding the lifetime and reactivity of such a state. Koizumi and coworkers<sup>18</sup> investigated biacetyl quenching of fluorescence and photoreduction of acridine in 2-propanol. A Stern-Volmer plot for biacetyl quenching of fluorescence gave a slope of 10 l. mol<sup>-1</sup> while a similar plot for the quenching of photoreduction gave a slope of approximately 17 l. mol<sup>-1</sup>. Assuming biacetyl can quench both of the singlets in the proposed reaction scheme, the equation for the second plot should be

$$\frac{\varphi_{-A}^0/\varphi_{-A}}{d(B)} = 1 + k_q \tau_s^\pi(B) + k_q' \tau_s^n(B) + k_q \tau_s^\pi k_q' \tau_s^n(B)^2 \quad (17)$$

where  $k_q$  and  $k_q'$  are the rate constants for biacetyl quenching of  $A^{1*}$  and  $A_n^{1*}$ , respectively, and (B) is the concentration of biacetyl. Equation 17 predicts the plot to give a curved line whose slope would be given by eq 18; the actual data reported are scattered so it is impossible to determine if there is marked curvature.

$$\frac{d(\varphi_{-A}^0/\varphi_{-A})}{d(B)} = k_q \tau_s^\pi + k_q' \tau_s^n + 2k_q k_q' \tau_s^\pi \tau_s^n(B) \quad (18)$$

Determination of  $k_q' \tau_s^n$  from the previously published plot using the value of  $k_q \tau_s^\pi = 10$  l. mol<sup>-1</sup> and eq 17 yields a value of  $5.4 \pm 1.4$  l. mol<sup>-1</sup>. If, as has been frequently assumed,<sup>44,45</sup> biacetyl quenches higher energy singlets at a diffusion-controlled rate, then a value of  $1.7 \times 10^{-9}$  sec is calculated for the lifetime of the  $^1n, \pi^*$  state in 2-propanol.<sup>46</sup> Using the value of 0.135 for  $k_r \tau_s^n$  in 2-propanol (the intercept/slope ratio in Table III), the lifetime of the  $^1n, \pi^*$  state,  $\tau_s^n$ , is calculated to be  $4.7 \times 10^{-9}$  sec. From the above calculated lifetime, a value for  $k_r$  of  $2.88 \times 10^7$  l. mol<sup>-1</sup> sec<sup>-1</sup> is calculated for the reaction of excited acridine with 2-propanol.

The mechanism of reaction of the  $^1n, \pi^*$  state with the various hydrogen atom donors is perhaps open to question. As mentioned previously, the nature of the products suggests hydrogen-atom abstraction. What appears to be a borderline primary isotope effect for perdeuteriotoluene suggests that hydrogen abstraction is the likely route in this case. Although previous studies indicate that PMA should yield readily hydrogen atoms from the ring methyl group,<sup>48</sup> our studies show a surprisingly low isotope effect for reaction with excited acridine. This result suggests either (a) that

(43) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

(44) J. T. Dubois and B. Stevens in "Luminescence of Organic and Inorganic Materials," H. P. Kallman and G. M. Spruch, Ed., Wiley, New York, N. Y., 1962, p 115.

(45) N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, **90**, 4194 (1968).

(46)  $k_{\text{diff}}$  for 2-propanol is calculated<sup>47</sup> to be  $3.2 \times 10^9$  l. mol<sup>-1</sup> sec<sup>-1</sup>.

(47) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

(48) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3361 (1965).

$\tau_{\text{sn}}$  is quite different in PMA-benzene-*tert*-butyl alcohol solutions from the value in 2-propanol and that reaction with PMA is nearly diffusion controlled or (b) that initial interaction between excited acridine and PMA does not involve rate-determining hydrogen atom transfer. Since an altered fluorescence was observed with PMA, the latter possibility is not unlikely. Neither anisole nor toluene alters or quenches acridine fluorescence or gives other evidence of complex formation; however it is likely that PMA is a better electron donor than either of the aforementioned compounds. Possibly then, the change of fluorescence indicated for PMA could be the superposition of acridine fluorescence on fluorescence from a PMA-acridine charge-transfer complex. Such excited-state complex formation has been well documented for several types of molecules; in the case of excited ketones and amines electron transfer complex formation is frequently followed by proton transfer to yield subsequently isolable reduction products.<sup>49,50</sup> Relatively broad, structureless fluorescence from excited-state donor-acceptor complexes is characteristic in nonpolar media.<sup>51</sup> Electron transfer or complex formation with an  $^1n, \pi^*$  state is not a surprising reaction; whether or not it actually operates in this case is uncertain. Interestingly, recent studies on energy-transfer mechanisms using the isotope effect as a probe indicate very little secondary isotope effect in electron-transfer processes.<sup>52</sup>

Our experiments demonstrate that decay of the fluorescent  $^1\pi, \pi^*$  state to a lower lying  $^1n, \pi^*$  state is a very important path for acridine and other N-heteroaromatic compounds; the fluorescence quenching experiments suggest that the process is reversible to a small extent although equilibrium is not attained. Our kinetic studies give no evidence as to the actual energy of the  $^1n, \pi^*$  state or to its fate other than the photoreduction. However, comparison of our limited flash studies in reducing and nonreducing solvents does provide some useful information. The fact that the initial intensity of the triplet-triplet absorption is considerably less in toluene than in benzene, even though the lifetimes are similar, indicates that hydrogen abstraction reduces the efficiency of reaching the triplet state. A similar situation is observed for 2-propanol compared to *tert*-butyl alcohol. Hence it is likely that the  $^1n, \pi^*$  state finds intersystem crossing, ultimately to the lowest triplet, an important path of decay.

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