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Citation: The Journal of Chemical Physics **84**, 6808 (1986); doi: 10.1063/1.450684 View online: http://dx.doi.org/10.1063/1.450684 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/84/12?ver=pdfcov Published by the AIP Publishing

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# Photoionization and photocyanation of 9-phenylanthracene

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(Received 3 February 1986; accepted 10 March 1986)

The photoinization of 9-phenylanthracene (PhA) and the role of the radical cation in the photocyanation reaction is reported. Radical cations are produced by two processes: (a) biphotonic unimolecular ionization under high intensity laser excitation and (b) a monophotonic bimolecular electron-transfer process in the presence of dicyanobenzene (DCB). In both cases, the singlet excited state is the precursor to the radical cation.

## **I. INTRODUCTION**

Nucleophilic photosubstitution reactions of aromatic compounds have been studied extensively.<sup>1</sup> It was observed that electron-donating substituents on the aromatic ring functioned as activators, when it was supposed that the primary reaction step was a photoionization. The resulting radical cation was assumed to be a reactive photochemical intermediate. Similar studies of other aromatic systems also suggested that photoionization to the radical cation was an initial reaction step. As a result, these reactions, all of them promoted by electron donating groups, were classified<sup>1</sup> as  $S_{R+N}Ar^*$ .

Studies of the multiplicity of the reactive excited state of the neutral molecule (i.e., that state that is intermediate to photoionization) were inconclusive. It was thought that photoionization involved the interaction of a low-lying triplet state (specifically the  $T_1$  state). However, the possibility of singlet intermediacy could not be ruled out completely.

Several groups have discussed the photocyanation of aromatic compounds:

- Suzuki et al.<sup>2</sup> report that photocyanation of anisole proceeds via a singlet excited state in the presence of 1,4-dicyanobenzene (DCB), which is a good electron acceptor, and via triplet excited states in the absence of DCB.
- (2) Bunce *et al.*<sup>3</sup> suggest that formation of a singlet excimer is the first step in the photoionization of naphthalene and biphenyl and, hence, in the photocyanation reaction. In the presence of DCB, however, these latter authors suggest that radical ions are formed from a singlet excited state via an electrontransfer mechanism.
- (3) Yasuda *et al.*<sup>4</sup> report that the photocyanation of arenes proceeds more efficiently in the presence of electron acceptors and, as a result, they suggest an electron-transfer mechanism involving an excited singlet state of the arene molecule.
- (4) Lemmetyinen et al.<sup>5</sup> studied the photocyanation of phenanthrene and concluded that a singlet state mechanism is operative in the presence of DCB whereas a triplet state mechanism is operative in the absence of DCB.

Four conclusions may be drawn from these last observations: (a) Radical cation formation is not restricted to aromatic compounds with electron donating substituents; (b) radical cations form via a singlet excited state in the presence of DCB; (c) in the absence of DCB, the results with respect to multiplicity of the excited state that is precursor to the radical cations are ambiguous; and (d) there is general agreement on the intermediacy of radical cations in photocyanation reaction.

The aim of this present work is to clarify the mechanism of photosubstitution of PhA. Since it is realized that photoionization and/or electron-transfer processes may play important roles in the photosubstitution reaction, particular attention is devoted to the detailed mechanism of photoionization and to the reactivity of the resulting radical cation in the photosubstitution reaction process.

### **II. EXPERIMENTAL**

### A. Steady state measurements

Small scale irradiation experiments were performed in a quartz cell of 1 cm path length. These cells, filled with the reaction mixture, were irradiated with a Phillips HP 125 W mercury lamp. The system was cooled during irradiation by circulating tap water around the cell compartment in order to minimize thermal side reactions. The progress of photo-chemistry was monitored by UV-vis absorptivity using a Cary 219 spectrophotometer. The cell compartment of the reactor was shuttered at certain time intervals and the reaction cell was transferred, in darkness, to the spectrophotometer. The spectrum obtained after various irradiation times is shown in Fig. 1.

Fluorescence quenching studies were conducted on a Perkin Elmer MPF-2A fluorescence spectrophotometer.

#### **B.** Laser photolysis measurements

A detailed description of the laser photolysis apparatus is given in an earlier report.<sup>6</sup> The third harmonic (355 nm) of a Nd:YAG laser (Quantel YG 481) was the excitation source, the pulse characteristics being 11 ns (FWHM) and 120 mJ (maximum output energy). The detection system comprised a photomultiplier (Hamamatsu R 928), a waveform digitizer (Biomation 8100), and an on-line computer (PDP 11/70).

## III. RESULTS AND DISCUSSION A. Steady state experiments

The change of absorption spectrum of PhA caused by irradiation in the presence of both a nucleophile  $(CN^{-})$  and



FIG. 1. Absorption spectra of 9-phenylanthracene ( $\sim 10^{-4}$  M) in solvent dimethylformamide in the presence of 1,4-dicyanobenzene ( $\sim 0.05$  M). The solution was saturated with respect to the nucleophile CN<sup>-</sup> ( $\sim 0.1$  M). Irradiation times of 0, 10, 25, 40, 70, 105, and 180 s were used, as shown in the figure.

an electron acceptor (DCB) are shown in Fig. 1. A new absorption band appears at  $\sim 410$  nm. After 3 min of irradiation, all absorption features of PhA have shifted to longer wavelengths. The new spectrum is characteristic of cyano substitution in the meso position of the anthracene ring.





9-Phenyl-10-cyanoanthracene

The fluorescence spectrum of PhA recorded in toluene with increasing concentration of DCB is shown in Fig. 2. The presence of an isosbestic point at  $\sim$ 470 nm indicates that an exciplex of PhA and DCB is formed.

In acetonitrile, because of the higher solubility of DCB in this solvent, fluorescence quenching is very efficient and no isosbestic point is observed. Laser photolysis indicates that radical cations form at considerably higher yields in acetonitrile when DCB is present, presumably because of the higher probability of electron-transfer fluorescence quenching:

 $^{1}PhA^{*} + DCB \rightarrow ^{2}PhA^{+} + ^{2}DCB^{-}$ .

Any specific interaction between <sup>3</sup>PhA\* and DCB may

Object Density 0.02 0.02 0.04 0.04 0.04 0.04 0.05 0.05 0.06 0.

FIG. 2. Fluorescence quenching of PhA by DCB in toluene. The concentration of PhA was  $\sim 1.5 \times 10^{-4}$  M. Concentrations of DCB were 0, 0.02, 0.04, and 0.06 M, as shown in the figure. An isosbestic point is clearly evident at  $\sim$ 470 nm.

be ruled out as a result of laser photolytic observations which reveal that the addition of DCB does not affect triplet decay times in any significant way. These latter results establish the fact that DCB is an exclusive singlet excited state quencher for PhA and that, in acetonitrile, this quenching produces radical cations.

Stern-Volmer analysis of the kinetics in an acetonitrile solvent postulates a reaction mechanism that involves competition between the unimolecular decay of PhA and a bimolecular quenching induced by DCB. If we define the quantum yields of emission in the absence and presence of DCB as  $\phi^0$  and  $\phi_c$ , respectively, then

$$\phi_{f}^{0} = k_{f} / (k_{f} + k_{isc} + k_{ic}) ,$$
  

$$\phi_{f} = k_{f} / (k_{f} + k_{isc} + k_{ic} + k_{q} [DCB]) ,$$
  

$$\phi_{f} / \phi_{f}^{0} = 1 + k_{q} [DCB] / (k_{f} + k_{isc} + k_{ic})$$
  

$$= 1 + \tau_{f} k_{q} [DCB] ,$$

where k is a rate constant; where the subscripts f, isc, ic, and q refer to fluorescence, intersystem crossing, internal conversion, and bimolecular quenching, respectively; where [DCB] is the concentration of dicyanobenzene; and where  $\tau_{f}$  is the lifetime of PhA in the absence of the DCB quencher. The fluorescence quantum yield  $\phi_f$  is defined as the ratio of quanta emitted  $(S_1 \rightarrow S_0)$  to quanta absorbed  $(S_1 \leftarrow S_0)$ . Since the quencher DCB does not absorb at the excitation wavelengths used for this work, the fluorescence intensities  $I_{f}$  can be taken as relative measures of the fluorescence efficiency. Thus, a plot of  $I_f^0/I_f$  vs [DCB] should yield a straight line of slope  $\tau_f k_q$  and intercept unity. Such a plot is given in Fig. 3. The value of  $k_q$  calculated from the slope and from the additional datum  $\tau_f = 7 \times 10^{-9}$  s is  $k_q = 8 \times 10^9 \ell$  $mol^{-1} s^{-1}$ . This value is of an order of magnitude appropriate for diffusion controlled quenching: In perylene, for ex-



FIG. 3. Stern-Volmer plot for the quenching of PhA fluorescence by DCB in an acetonitrile solvent.

ample, the diffusional rate constant, as obtained from fluorescence quenching,<sup>10</sup> is  $k_{\text{diff}} = 2 \times 10^{10} \, \ell \text{mol}^{-1} \text{ s}^{-1}$ . Thus, for PhA, we conclude that  $k_q$  is essentially diffusion controlled.

#### **B. Laser photolysis experiments**

The transient absorption spectra of PhA, as recorded in toluene (dielectric constant  $\epsilon = 2.4$ ) and in acetonitrile ( $\epsilon = 36$ ), are shown in Figs. 4(a) and 4(b), respectively. In toluene, one dominant absorption band, for which  $\lambda_{max} \approx 440-450$  nm, is observed. In acetonitrile, a similar absorption band, for which  $\lambda_{max} \approx 430$  nm, as well as an additional broad absorption band in the region 550-700 nm are observed. This latter band has an absorption maximum at 640 nm. The identification of the species responsible for these maxima is based on the following considerations:

(i) When the solution of PhA in toluene is purged with oxygen, the 440 nm absorption is completely quenched.

(ii) The  $T_j \leftarrow T_1$  absorption spectrum of PhA is reported<sup>7</sup> to exhibit maxima at 428 and 434 nm in isopropanol and liquid paraffin, respectively.

(iii) The 430-440 nm absorption band, based on observations (i) and (ii), must be assigned to the  $T_1$  triplet excited state absorptivity of PhA.

(iv) The absorption spectrum of PhA radical cation is reported<sup>8</sup> to exhibit three absorption maxima: 585 nm ( $\epsilon \approx 8000 \ \ell \ mol^{-1} cm^{-1}$ ); 645 nm ( $\epsilon \approx 9000 \ \ell \ mol^{-1} cm^{-1}$ ); and 715 nm ( $\epsilon \approx 10\ 000\ \ell \ mol^{-1} cm^{-1}$ ).

(v) An increase of DCB concentrations leads to an enhancement of the transient absorptivity at these three longer wavelengths.

(vi) The long wavelength absorption band, based on observations (iv) and (v), must be assigned to the radical cation of PhA. This cation is observed only in the polar solvent acetonitrile; it appears to be completely absent in to-luene.

The identification of transient species in the toluene sol-



FIG. 4. (a) Transient absorption spectra of PhA in toluene solvent. Delay times of 2, 8, 20, and  $64 \,\mu$ s after the laser pulse were used and the resulting spectra are so denoted; (b) transient absorption spectra of PhA in acetoni-trile solvent. Delay times of 0.4, 1.0, 1.7, 2.7, 3.7, and 5.45  $\mu$ s after the laser pulse were used and the resulting spectra are so denoted.

vent is straightforward. However, further investigation of the acetonitrile solvent suggests that the 430 nm absorption band may be more complex than item (iii) above infers. This complexity, and inferences from it, will now be discussed;

(vii) When DCB is added to an acetonitrile solution of PhA, absorptivity is enchanced not only in the 500-700 nm region but also at 430 nm. This effect may be attributed either to an enhancement of triplet concentrations by the addition of DCB or to an additive contribution of the PhA<sup>+</sup> moiety to the absorptivity at 430 nm. The possible effects of DCB on triplet absorptivity may be schematized as

(1)

<sup>1</sup>PhA\* 
$$\rightarrow$$
 PhA +  $hv_f$ ,  
<sup>1</sup>PhA\*  $\xrightarrow{(2)}{}^{3}$ PhA\*,  
<sup>1</sup>PhA\* + DCB  $\xrightarrow{(3)}{}$  (PhA+...DCB<sup>-</sup>)  $\rightarrow$  PhA+ + DCB<sup>-</sup>  
(4) (5) (6) (7)  
<sup>3</sup>PhA\* + DCB  $\rightarrow$  PhA + DCB

where, in the presence of DCB, processes (2) and (3) are two obviously competitive processes. Although the formation of triplets via process (2) is quenched to some extent in the presence of DCB, the two new routes (4) and (5) are enhanced. Thus, the net effect of DCB on triplet yield depends on the rate constants of processes (1) through (7). Since the values of these rate constants are not available, another method, one which employs selective quenching, was used in an effort to analyze the complexity of the 430 nm absorption.

(viii) Molecular oxygen is recognized as an efficient quencher of both singlet and triplet excited molecules. The quenching rate constant usually falls within an order of magnitude of that for diffusional quenching and it does not appear to differ greatly for either singlets or triplets. However, because of the shorter lifetime of excited singlet states, their reactions with oxygen are expected to be less important than are those of the triplet states. Now, the O<sub>2</sub> concentration in a nondegassed, air-equilibrated solvent at room temperature and atmospheric pressure<sup>11</sup> is of the order of  $\sim 1 \times 10^{-3}$  M. Indeed, for most organic solvents saturated with oxygen, the  $O_2$  concentration is  $[O]_2 \sim 10^{-2}$  M. Thus, for the diffusioncontrolled oxygen quenching rate, we obtain

$$k_a[O_2] \simeq (1 \times 10^{10}) \times (1 \times 10^{-2}) \simeq 1 \times 10^8 \text{ s}^{-1}$$
.

(ix) When an acetonitrile solution of PhA is saturated with oxygen, the 430 nm absorptivity decreases in intensity and exhibits a faster decay. The analysis of the decay kinetics at 430 and 640 nm in oxygen-saturated solutions demonstrates that both species decay by second order kinetics. Second order kinetics imply that the decay mode of the transient species is a bimolecular process. Now, the rate constant of a second order decay depends on the intial concentration of the transient species, as is reflected in the units of rate constant, namely k ( $\ell mol^{-1} s^{-1}$ ). Since the real concentration of the transient species are not known, we used the optical density values, D, as a measure of their concentration. In doing so, we use the second order rate constants merely for comparison of relative magnitudes and not absolute values. The second order rate constants thus obtained for the two wavelengths mentioned are:  $k_2 = 2 \times 10^7 \text{ s}^{-1} \text{ D}^{-1}$  and  $k_2 = 1.8 \times 10^7 \text{ s}^{-1} \text{ D}^{-1}$ . These decay constants are ~10 times less than that estimated above for diffusion-controlled oxygen quenching. In other words, in oxygen-saturated solutions, the transients that are observed at 430 nm and that

decay such that  $k < 10^8 \text{ s}^{-1} \text{ D}^{-1}$  are not likely to be triplets. These results suggest that the radical cation possesses an additional absorptivity, one that overlaps the 430 nm  $T_i \leftarrow T_1$ absorptivity. No PhA+ absorptivity has been cited in this spectral region.<sup>8</sup> However, a similar compound, the 9,10diphenylanthracene radical cation is reported<sup>9</sup> to absorb at 445 nm as well as at 600, 660, and 730 nm. Thus, in our experiments, the long-time, residual absorbance at 430 nm that remains after total quenching of  $T_1$  can be attributed to PhA<sup>+</sup> absorptivity.

These results permit the identification of all short-lived transients that appear in irradiated solutions of PhA. In acetonitrile, even in the absence of DCB, the radical cation absorption is clearly observed. In toluene, on the other hand, no such ions are detected. However, it is known that photoionization does occur in nonpolar solvents, but to a lesser extent than in polar solvents, mainly because of (a) the high solvation probability of ions in polar solvents, and (b) the efficient geminate recombination that characterizes nonpolar solvents. Thus, the detection of the extremely low ion concentration in a toluene solvent will require a more sensitive detection system than is available to us.

Two basic questions must be addressed in all mechanistic photophysical and photochemical studies: (1) What is the nature of the photoactive excited state (singlet or triplet) of the parent molecule; and (2) How many photons are required to complete the photoprocess (i.e., is the reaction mono- or biphotonic)? Consequently, we now proceed to address both of these questions.

#### 1. Singlet vs triplet mechanism

Two sets of experiments to determine whether the singlet  $S_1$  or triplet state  $T_1$  or both are precursor to the ion formation process have been carried out. They are:

(i) The effect of fluorescence quencher  $(I^{-})$  on ion formation: Triplet and ion absorptivities as well as the fluorescence intensity have been monitored for  $\sim 10^{-4}$  M PhA solution in acetonitrile in the absence and presence of a fluorescence quencher  $(I^{-})$ . The results are given in Table I. In the presence of this fluorescence quencher, it was found that  $\phi_f$  decreases and  $\phi_i$  increases, implying that  $\phi_{isc}$  is enhanced by heavy atom spin-orbit coupling induction of the  $S_1 \longrightarrow T_1$  intersystem crossing process

PhA\* 
$$^{(I^-)}$$
 <sup>3</sup>PhA\*.

The quantum yield  $\phi_{PhA^+}$  is found to decrease in the presence of quencher. This depletion suggests that the singlet excited state is precursor to ion formation. In the presence of quencher, PhA<sup>+</sup> lifetime does not change significantly,

TABLE I. The effect of  $I^-$  on fluorescence  $(\phi_f)$ , triplet  $(\phi_i)$ , and ion  $(\phi_{PhA^+})$  yields for an acetonitrile solution of  $10^{-4}$  M PhA.

[1-]	$\phi_{_{\mathrm{PhA}}+}$	φ,	$\phi_f$
O	≡1 0.26	=1	≡1 0.41
saturateo	0.20	2.5	0.41

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indicating that no specific interaction occurs between  $I^-$  and PhA\*.

(ii) The effect of  $O_2$  quenching on the ion formation: As mentioned in Sec. III B above, oxygen quenches both singlet and triplet excited states. However, because of longer lifetimes, triplets are quenched more efficiently than singlets. Thus, oxygen quenching studies can be used to monitor the role of triplets in a photoprocess. Some of the decay channels that are available for triplets are

$$isc$$
 PhA , (1)

$$^{3}PhA^{*}$$
  $\xrightarrow{O_{2}}$  PhA , (2)

$$\rightarrow PhA^+ + PhA^- , \quad (3)$$

$$\xrightarrow{h\nu} {}^{3}\text{PhA}^{**} \rightarrow \text{PhA}^{+} + e^{-} \quad . \tag{4}$$

In oxygen-saturated solutions, process (2) is competitive with processes (3) and (4).

Consider process (3) first: Bimolecular triplet-triplet annihilation is a diffusion-controlled process, the rate of which depends on triplet concentrations. Since triplet concentrations in this study are much lower than the oxygen concentrations, process (3) is, in effect, totally quenched in the presence of oxygen.

Process (4) is a biphotonic ionization of the  $T_1$  state. Since second photon absorption must be complete within the time duration of the laser pulse, namely 11 ns, the time scale is too short for effective oxygen competition. Consequently,  $O_2$  quenching studies can provide no information concerning process (4).

The results of our oxygen quenching experiments are given in Table II. In  $O_2$  saturated solutions, the triplets are totally quenched but the ion yield decreases only by  $\sim 30\%$ . The results given in Table I and II point in the same direction, namely that triplets do not play any major role in ion formation.

#### 2. Monophotonic vs biphotonic mechanism

Two different experiments to determine whether ions are formed in a single photon or two photon process have been performed. They are:

(i) The effect of PhA concentration on ion formation: We have studied a set of acetonitrile solutions in which PhA concentrations ranged from  $1.0 \times 10^4$  to  $5.2 \times 10^{-3}$  M. The triplet absorption was monitored at 430 nm and the cation absorption was monitored at 640 nm for each solution. The results are given in Table III.

At low concentrations, both monophotonic and bipho-

TABLE II. The effect of oxygen quenching on the relative yields of triplet  $(\phi_i)$  and ions  $(\phi_{PhA+})$  for an acetonitrile solution of  $10^{-4}$  M PhA.

Saturating gas	$\phi_i$	$\phi_{PhA^+}$
N2	=1	=1
<b>O</b> <sub>2</sub>	~0	~0.7

TABLE III. The effect of PhA concentration on triplet ( $\phi_i$ ) and ion ( $\phi_{PhA+}$ ) yields for an acetonitrile solution of 10<sup>-4</sup> M PhA.

[PhA] ×10 <sup>3</sup> mol ℓ <sup>-1</sup>	$\phi_i$	$\phi_{_{\mathrm{PhA}}+}$
0.10	0.58	1.00
0.26	0.72	1.00
0.52	0.84	0.94
1.0	1.00	0.83
1.3	0.94	0.67
1.6	0.81	0.39
5.2	0.16	0.00

tonic processes may be operative. However, at high concentrations, the ground state PhA absorptivity should become competitive with the biphotonic process and decrease its relative importance. Figure 5 shows a simplified three-level energy diagram on which the relevant transitions are denoted by vertical arrows. Whether process (a), (b), or (c) dominates depends on factors such as PhA concentration, [PhA]; laser intensity,  $I_{355}$ ; quantum yield of intersystem crossing  $(S_{1}^{nn}T_1)$ ,  $\phi_{isc}$ ; and the molar absorptivity of each absorptive act at 355 nm, namely

$$\epsilon_{355}^{S_0}$$
,  $\epsilon_{355}^{S_1}$ ,  $\epsilon_{355}^{T_1}$ .

Since all variables other than [PhA] remain constant, we can compare the effect of [PhA] on both triplet and ion yields.

(1) As [PhA] increases from  $10^{-4}$  to  $10^{-3}$  M,  $\phi_t$  increases about 100% (Table III), whereas  $\phi_{PhA+}$  decreases ~17%. These results indicate that as [PhA] increases, the monophotonic process  $(S_1 \rightsquigarrow T_1)$  is enhanced at the expense of the biphotonic process (<sup>1</sup>PhA\* $\rightarrow$ PhA<sup>+</sup> +  $e^-$ ).

(2) The results given in Table III for the [PhA] range  $1 \times 10^{-3} - 5 \times 10^{-3}$  reveal that, at higher concentrations,  $\phi_t$  starts to decrease in synchrony with  $\phi_{PhA^+}$ . This effect may be the result of a concentration quenching of phenylanthracene excited state molecules which competes effectively with the intersystem crossing  $(S_1 \longrightarrow T_1)$  quenching route.

(ii) The effect of laser intensity on ion formation: The relationship of laser intensity to photoproduct yield is often used to identify a photoprocess as either monophotonic or biphotonic. However, considerable difficulties are encountered in the interpretation of the results<sup>12-14</sup> and the prosecution of an unambiguous experiment is by no means a simple



FIG. 5. Three-level energy diagram for PhA. The thickness of the arrows represents the probability of transition between any two levels. The righthand side of the diagram depicts the relative effects of an increase of the ground state concentration on the probability of the various transitions.

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process.

A logarithmic plot of the optical density, D, of ion absorptivity vs laser intensity, I, is given in Fig. 6(a). Wire mesh filters were placed in the laser beam such that the maximum pulse energy incident on the sample could be varied between 2.4 and 120 mJ.

For laser energies 13.6 to 120 mJ, the relation between optical density and laser intensity is linear (slope = 1). However, at lower energies, 2.4 to 7.7 mJ, the relation becomes quadratic (slope = 2). These results suggest that ion formation is a two-photon process, as seen from the quadratic dependence observed at low laser energies. At higher energies, it is difficult to draw any conclusion solely from the data of Fig. 6(a): The linear dependence may indicate either (a) that the process is monophotonic or (b) that it is biphotonic but that the absorptivities of the two implicated levels are very different.<sup>12</sup>

In order to differentiate between process (a) and (b), another set of experiments, one which utilized an internal standard, was conducted. Since triplet formation is a onephoton process and since the involvement of triplets in the ionization process has already been ruled out by our experiments, a plot of optical density of ion absorptivity vs that of triplet absorptivity should contain information on the number of photons involved in the ion formation process. Such a plot is given in Fig. 6(b).

The absorptivity at 430 nm is predominantly triplet with some contribution from the ion. The optical density, D, of triplets at this wavelength was calculated using the expression

 $D({}^{3}PhA^{*}){}^{430} = D({}^{3}PhA^{*})_{\text{measured}} - D(PhA^{+}){}^{640}/3$ which implies that the ion absorptivity at 430 nm is 1/3 that of the ion absorptivity at 640 nm. The slope of the straight line of Fig. 6(b) is 2.3, indicating rather strongly that ions form in a two-photon process.

#### 3. The mechanism of photocyanation

We have recorded the transient absorption spectra of PhA in acetonitrile in the presence of DCB and CN<sup>-</sup>. Two regions of the spectrum are of interest: one at 440 nm, the other being a broad absorption at 500–700 nm. Figure 7(a) shows the long wavelength region of the spectrum. Close inspection of this figure shows that the absorption intensity grows with time, achieves maximum at  $\sim 3.4 \ \mu s$ , and declines thereafter. This temporal behavior is also evident in the transient profile of the 600 nm [Fig. 7(b)] absorption maximum.

Another important feature emerges from a study of the 410 nm region where the steady state results of Fig. 1 suggest that a new absorption band due to the stable product, 9phenyl-10-cyanoanthracene, should appear. Figure 8 shows the long-time behavior of the species that absorbs at 410 nm. Inspection of this figure, even at much longer times, shows no indication of any decay. Thus, product formation that exhibits absorptivity at 410 nm is consistent in both the steady-state and time-resolved experiments.

The temporal behavior of both the 600 and 410 nm absorptivities are found to depend on the presence or absence of an oxidizing agent ( $O_2$  or DCB). In carefully degassed solutions, in the absence of DCB, product growth is slower and the yield is significantly lower. In air-equilibrated solutions in the presence of DCB, product growth reaches its maximum.

In  $CN^-$  saturated solution, no fast formation of ions in the region 500–700 nm is observed. Indeed, the formation and decay of intermediates take place on the time scale shown below:



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FIG. 7. (a) Transient absorption spectra of PhA in acetonitrile solvent in the presence of ~0.1 M DCB and ~0.1 M CN<sup>-</sup>. Delay times of 0.2, 1.4, 3.4, 6.4, and 26.9  $\mu$ s after the laser pulse were used and are denoted on the various spectra; (b) transient profile of absorbing species at 600 nm as shown in (a). The dots are the experimental points; the two solid lines are plots of two exponential functions that supply the best fits ( $k_{growth} = 8.8 \times 10^5 \text{ s}^{-1}$ ,  $k_{decay} = 2.8 \times 10^4 \text{ s}^{-1}$ ).

where "X" is an unknown chemical intermediate.

No interaction of CN with PhA appears to occur; indeed, no fluorescence quenching is observed even in solutions of PhA which are saturated with respect to  $CN^{-}$ .

Based on the above observations, we propose the following mechanism for the photocyanation of PhA:





FIG. 8. Transient profile of the absorbing species at 410 nm. The dots are the experimental points; the solid line is a plot of the exponential function that supplies the best fit  $(k_{\text{growth}} = 3.3 \times 10^4 \text{ s}^{-1})$ .

where "X" is an intermediate formed by nucleophilic attack on PhA<sup>+</sup> and which decays to the stable reaction product. The transient profiles at 600 and 410 nm are compared in Fig. 9. The rate of formation of the product is congruent with the initial fast decay at 600 nm. However, even after this initial fast decay, the 600 nm absorption continues its decay,



FIG. 9. Transient absorption profiles for 600 (upper curve) and 410 nm (lower curve) for solutions of PhA to which  $CN^-$  had been added.

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but at a considerably slower rate. We interpret these results in terms of two decay channels for the intermediate "X": Decay channel (1) constitutes the initial fast process associated with product growth. Decay channel (2) is a bimolecular process and its rate is determined by the limiting factors of diffusion control and concentration of "X". Of course, the slow decay of the 600 nm absorptivity could well be due to another absorbing species, "Y," which is not an intermediate in the photocyanation reaction.

### **IV. CONCLUSION**

The basic conclusions that derive from this study are: (1) Radical cations of PhA form biphotonically from an

excited singlet state under high intensity excitation.

(2) Radical cations form via bimolecular electrontransfer quenching of PhA by DCB under low to medium intensity excitation.

(3) Efficient photocyanation of PhA requires (a) the formation of PhA<sup>+</sup> via one of the routes described above and (b) the presence of an oxidizing agent such as  $O_2$  or DCB.

Our results, although confined to only one compound, outline one possible mechanism for photosubstitution of a large number of aromatic hydrocarbons. In any photoreaction, the reactivity of an excited state (singlet or triplet) may depend on many factors such as the energy, the nature of the excited state, the solvent, the presence or absence of sensitizers or quenchers, and the lifetime of the excited state. In earlier studies, it was postulated that photocyanation of aromatic hydrocarbons proceeded via an excited triplet state because of their longer lifetimes compared to excited singlet states. However, this work clearly shows that the singlet excited state of phenylanthracene undergoes photocyanation efficiently, provided the other requirements, as already mentioned, are met.

## ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy. Part of this work was performed at the Center for Fast Kinetics Research (CFKR) at the University of Texas at Austin. The CFKR is jointly supported by the Biotechnology Branch of the Division of Research Resources of NIH and by the University of Texas at Austin. We are grateful to all these parties.

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