Spectroscopic signatures of protonated perylene in concentrated sulfuric acid

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Abstract

Protonated perylene is an important intermediate in the oxidation of perylene to its radical cation in oxidizing environments, and has been implicated in recent investigations of photoinitiated reaction kinetics in nonpolar solvents. The literature on its spectral signatures in concentrated sulfuric acid provides a well-characterized absorbance spectrum, but its emission characteristics remain ambiguous. In this paper we present the absorbance and emission spectrum of protonated perylene in concentrated sulfuric acid. We demonstrate that dissolution of perylene in concentrated sulfuric acid occurs through the protonated perylene intermediate, which is completely oxidized to the radical cation in the air-saturated liquid within 1 h after dissolution of solid perylene. During this time it is possible to selectively excite protonated perylene in the presence of other absorbing species, and we use this fact to measure the emission spectrum of protonated perylene in concentrated sulfuric acid. Protonated perylene's emission spectrum has a peak at 670 nm. The fluorescence decay of this species exhibits single-exponential behavior when excited at 625 nm, which demonstrates that a single emissive species is prepared.
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1. Introduction

Protonated perylene (PeH$^+$) has played a role in several recent investigations of PAH dynamics in unusual environments. In a recent study of the excited state dynamics of perylene radical cation in oxidizing environments, Gumy and Vauthey [1] observed emission from a solution of perylene in concentrated sulfuric acid (hereafter we will refer to room temperature 18 M liquid sulfuric acid as CSA). They assigned the 620 nm emission to protonated perylene on the basis of the excitation spectrum of the 620 nm feature, which exhibited a peak at about 580 nm. They reasoned that, though the concentration of this species was too low to be observable in absorption in the presence of the strongly absorbing radical cation, PeH$^+$ was still present in sufficient concentration to give rise to measurable emission. Thomas and coworkers [2] have also observed both absorption and emission spectra of a perylene species in zeolites that was assigned to PeH$^+$. In their study proton donating zeolites were bathed in solutions of PAHs dissolved in a nonpolar solvent. Because PAHs have relatively large proton affinities (for example, perylene's gas phase proton affinity is

213 kcal/mol [3,4]) they anticipated formation of protonated arenes. Absorption spectra of perylene in this environment were identical to previously reported spectra of protonated perylene prepared in anhydrous HF [5,6], with distinct absorption features in the 400 and 627 nm regions. Thomas and coworkers [2] measured the emission spectrum of this species, and observed a broad feature that peaked at 670 nm. Prior to their report, emission from the protonated species had not been reported to our knowledge.

The chemistry of perylene in acidic and oxidizing environments has been thoroughly investigated, and the radical cation is the primary perylenic species in CSA [2,5,7–13]. Buck et al. [14] and Aalbersberg et al. [6,15] have demonstrated that protonated arenes are in equilibrium with the oxidized species when an oxidizer is present in solution, and the equilibrium depends on the basicity constant of the arenes as well as their oxidation potentials [16,17]. Shine and coworkers have published a series of papers enumerating the reactive pathways of the perylene radical cation [18–20], and offered pathways to the formation of hydroxylated perylene, dihydroxy-perylene and ketones of perylene. The postulated reaction pathways involve intermediates composed of mixed dimers of neutral perylene with reactive perylene derivatives.

In a recent study of femtosecond ionization of perylene in nonpolar solvents, we postulated that the excited perylene

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radical cation can engage in photochemistry with the solvent. On the basis of Gumy and Vauthey's spectral assignment of the 620 nm emission from perylene in CSA, we suggested that hydrogen abstraction may be a viable relaxation pathway. However, the apparent discrepancy between the PeH$^+$ spectrum reported by Gumy and Vauthey [1] in CSA and the PeH$^+$ spectrum reported by Thomas and coworkers [2] in acidic zeolites has motivated us to investigate the spectral properties of perylene radical cation and its reaction products in CSA. In this paper we demonstrate that perylene solubilizes into CSA as the protonated cation, and is then oxidized to the radical cation over a period of about 30 min. The absorption spectrum of the protonated cation is well separated from the dominant features of the radical cation spectrum. Thus, we can selectively excite the protonated perylene, and measure its emission spectrum shortly after preparation of the sample. This allows us to make an unambiguous assignment of the protonated perylene emission spectrum in CSA. We demonstrate that the resulting emission spectrum exhibits time-dependent behavior on a timescale of tens of minutes that is commensurate to the behavior observed in the absorption spectrum of the protonated cation. We also measure the fluorescence decay of the protonated perylene emission with picosecond time resolution. Excellent fit to a single exponential model function demonstrates that the emission arises from a single emissive species.

2. Experimental

Perylene (>99%) used was obtained from Fluka. The solid was pulverized into a fine powder prior to addition to CSA when samples were prepared by addition of the solid to CSA. Samples were also prepared by extraction of perylene into CSA from a hexane solution. The solvents used were obtained in the purest commercially available form, and used without further purification. Absorbance spectra were collected on a HP 8453 diode array spectrometer with 1 nm spectral resolution. Cells with an optical path length of 1 mm were used due to the strong absorbance of the perylene radical cation.

Steady-state fluorescence emission spectra were collected in a home-built scanning T-format fluorometer. The dispersed emission spectrum was collected through a monochromator in one arm of the instrument, and the fluorescence at a fixed wavelength was collected synchronously and simultaneously through the other arm to correct for fluctuations in the emission intensity due to sample and instrumental conditions. The emission slit widths were set at 1 mm, giving 4 nm resolution. Excitation spectra were obtained with a computer-controlled monochromator with a bandpass of 8 nm. Real time emission decays were measured at the peak of the emission spectrum, and the intensity was measured every 30 s. Fluorescence lifetime measurements via time-correlated photon counting utilized a mode-locked diode pumped Nd:YAG laser coupled to a dye

laser, cavity dumped at 4 MHz. The 625 nm excitation beam was vertically polarized and the emission was collected at the magic angle. The emission wavelength was selected with a colored glass filter (long pass 665 nm cutoff), and was collected by a microchannel plate PMT (Hamamatsu, R 3809U-50). The timing electronics have been described previously [21]. A typical instrument function has a 70 ps full-width at half-maximum. The data were analyzed by the iterative reconvolution method using software of our own design that utilizes the Marquardt–Levenberg algorithm to minimize chi-square.

3. Results

Visually, perylene exhibits several distinct color transformations as it dissolves in CSA. When large (as received) crystalline material is added to CSA, the solution immediately turns purple, which is characteristic of the presence of the radical cation. The crystallites dissolve slowly over a period of many minutes, giving rise to intricate visible patterns in solution. However, if the solid is pulverized prior to addition to CSA, it dissolves rapidly, and the solution initially appears green (Aalbersberg et al. [15] also observed the green initial color). Over the course of about 10 min the green solution turns light blue and then purple. The evolution of the solution's absorption spectrum is shown in Fig. 1. The prominent, sharp peak at 535 nm is the well-known radical cation $D_0 \rightarrow D_5$ absorption [22,23]. The features at 400 and 627 nm arise from the protonated perylene. These features are identical to the features in Aalbersberg's et al. [6] spectrum of Pe in anhydrous HF as well as the spectrum of the species observed in zeolites by Thomas and coworkers [2]. At early times the three features at 400, 535 and 627 nm cover most of the visible spectrum, with the notable exception of the 425–500 nm region, giving rise to the blue solution. Fast absorbance measurements indicate that the initial green color, which only lasts an instant, is the color of a solution of protonated perylene alone, with very little perylene radical cation present. These measurements cannot be made in ordinary cuvettes, because the strong Pe$^{\bullet+}$ absorbance is large within the timescale of the preparation of the solution. We have measured the early time absorbance spectrum by coating a microscope slide with solid perylene, and then contacting it with a drop of CSA on another microscope slide while collecting spectra with a 20 μs dwell time. The strong absorbance at 535 nm begins to grow in approximately 100 μs after initial contact. As time passes the PeH$^+$ features diminish, and the Pe$^+$ feature increases in intensity as shown in Fig. 1, reflecting the fact that PeH$^+$ is being oxidized. Within 20 min, the PeH$^+$ absorbance is no longer apparent, though fluorescence from the sample can be observed for 30–40 min after sample preparation. These observations indicate that formation of protonated perylene during solubilization of the solid or extraction from organic solvents is kinetically favored, even though
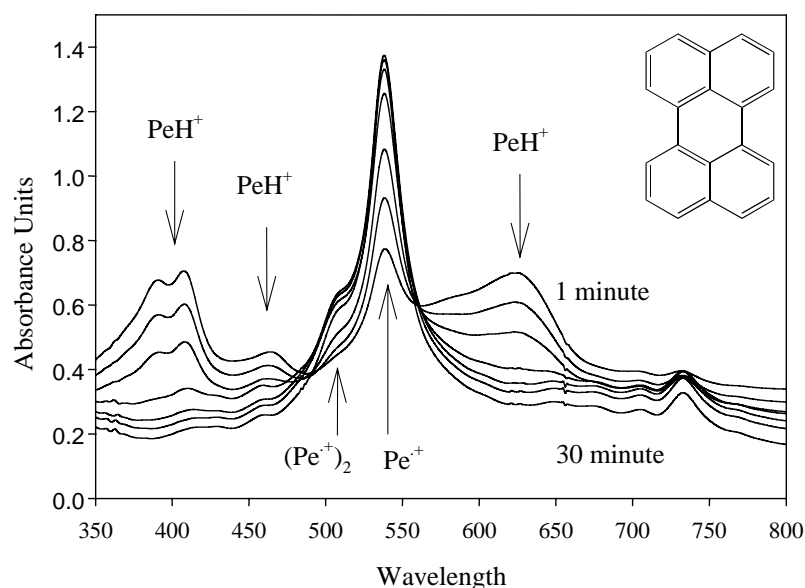
Fig. 1. Absorbance spectrum of perylene vs. time after extraction from hexane into concentrated sulfuric acid. The arrows indicate the evolution of spectral features as time increases. Time increments between addition of perylene to concentrated sulfuric acid and spectral collection time are 1, 3, 6, 10, 13, 20 and 30 min.

the radical cation is the thermodynamically stable species in CSA. Perylene radical cation has broad, weak absorptions across most of the red region of the spectrum from 540 to 800 nm, with a relatively strong feature at about 740 nm. When the concentration of the protonated form is low, it is difficult to identify absorbances related to this species, but prior to oxidation, the protonated species accounts for nearly all of the absorbance in the 620 nm region of the spectrum.

In bulk solution, we have observed an acceleration of the oxidation of protonated perylene when the initial mass of perylene added to the solution is increased. The concentration dependence of the oxidation suggests that protonated perylene can act as an oxidizing agent for another protonated perylene molecule. Herbst and Le Page [24] have shown that H atoms stick to PAH radical cations in the gas phase, reflecting the stability of protonated PAHs. Hirama et al. [25] have concluded from theoretical investigations that molecular hydrogen can be formed by reaction of protonated PAHs with atomic hydrogen through a nearly barrierless pathway. The PAH radical cation serves as a catalytic center that first captures an H atom to form the protonated species, and then catalyzes the formation of H_2 via reaction with a second H atom. They speculate that this reaction may be an important mechanism for H_2 formation in interstellar space. Our observation of concentration dependent oxidation of protonated perylene suggests that a bimolecular reaction of two protonated perylene ions may occur, with one molecule serving as the catalytic site, and the second serving as an H atom source. This hypothesis suggests that oxidation of protonated perylene in CSA may result in H_2 formation during the course of the dissolution process.

Fig. 2 shows the emission spectrum that is observed when PeH^+ is excited at 400 or 627 nm. The spectrum peaks at 670 nm and is consistent with the observation of PeH^+ in zeolites by Thomas and coworkers [2]. This is remarkable, given the considerable differences between the bulk environments of these systems. Equally important is the fact that this emission is shifted about 40 nm away from the peak position of the feature observed by Gumy and Vauthey [1]. To confirm the assignment, we have measured the fluorescence excitation spectrum of the 670 nm peak, which is shown in Fig. 3. The spectrum has been divided by the light source power spectrum and scaled to match the absorbance at 625 nm. Superimposed on this spectrum is the absorption spectrum of the perylene/CSA solution measured within 1 min of preparation. The 400 nm feature and the 627 nm feature in the absorption spectrum are observed. Slight intensity variations probably result from the 4 nm spectral bandwidth of the light source. The 670 nm scattered light appears as a shoulder on the 625 nm band. There is no sharp excitation feature at 580 nm, indicating that the 620 nm emission observed by Gumy and Vauthey [1] does not arise from PeH^+. The time dependent behavior of the excitation spectrum mimics that of the absorption and emission spectra. Real time decays of these three spectral signatures are presented in Fig. 4. The rise of the prominent radical cation feature monitored at 538 nm is commensurate with both the decay of the PeH^+ absorbance monitored at 393 nm, and the decay of the PeH^+ emission monitored at 665 nm. The exponential time constants for all four features are given in Fig. 4, and are identical to one another within the uncertainty of the measurement. This indicates that the loss of PeH^+ is correlated with the increase in $Pe^{\bullet+}$ concentration,
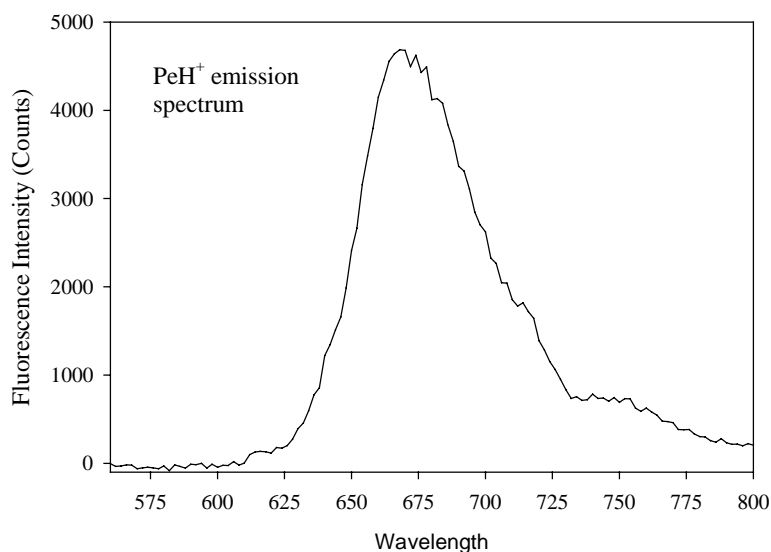
Fig. 2. Emission spectrum of PeH$^+$ collected from a freshly prepared sample of perylene in concentrated sulfuric acid, with 625 nm excitation.
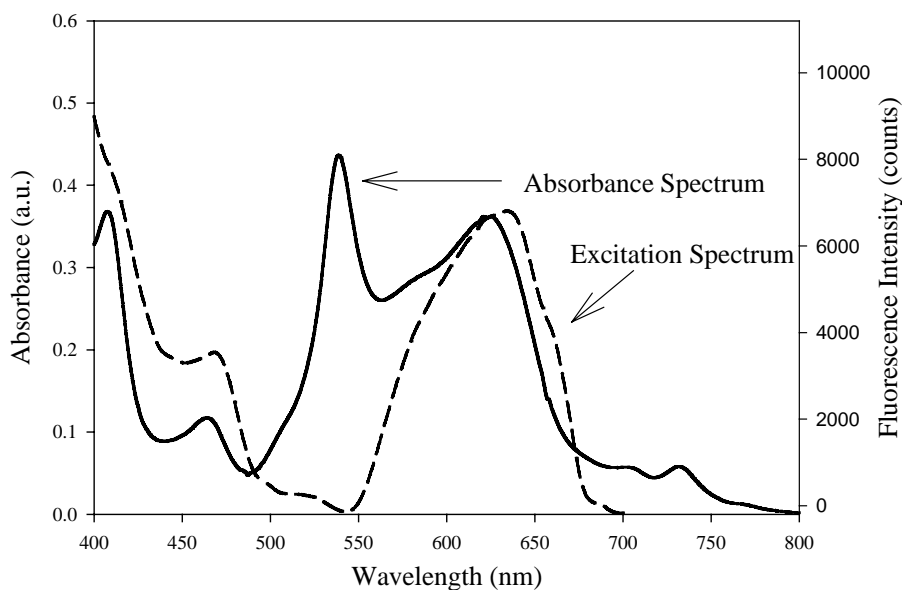

Fig. 3. Absorbance and excitation spectra of perylene in concentrated sulfuric acid. Spectra were taken 3 min after addition of perylene to concentrated sulfuric acid.

and is consistent with the postulate that protonated perylene is oxidized directly to the radical cation. Kinetic modeling of this reaction is currently in progress.

The fluorescence decay profile of the 670 nm emission is shown in Fig. 5 along with the instrument function and an exponential model function convoluted with the instrument function. The measurement was made on a freshly prepared sample of perylene in CSA excited at 620 nm, and was completed within about 5 min of initial preparation of the solution. The emission exhibits single exponential decay, with a time constant of 5.78 ns, and a χ^2 value of 1.07. The decay indicates that the 670 nm emission arises from a single species in solution, protonated perylene.

4. Discussion

Our results provide unambiguous evidence that protonated perylene emits at 670 nm in CSA. However, we have also observed the 620 nm emission reported by Gumy and Vauthey [1] when the solution is excited in the 530–610 nm region. Two peaks are evident, one at ∼580 nm and the other at 620 nm. The relative intensity of the peaks depends on the age of the sample, and in fact old samples (>2 weeks after preparation) show a strong third peak at ∼635 nm. Excitation spectra of the 580 and 620 nm features appear to exhibit continually shifting excitation maxima as the emission wavelength is shifted, which is characteristic of strongly overlapped spectral features, and may also reflect the sen-
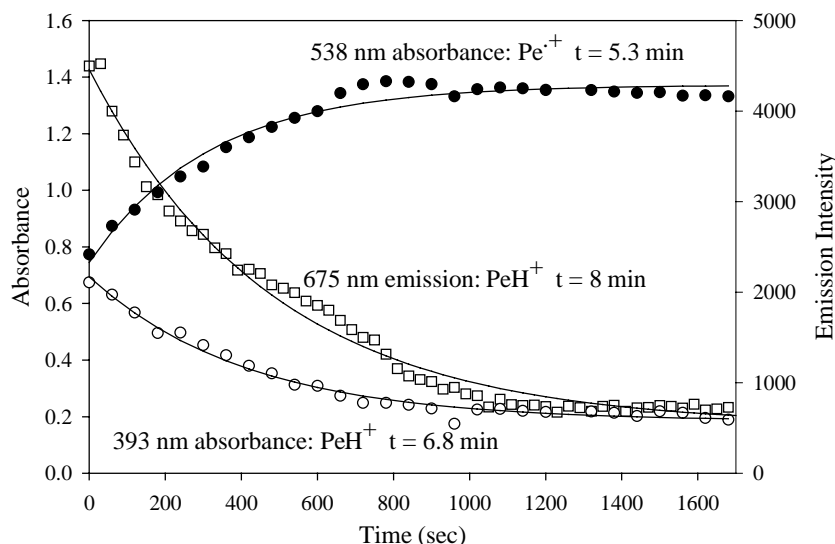
Fig. 4. Real time evolution of absorbance and emission spectral features. Commensurate decay and rise times are consistent with direct conversion of PeH$^+$ to Pe$^{\bullet+}$.
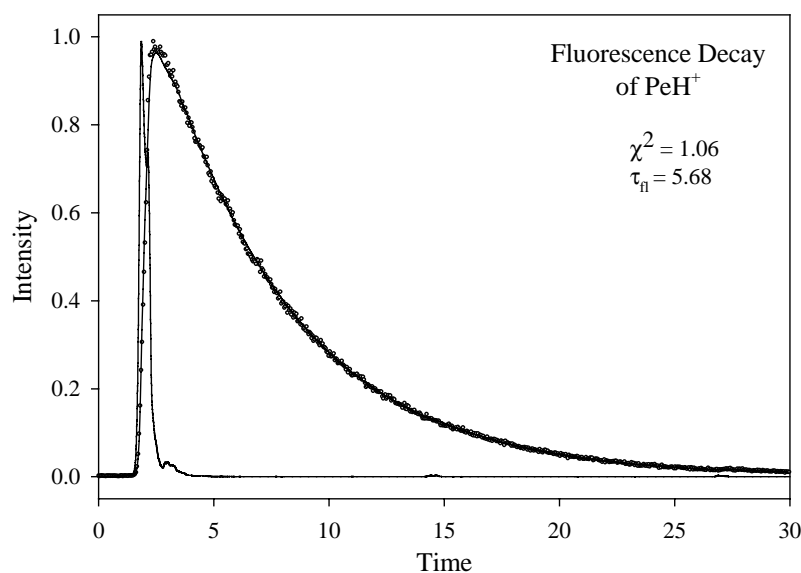

Fig. 5. Fluorescence decay of PeH$^+$ in concentrated sulfuric acid. The decay was collected through a 665 nm cutoff filter with 625 nm excitation. The measurement was completed within ~10 min of sample preparation.

sitivity of the emissive species to specific solvent environments. These results suggest that the 580 and 620 nm peaks result from two distinct species, though we have not yet confirmed the species responsible for the emission. They may result from stable ionic dimers, possibly including a dimer composed of a neutral and a radical cation (Pe$^{\bullet}$Pe$^{\bullet+}$) or a dimer composed of two radical cations (Pe$^{\bullet+}$)$_2$. The former has been observed by Meot-Ner in the gas phase, who has measured the free energy of association in the gas phase as ~35 kJ/mol [26]. The latter species is known to be stable in CSA, with a free energy of association of ~17 kJ/mol [27]. This species gives rise to absorption at 508 nm, which is ob-

served as a shoulder in Fig. 1. Excitation of this prominent absorption feature does not result in strong emission in the 580–620 nm region. The emission quantum yields of these species may also be sensitive to the excitation wavelength due to the possibility of dimer or proton dissociation at relatively high excitation energies. These issues are still under investigation.

The fluorescence lifetime of PeH$^+$ is similar to the 4.5 ns fluorescence lifetime of the neutral parent, in contrast to the fluorescence decay of protonated anthracene and pyrene in zeolites reported by Thomas and coworkers [2]. In zeolites the fluorescence lifetime of protonated anthracene is

1 ns, compared to the 5 ns lifetime of the neutral parent in liquid solution, and the fluorescence lifetime of protonated pyrene is 4 ns, compared with ∼250 ns lifetime of the neutral parent in liquid solution. These comparisons suggest that protonated arenes in zeolites may relax by nonradiative mechanisms that are not operative in liquid solution. We are testing this postulate further via studies of the fluorescence lifetimes of protonated anthracene and pyrene in CSA.

Acknowledgements

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