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# Enhanced photoreactivity of acenaphthylene in water: a product and mechanism study

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## Abstract

Acenaphthylene undergoes direct photolysis in dilute aqueous solutions at concentrations as low as $5\times10^{-7}$ M. The reactivity observed for acenaphthylene in water greatly exceeds that observed in organic solvents. The major products from direct photolysis in aerated aqueous solutions at concentrations above $5\times10^{-5}$ M are the cis and trans dimers of acenaphthylene. Triplet-sensitized dimerization in water produces a large excess of cis dimer (cis/trans = 14); however, direct photolysis initially produces a small excess of cis dimer (cis/trans = 1.5) and upon further conversion the ratio changes to favor the trans dimer (cis/trans = 0.6). The origin of the trans dimer is assigned to photolysis of crystalline acenaphthylene which is thought to form as a coprecipitate with cis dimer during photolysis. The origin of the cis dimer is assigned to dimerization from the triplet manifold. The increased efficiency of acenaphthylene photolysis is attributed to a hydrophobic effect and partly to an enhanced efficiency of dimerization in crystalline acenaphthylene.

*Keywords:* Acenaphthylene; Photochemistry; Aqueous solutions; Photooxidation; Photodimerization

## 1. Introduction

Acenaphthylene (Ac) is classified as an EPA (Environmental Protection Agency) priority pollutant for which photolysis has been predicted to be environmentally insignificant [1,2]. Earlier reports estimate the quantum efficiency of direct photolysis of Ac in aqueous systems as $5\times10^{-3}$ [1]. Experimental measurements have not been reported to date that substantiate these predictions and information is not available concerning the role of photolysis in controlling the fate of Ac in aqueous systems. The rate of Ac reaction with singlet molecular oxygen has been estimated as $4\times10^{7}$ $M^{-1}$ $h^{-1}$ [1]; however, we are not aware of any reports in the literature which describe the formation of oxidation products from direct photolysis of Ac in solution.

Details of the aqueous photochemistry of anthracene have previously been reported [3]. In this paper we present the results of our investigation into the aqueous photochemistry of acenaphthylene (Ac). The aqueous solubility of Ac ($8.1\times10^{-5}$ M) [4] is considerably greater than that of anthracene ($3\times10^{-7}$ M) [4] and the observed photochemistries of these two photoactive hydrocarbons (PAHs) also differ dramatically. Water has been shown to be a unique medium that can influence the efficiency of chemical reactions by promoting ground state association of organic solutes through a hydrophobic effect [5]. However, the 9,10-photodimer of anthracene was not observed upon photolysis in water. This result suggests that anthracene ground state pairing is not induced in aqueous media [3]. Anthracene has been shown to undergo photodimerization in the crystalline form and undissolved microcrystals in the aqueous samples would also be expected to result in dimer formation upon photolysis [6]. Aqueous solutions of anthracene thus appear to be free of ground state associated pairs and microcrystals. In contrast with the photochemistry observed for anthracene in water, dimer formation is the major reaction pathway for Ac consumption upon photolysis in aqueous media. In addition, we report the formation of oxidation products from direct photolysis of Ac in dilute aqueous solutions which correspond to the products that we have observed from the direct photolysis of Ac on $SiO_2$ [7].

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## 2. Experimental details

### 2.1. Materials

The Ac used in these studies was purchased from Aldrich Chemical Co. and further purified by recrystallization from ethanol followed by vacuum sublimation; m.p. 89–90 °C. The purified sample contained approximately 2%–3% residual acenaphthene. Photolysis was done with light sources and filters which allowed excitation of the Ac but not acenaphthene. Acenaphthenone was prepared from 1-hydroxyacenaphthene (Aldrich Chemical Co.; used as received) by oxidation in acetone with dropwise addition of Jones' reagent [8]. The crude ketone was isolated and further purified by vacuum sublimation; m.p. 118–120 °C (lit. 121–121.5 °C) [9]; $m/z$ 169 (12), 168 (100), 141 (9), 140 (84), 139 (70). Acenaphthenequinone, 1,8-naphthalic anhydride, 2,3-naphthalenedicarboxaldehyde, bibenzyl, perylene, methylene blue, acenaphthene and anthrone were purchased from Aldrich Chemical Co. and used as received. Naphthalene was purchased from Aldrich Chemical Co. and further purified by vacuum sublimation. All solvents used were high performance liquid chromatography (HPLC) grade from Baxter Healthcare Corporation, Burdick and Jackson Division, and were used without further purification.

The cis and trans dimers of Ac were prepared as follows. A solution of Ac (306 mg in 20 ml of methylene chloride) was photolyzed for 12 h in a Rayonet RPR-208 photoreactor (Southern New England Ultraviolet Company, Bradford, CT) fitted with 350 nm bulbs. A precipitate of white needles which formed during the photolysis was removed by filtration and determined by gas chromatography (GC) to be greater than 90% trans dimer. Recrystallization from benzene gave pure trans dimer, m.p. 305–307 °C (lit. 307 °C) [10]. The solvent was removed from the filtrate and the residue was recrystallized from cyclohexane to give pure cis dimer, m.p. 230–235 °C (lit. 234 °C) [10].

### 2.2. Methods

Solutions were prepared by stirring Ac in water for a minimum of 12 h with subsequent filtration through a 0.45 μm cellulose acetate filter to remove undissolved PAH. Photoproducts were extracted from water into methylene chloride for analysis. The initial and final concentrations of Ac were determined by HPLC. Product quantitation was done by GC and HPLC. Analysis by GC was done on a Hewlett–Packard model 5890 gas chromatograph fitted with a 5 m × 0.53 mm (0.25 μm film thickness) Hewlett–Packard HP-1 bonded phase silica column and a flame ionization detector. An internal standard method was used for GC quantitation and response factors were calculated from solutions of authentic materials. GC calibration for 1,8-naphthalenedicarboxaldehyde was done with 1,2-naphthalenedicarboxaldehyde. Gas chromatography–mass spectrometry (GC–MS) analysis was done on a Hewlett–Packard model 5995A instrument fitted with a 30 m × 0.25 mm (0.25 μm film thickness) J&W DB-1 bonded phase silica column. HPLC analysis was performed on a Hewlett–Packard model 1090 instrument equipped with a 200 mm × 2.1 mm Hewlett–Packard Hypersil ODS column and a diode array absorbance detector. Analyses were run in a 65:35 ratio of acetonitrile and water respectively. HPLC calibration was done with solutions of authentic materials.

A high pressure mercury lamp (Oriel Corporation, Stratford, CT) and a Rayonet RPR-100 photoreactor (Southern New England Ultraviolet Company, Bradford, CT) with 350 nm bulbs were used to photolyze aqueous samples of Ac in this work. The output from the Hg lamp was passed through an Oriel lp.34 glass cut-off filter (50% transmittance at 350 nm). Photolysis with the Rayonet photoreactor was done in Pyrex glass tubes (50% transmittance at 300 nm). Absorption spectra were measured on a Cary-4 spectrometer and fluorescence spectra were measured on a Spex Fluorolog fluorimeter with double monochromators in both the excitation and emission paths. The Hg lamp profile was digitized with the Spex fluorimeter by synchronously scanning the excitation and emission monochromators with an offset of 0 nm. The light was collected off the front face of a polytetrafluoroethylene (PTFE) disk (Varian; reflectivity greater than 96% in the range 200–2500 nm and reflectivity greater than 99% between 350 and 1800 nm) and corrected for nonlinearities in the excitation and emission monochromators and the detector using correction factors provided by the fluorimeter manufacturer. The Rayonet lamp profile was digitized from information provided by the manufacturer.

The photodepletion of dilute solutions of organics has been shown to follow first-order kinetics, with the wavelength-averaged quantum yield for photolysis given by [11]

$$\phi = \frac{(0.693)(6.02 \times 10^{20})}{(2.303)_{1/2} \Sigma_i \bar{\epsilon}_i F_i} \qquad (1)$$

The use of this equation for predicting environmental residence times requires that the quantum yield be wavelength independent. Wavelength independence of $\phi$ for several PAHs has been demonstrated either directly by photolysis at various wavelengths or indirectly by using $\phi$ values determined at a single wavelength in the laboratory to correctly predict rates of solar photolysis [11]. The value of $t_{1/2}$ in Eq. (1) is determined from the observed first-order photolysis rate, while the summation in the denominator accounts for the integrated overlap of the absorption spectrum of the reactant and the spectral profile of the exciting light source. In the summation, $\bar{\epsilon}_i$ is the average extinction coefficient in a given wavelength interval, denoted by subscript $i$, and $F_i$ is the integrated light flux over that same interval. The size of each wavelength interval, determined by the digitization of the absorption spectrum and the spectral profile of the lamp, was set to 1 nm for these studies. The intensity of the lamp at each digitized wavelength was also corrected for filters used in the photolysis. The photon flux was determined using a benzophenone–benzhydrol actinometer [12] and the measured photon flux was adjusted for the fraction of the lamp profile which was absorbed by the actinometer, giving a total lamp flux of $2.60 \times 10^{17}$ photons $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$ for the Hg lamp and $1.57 \times 10^{16}$ photons $\mathrm{cm}^{-2}\ \mathrm{s}^{-1}$ for the Rayonet photoreactor.

## 3. Results and discussion

### 3.1. Quantum yields

Investigations of Ac photochemistry in organic solvents have focused on factors affecting the production of two isomeric (cis and trans) photodimers. The quantum yield of dimerization, $\phi_D$, has been measured in organic solutions at concentrations ranging from greater than 1 M down to a few millimoles [13]. Submillimolar solutions of Ac in organic solvents have been reported to be photochemically unreactive under oxygen-deficient conditions [13e]. The presence of oxygen in organic solutions has two effects on the photochemistry of Ac. It lowers the efficiency of dimerization and changes the cis/trans dimer ratio resulting from photolysis [13]. Both these effects result from oxygen quenching of the triplet state of Ac. The concentrations of Ac previously studied in organic solvents are considerably higher than the saturation solubility of Ac in water. On the basis of this information it would be incorrect to anticipate that aqueous solutions of Ac would be photochemically stable as previously predicted [2].

We observe first-order decays of Ac upon photolysis in aerated water at concentrations ranging from $5 \times 10^{-7}$ M up to the saturation limit of $8.1 \times 10^{-5}$ M. Precipitation of both the cis and trans dimers during the reaction leads to some scatter in the kinetic data and an associated uncertainty of about 10% in the calculated quantum yields. The effects of non-absorbing particulate matter on rates of photochemical reactions through diffuse scattering of the incident light have been reported [11e]. The maximum theoretical rate enhancement by diffuse scattering is a factor of 2 over the rate in a non-scattering medium. The initial concentration of Ac employed in these experiments is low and the amount of precipitate is likewise small. Consequently, effects from light scattering on the quantum yield of Ac consumption are considered to be minor. No attempt has been made to correct the reported quantum yields for light-scattering effects. Fig. 1 shows the quantum yield for loss of Ac ($\phi_{-\mathrm{Ac}}$) as a function of initial concentration using both the Hg and Rayonet light sources. The lower efficiency determined for Ac consumption with the Rayonet photoreactor, as depicted by the differing slopes of the two lines in Fig. 1, can be attributed to dimer photodissociation (see below).

In our laboratory a $6.5 \times 10^{-5}$ M solution of Ac in methanol, aerated or nitrogen purged, failed to undergo any significant photoreaction upon irradiation over a 4.5 h period (Hg lamp) at wavelengths greater than 340 nm. The half-life for photolysis of Ac in aerated water under the same light flux and at similar concentrations is approximately 30 min. This result underscores the greatly enhanced reactivity observed in water. Likewise, addition of up to 43% water to a 25 mM solution of Ac in methanol has previously been reported to increase the quantum yield of dimerization in aerated solutions [13e].

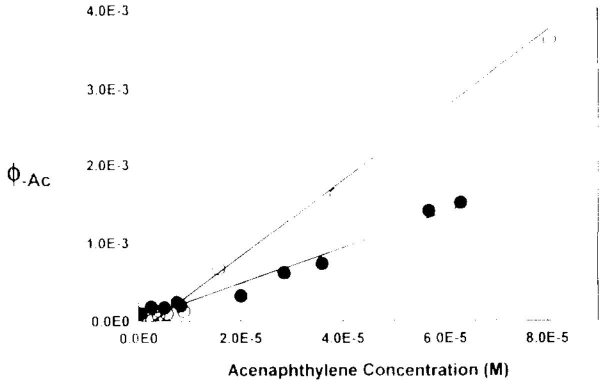


Fig. 1. Concentration dependence of Ac photodepletion in water, $\phi_{-\mathrm{Ac}}$: ○, Hg lamp with 340 nm cut-off filter (see Fig. 2); ●, Rayonet photoreactor through Pyrex (see Fig. 2).

### 3.2. Products

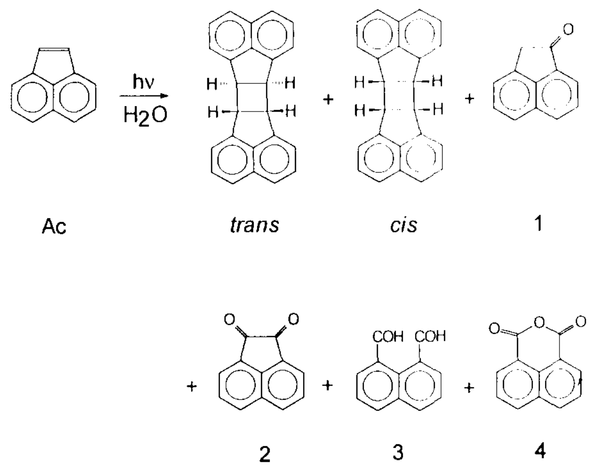
Cis and trans dimers account for more than 80% of the consumed reactant at initial Ac concentrations above $5 \times 10^{-5}$ M (Table 1). As direct photolysis of Ac in water proceeds, both dimers precipitate from solution and a white solid, which is greater than 80% trans dimer, is observed to form on the front and back cell walls in a pattern which images the exciting Hg light source. The remainder of the starting material is accounted for as oxidation products acenaphthenone (**1**), acenaphthenequinone (**2**), 1,8-naphthalenedicarboxaldehyde (**3**) and 1,8-naphthalic anhydride (**4**), each of which is formed in yields of only a few per cent (Scheme 1). At lower initial concentrations ($6.8 \times 10^{-6}$ M, Table 1) the dimers still account for 48% of the consumed Ac while oxidation product **3** accounts for 33% of the reacted material. Methylene-blue-sensitized photo-oxidation of Ac ($7.1 \times 10^{-5}$ M) in water results in the formation of 2-hydroxyacenaphthenone (identified by GC–MS) and **3** as the only products. Oxidation of Ac in methanol, sensitized by methylene blue, has previously been reported to yield products related to a presumed 1,2-dioxetane intermediate and products derived from oxidation of **3** [14]. Oxidation product **1** cannot be easily attributed to a singlet molecular oxygen mechanism and its origin is currently not known. Small amounts of oxidation products are also observed from direct photolysis in nitrogen-purged aqueous solutions; however, the dimers are the major products (Table 1). Incomplete oxygen removal is thought to be responsible for oxidation product formation in nitrogen-purged aqueous solutions.

Comparison of entries (b) and (j) or (d) and (k) in Table 1 reveals that nitrogen-purged solutions of Ac in water react 2–2.6 times more efficiently than aerated solutions (oxygen concentration equal to 0.26 mM) [15]. Similarly, a factor-

Table 1
Product yields from photolysis of Ac in water

| Table entry | Atmosphere | Time (min) | $[Ac]_{t=0} \times 10^5$ [a] | Mole per cent | | | | | | | Cis/trans | Per cent dimer [c] | Material balance |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Ac(*t*) [b] | **1** | **2** | **3** | **4** | Cis | Trans | | | |
| (a) | Air | 210 | 0.68 | 69.6 | 5.2 | 0.1 | 10.0 | 1.9 | 6.1 | 8.3 | 0.7 | 48.0 | 101.2 |
| (b) | Air | 36.5 | 3.40 | 88.0 | 4.4 | – | 4.4 | 1.1 | 2.8 | 1.9 | 1.5 | 39.0 | 102.6 |
| (c) | Air | 25.0 | 4.03 | 62.9 | 8.2 | 2.3 | 4.0 | – | 5.9 | 11.0 | 0.9 | 45.6 | 94.3 |
| (d) | Air | 36.5 | 4.35 | 76.3 | 2.7 | – | – | 0.8 | 7.7 | 9.4 | 0.8 | 72.0 | 96.9 |
| (e) | Air | 169.0 | 4.40 | 33.0 | 4.3 | 1.2 | 3.4 | 3.2 | 19.9 | 35.0 | 0.6 | 82.0 | 100.0 |
| (f) | Air | 64.0 | 4.70 | 54.0 | 3.9 | – | – | – | 18.4 | 23.4 | 0.8 | 91.0 | 99.8 |
| (g) | Air | 50.0 | 6.04 | 50.9 | 2.5 | 0.6 | 1.7 | 0.5 | 18.6 | 22.4 | 0.8 | 83.5 | 97.2 |
| (h) | $N_2$ | 20.0 | 2.96 | 76.8 | 1.5 | 1.9 | – | 1.8 | 8.4 | 6.4 | 1.3 | 63.7 | 96.8 |
| (i) | $N_2$ | 40.0 | 3.30 | 74.1 | 1.8 | – | – | 1.3 | 11.2 | 10.7 | 1.1 | 84.1 | 98.7 |
| (j) | $N_2$ | 36.5 | 3.70 | 68.7 | 4.3 | – | 2.6 | 2.2 | 14.9 | 11.6 | 1.2 | 84.5 | 104.3 |
| (k) | $N_2$ | 36.5 | 4.47 | 52.0 | 2.3 | – | 1.8 | 2.9 | 17.8 | 23.6 | 0.8 | 86.3 | 100.4 |

[a] Initial concentration of Ac (mol $l^{-1}$).
[b] Ac remaining after photolysis.
[c] Percentage of consumed Ac accounted for as total dimer.



Scheme 1.

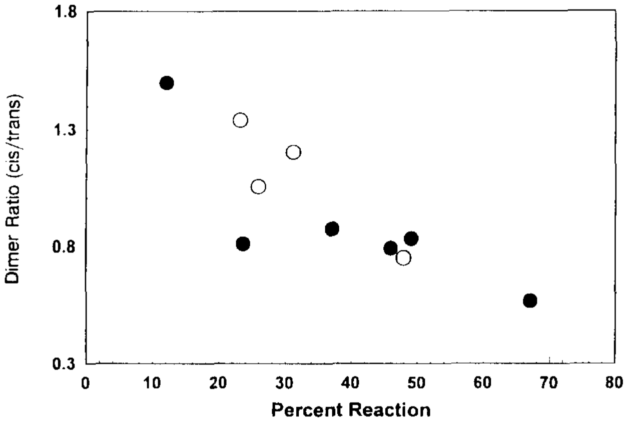


Fig. 2. Cis/trans dimer ratio as a function of per cent consumption of Ac upon direct photolysis in water: ○, nitrogen purged; ●, aerated.

of-2.2 change in $\phi_D$ has been reported for dimerization of Ac in benzene over a similar range of oxygen concentrations [13e]. The lifetime of the $S_1$ state of Ac is reported to be approximately 5 ns in cyclohexane [13e]. Diffusion-controlled quenching ($k_d = 5.9 \times 10^9$ $M^{-1}$ $s^{-1}$) of $S_1$ by oxygen (0.26 mM) in aerated water should be insignificant (about 1%). In fact, the $S_1$ state of anthracene, which has a similar lifetime (5.2 ns in methylcyclohexane) [16], shows approximately 1% quenching of $S_1$ in aerated aqueous solution [17]. Consequently, the observed effect of oxygen on $\phi_{-Ac}$ is not consistent with quenching of the $S_1$ state of Ac. The data are consistent with oxygen quenching of the $T_1$ state of Ac which has a much longer lifetime (6 μs in cyclohexane) [18].

The material balances reported in Table 1 account for all the starting Ac within experimental error. The effect of nitrogen purging on the cis/trans dimer ratio is also revealed by entries (b) and (j) or (d) and (k) in Table 1. The data indicate that nitrogen purging has little or no effect on the dimer ratio. The absence of a large effect of oxygen on the cis/trans dimer ratio is unusual for Ac photochemistry and the result indicates that both dimers come from an intermediate which is quenchable by oxygen, approximately the triplet state of Ac [13]. This is consistent with results from oxygen-quenched studies (see above). The dimer ratio does appear to change significantly with per cent conversion of the starting material (Table 1 and Fig. 2). The data in Table 1 also indicate that there is a concentration effect on the ratio of dimers to oxidation products. As the initial concentration of Ac is reduced in aerated solutions, a higher percentage of oxidation products is observed. The data in Table 1 do not reveal a large effect of concentration on the cis/trans dimer ratio.

### 3.3. Dimer formation

A considerable amount of information is known about the photochemical dimerization of Ac. Dimerization of Ac occurs from both the $S_1$ and $T_1$ electronic states [13]. Reaction of $S_1$ with ground state Ac leads almost exclusively to cis dimer, whereas reaction of $T_1$ with the ground state yields both cis and trans dimers [13d,f]. The ratio of dimers (cis/

trans) formed from triplet sensitization by rose bengal in a series of organic solvents has been reported to be a linear function of the Kirkwood–Onsager solvent parameter [13c]. Extrapolation of the trend in sensitized dimer ratio predicts a 75:1 (cis/trans) ratio in water. We observe a 14:1 (cis/trans) ratio from the rose-bengal-sensitized dimerization of Ac in a nitrogen-purged aqueous solution ($\lambda_{ex}$ > 540 nm). The large excess of cis dimer observed from the triplet-sensitized photolysis is qualitatively consistent with the predicted trend in cis/trans ratio in solvents of high polarity. The ratio of dimers (cis/trans) formed from direct photolysis in water starts near a value of 1.5 and decreases with increasing photolysis time or per cent conversion of Ac (Fig. 2). We have shown that triplet sensitization in water gives excess cis dimer and dimerization of Ac from $S_1$ is also known to give primarily cis dimer; thus trans dimer formed from direct photolysis in aqueous solution must come from yet another source.

The ratio of dimers (cis/trans) formed from photolysis of Ac has previously been reported to decrease during photolysis in both 60 and 20 mM toluene solutions [19]. The change in dimer composition with photolysis time in organic solvents was attributed to reaction of $S_1$ with ground state Ac only during the early stages of photolysis. Owing to the decreasing concentration of the starting material and the short lifetime of $S_1$, reaction from $S_1$ cannot continue to compete with dimerization from $T_1$ as photolysis proceeds [13,20,21]. The low solubility of Ac in water and the observed formation of excess cis dimer from the $T_1$ state argue that the same explanation cannot account for the observed change in cis/trans ratio during photolysis in aqueous solution.

It is known that photolysis of crystalline Ac at room temperature leads primarily to trans dimer formation [22]. This suggests that photolysis of microcrystals of Ac at ambient temperature would lead to large amounts of trans dimer. The quantum yield for dimerization to trans dimer, $\phi_{D,trans}$, in crystalline Ac has been reported to be $4.1 \times 10^{-3}$ at 20 °C [23]. The observed values of $\phi_{-Ac}$ in water at high concentrations (about $8 \times 10^{-5}$ M, Hg lamp) approach the limiting value of $2\phi_{D,trans}$ but remain somewhat smaller (Fig. 1). Reports on the dimerization of crystalline Ac show that as the temperature is raised, the ratio of cis/trans dimer increases dramatically, as does the quantum yield for total dimer formation [23]. A 50% decrease in $\phi_{-Ac}$ is observed from photolysis in water when the temperature is increased from 23 to 71 °C. When photolysis is done at higher temperatures in aqueous solutions, the cis/trans dimer ratio, though somewhat erratic, is observed to increase (Fig. 3).

A possible explanation for the observed change in cis/trans dimer ratio during photolysis of aqueous samples involves crystalline Ac formation as a coprecipitate on seed crystals of cis dimer that form early in the reaction. The initially formed dimer which precipitates probably arises from reaction of Ac ground state pairs or as the result of a bimolecular reaction from $T_1$ (giving primarily cis dimer in water). A coprecipitation mechanism would account for the change in dimer ratio that is observed as the reaction proceeds. The decrease in $\phi_{-Ac}$ with increasing temperature can be explained by reduced crystallization of Ac on to the seed crystals of cis dimer at higher temperatures. Similarly, the increase in cis/trans ratio with increasing temperature could arise from the change in the ratio observed for dimerization of crystalline Ac at elevated temperatures [23] and/or by an increase in dimerization of monomeric Ac in solution. Conversely, when a supersaturated solution of Ac in water was cooled to 10 °C, precipitation of Ac was observed and photolysis led to highly efficient consumption of Ac and a large excess of trans dimer (cis/trans ratio of 0.1).

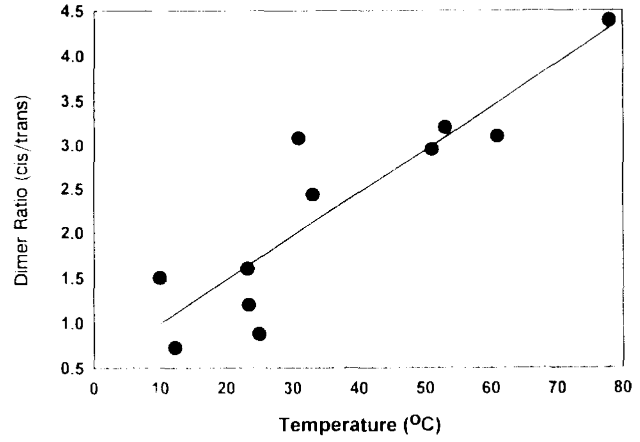


Fig. 3. Temperature dependence of observed cis/trans dimer ratio from photolysis of Ac in water ([Ac] = $6 \times 10^{-5}$ M, photolysis time 45 min for all samples).

This explanation is not inconsistent with our observation of Beer's law behavior for aqueous solutions of Ac (Fig. 4). This figure shows the absorbance per centimeter path length for a series of aqueous Ac solutions. The figure includes data taken at six wavelengths beginning at the first UV–visible maximum (322 nm) and progressing to the red edge of the spectrum. Deviations from Beer's law due to microcrystals or ground state pairs in solution should be most significant at the longer wavelengths. Data taken at each wavelength are highly linear. Homogeneous solutions are expected to obey Beer's law and previous work has shown that ground state

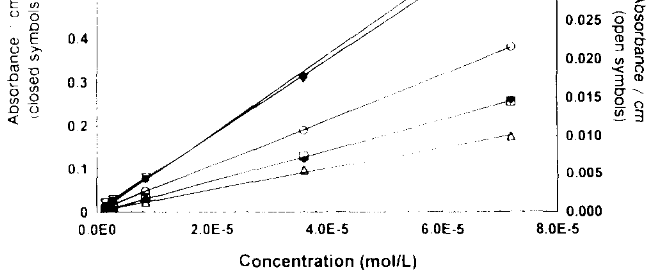


Fig. 4. Absorbance per centimeter path length vs. concentration for absorption of light by aqueous solutions of Ac at various wavelengths: ●, 322 nm; ◆, 338 nm; ▽, 350 nm; ○, 370 nm; □, 400 nm; △, 420 nm.

pairing will not necessarily be observed by this technique [5]; however, the presence of microcrystals should produce non-linearity in Fig. 4. Aqueous solutions of Ac are also observed to show no changes in optical density or spectral profile upon heating to 90 °C in a closed system. Microcrystals of Ac, if initially present in the aqueous solutions, should dissolve on heating and result in changes in optical density or spectral profile. Furthermore, photolysis of unsaturated Ac solutions which have been heated to dissolve microcrystals and subsequently cooled to room temperature leads to no change in the cis/trans ratio. These results diminish the possibility that trans dimer results from photolysis of crystalline Ac initially present in solution. Our previous work with aqueous solutions of anthracene also failed to produce any evidence of microcrystals or ground state pairing [3a].

An alternative mechanism for trans dimer formation by photolysis of crystalline Ac is the photodissociation of precipitated cis dimer to generate undissolved Ac that could subsequently undergo a second dimerization reaction to give trans dimer. Photolysis of cis dimer in the solid state (in air) did not lead to dimer dissociation or cis–trans interconversion with either the Hg or Rayonet light source. Both dimers are highly insoluble in water and only the cis isomer could be dissolved (with the aid of 5% acetonitrile co-solvent) in sufficient quantity to determine whether photodissociation was occurring prior to crystallization. Cis dimer photodissociation in water (5% acetonitrile) was experimentally shown not to occur during photolysis with the Hg lamp through a long-pass 340 nm cut-off filter; however, cis dimer dissociation did occur upon photolysis with the Rayonet photoreactor through Pyrex glass. The efficiency of Ac dimerization is expected to be concentration dependent, while the dimer photodissociation, a unimolecular process, is concentration independent as demonstrated by Livingston and Wei [13e]. This difference in concentration dependence for Ac and dimer photolysis, in addition to the fact that dimer is photodissociated with the Rayonet but not the Hg lamp, is responsible for the divergence of the two lines in Fig. 1.

To test the possible involvement of the cell wall in catalyzing an interface-specific reaction leading to build-up of trans dimer, we photolyzed Ac on silica gel which was dry and on silica gel which contained a monolayer of water. At a surface loading of $3.5 \times 10^{-6}$ mol $g^{-1}$ on dry silica gel, photolysis led to cis/trans ratio of 2.1 which is in agreement with our previous observations [7]. However, photolysis on silica ($3.5 \times 10^{-6}$ mol $g^{-1}$) in the presence of a monolayer of water led to a cis/trans ratio of 13.8. We attribute the dramatic increase in the observed cis/trans ratio in the presence of a monolayer of water to bimolecular dimerization from $T_1$ by Ac monomers with increased mobility on the $SiO_2$ surface. Although Pyrex and quartz glasses differ from silica gel, this result does not support the concept of an interface-specific reaction leading to trans dimer.

On the basis of the preceding arguments we believe that the most defendable mechanism of trans dimer formation involves the photolysis of crystalline Ac formed by co-crystallization on precipitated dimer. The observed high reactivity of Ac in water is partially accounted for by the increased efficiency of dimerization in the crystalline form as previously shown [23].

### 3.4. Emission spectroscopy

Ac has a very low fluorescence quantum yield (about $1 \times 10^{-4}$ [13e]) and is therefore not suitable for analysis even by this sensitive technique. However, acenaphthene and naphthalene have aqueous solubilities and structural characteristics similar to Ac and each exhibits strong fluorescence. Fig. 5 shows the fluorescence from acenaphthene in water ($2.9 \times 10^{-5}$ M, curve a) and methanol ($2.0 \times 10^{-4}$ M, curve b) and from crystalline acenaphthene (curve c). The normalized solution fluorescence curves (a and b) show no evidence for significant contributions from crystalline material which has a significantly red-shifted maximum. Furthermore, the aqueous spectral profile shows no detectable contribution from an excimer which was observed in concentrated organic solutions of acenaphthene [24]. Aqueous solutions of naphthalene exhibit similar behavior.

The absence of excimer emission alone does not rule out the existence of ground state pairs. The concentration of ground state pairs could be too small to lead to observable excimer emission as suggested by Livingston and Wei [13e]. Alternatively, ground state pairs could exist in a conformation that is dissociative on the excited state surface or the barrier to excimer formation imposed by reorganization could be prohibitive. For example, the delayed fluorescence from acenaphthene triplet–triplet annihilation fails to show any excimer component, while the delayed fluorescence from pyrene shows a significantly enhanced excimer emission [25]. Given that excimer is the presumed precursor to cis dimer formation from $S_1$, failure to observe excimer emission from acenaphthene delayed emission suggests that Ac ground state pairs in a less than ideal orientation would not lead to dimer upon photolysis [13]. In addition, on the strength of

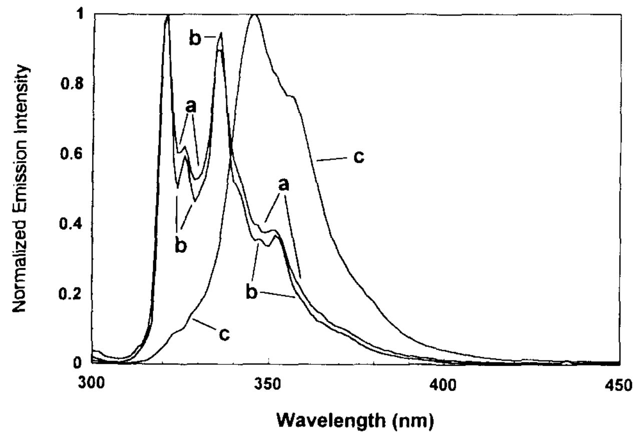


Fig. 5. Fluorescence from acenaphthene in water (curve a, $2.9 \times 10^{-5}$ M) and methanol (curve b, $2.0 \times 10^{-4}$ M) and from crystalline acenaphthene (curve c). Excitation wavelength of 290 nm used for all spectra.

our ability to achieve high conversions of Ac to cis dimer under triplet-sensitized conditions and the observed oxygen effect on $\phi_{-\mathrm{Ac}}$, we favor cis dimer formation from $T_1$. The possibility of reaction from the triplet manifold by ground stage pairs is not rigorously excluded.

## 4. Conclusions

The photolysis of Ac in aqueous solutions proceeds with an efficiency which greatly exceeds that observed in organic solvents. At concentrations above $5\times10^{-5}$ M, photolysis proceeds to give primarily cis and trans dimers. Triplet-sensitized dimerization of Ac in aqueous solution gives a large excess of cis dimer, whereas direct photolysis initially gives a small excess of cis dimer and eventually gives an excess of trans dimer as the reaction proceeds. Formation of trans dimer probably results from photolysis of crystalline Ac as it coprecipitates with the initially formed cis dimer. Part of the acceleration of Ac photolysis in water could be attributed to a hydrophobic effect that is approximately of the same order of magnitude as previously observed for dimethylthymine dimerization in aqueous solutions [5a,b]. The remainder of the acceleration is attributed to the increased efficiency which has previously been observed for dimerization in crystalline Ac.

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