

$\Delta S^\circ_{\text{mic}}$  and  $\Delta H^\circ_{\text{mic}}$  of ED, lower than those of nonionic  $\text{RD}_2$ , can probably be attributed to the slight differences between the hydrophobicity of the two nitrogens present in the  $\text{RD}_2$  with respect to the two oxygens of the ED molecules and/or to the different flexibility of the rings of the heterocyclic ether and the monoether chains.

We finally consider the thermodynamic parameters for the adsorption process summarized in Table VI.

Note that the thermodynamic parameters of adsorption have the same sign but greater absolute values as those for the micellization. This result reflects the different geometrical organ-

ization of the surfactant molecules in the micellar aggregates and in the monolayer films at the air-water interfaces.<sup>42</sup> It can be rationalized considering that the major contribution to the thermodynamic parameters of adsorption and of micellization comes from the interactions of the chains with interfaces in the former case but from the interactions between the chains in the latter.<sup>23</sup>

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## Solvent Effects on the Photophysical Properties of Pyrene-3-carboxylic Acid

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The photophysical properties of pyrenecarboxylic acid  $\text{PCOOH}$  have been studied in liquids of different polarity. In polar solvents the excited free acid  $\text{PCOOH}$  and anion  $\text{PCOO}^-$  are observed along with a protonated form of the excited acid  $\text{PCOOH}_2^+$ . The  $\text{pK}$  measured in water are  $\text{pK} = 5.2$  for  $\text{PCOO}^- + \text{H}^+ \rightleftharpoons \text{PCOOH}$  and  $\text{pK} = 6.1$  for  $\text{PCOOH} + \text{H}^+ \rightleftharpoons \text{PCOOH}_2^+$ . In moderately polar media such as methanol the excimer of  $\text{PCOOH}$  is formed via interaction of the excited dimer with  $\text{H}^+$ . No excimer is observed in nonpolar media. The established photophysical properties of  $\text{PCOOH}$  are used to illustrate its possible use as a monitor of vicinal and geminal OH groups readily distinguishable on silicas.

### Introduction

A number of luminescence probes have been developed for characterizing the properties of various microheterogeneous systems in solvents over a wide range of polarity.<sup>2-4</sup> By virtue of their photophysical properties, pyrene derivatives have gained a significant place among luminescence probes. For example, the vibronic band intensities in pyrene's monomer fluorescence are strongly dependent on the solvent dipole moment; thus, the so-called  $\text{III/I}$  ratio is an excellent probe for the microenvironment's polarity. The kinetic data of the pyrene excimer formation comments on its mobility in various microheterogeneous systems. Long-chain pyrenecarboxylic acids (the pyrene ring of which is separated from the carboxylic group by four or more  $\text{CH}_2$  groups) were successfully utilized to study the interaction of acids with colloidal surfaces.<sup>4,5</sup> Aminopyrene was recently used<sup>6</sup> to investigate the relative contributions of geminal and vicinal OH groups on silica surfaces; the different acidities of the two types of groups produced either the excited aminopyrene or the excited protonated forms of the probe.

Pyrenecarboxylic acid (PCA) may also prove to be a useful probe, as the two chromophores being in close proximity may produce interesting features on surfaces. Previous work<sup>7,8</sup> on the photophysics of PCA showed large discrepancies in the values of the protolytic equilibrium constants of the excited singlet state, which raised some concern about the applicability of the Förster cycle when applied to weak aromatic bases and acids.<sup>9</sup> Hence, the photophysics of PCA should be clarified before it can be used reliably as a luminescence probe. This paper deals with medium effects on the protolytic equilibria of both the ground and excited states of PCA and reports relevant spectra, and kinetic data. Initial studies of the probe in complex systems are also reported.

### Experimental Section

**Materials.** PCA (Molecular Probes), methanol and HCl (Fisher), benzene and cyclohexane (Aldrich), and glycerol

(Sargent-Welch) were of reagent grade and were used without further purification.

**Instruments.** A PRA nitrogen laser LN-1000 with a wavelength of 337.1 nm, a pulse width of 1 ns, and an energy of 1 mJ/pulse was used as an excitation source for PCA emission decay measurements. A Hamamatsu Photonics multichannel plate photodetector R 1644 U (0.3-ns rise time) connected to a Tektronics 7912 AD transient capture device was used to monitor the short-lived species formed. The data were subsequently analyzed on a Tektronics 4052 A microcomputer. Steady-state absorption and emission spectra were recorded on a Perkin-Elmer 552 spectrophotometer and a Perkin-Elmer MPF 44B spectrofluorometer, respectively.

### Results and Discussion

**Aqueous Solution.** Figure 1a shows the absorption and emission spectra of PCA in water at pH 13. It can be observed that in a basic medium the absorption and emission spectra are mirror images of each other and resemble that of pyrene. A small bathochromic shift in the absorption spectrum, a slight increase in the extinction coefficient of  $^1\text{A}_g \rightarrow ^1\text{L}_b$  transition, and a well-structured emission spectrum indicate a weak influence of the carboxylic anion on the  $\pi$  electrons of the pyrene ring. Figure 1b shows the absorption and emission spectra of PCA at pH 3.3. It can be noted that the extinction coefficient of the  $^1\text{A}_g \rightarrow ^1\text{L}_b$  transition has grown 1 order of magnitude with respect to the anionic form and that the second singlet state  $^1\text{L}_a$  has a less pronounced vibrational structure. This can be understood as a

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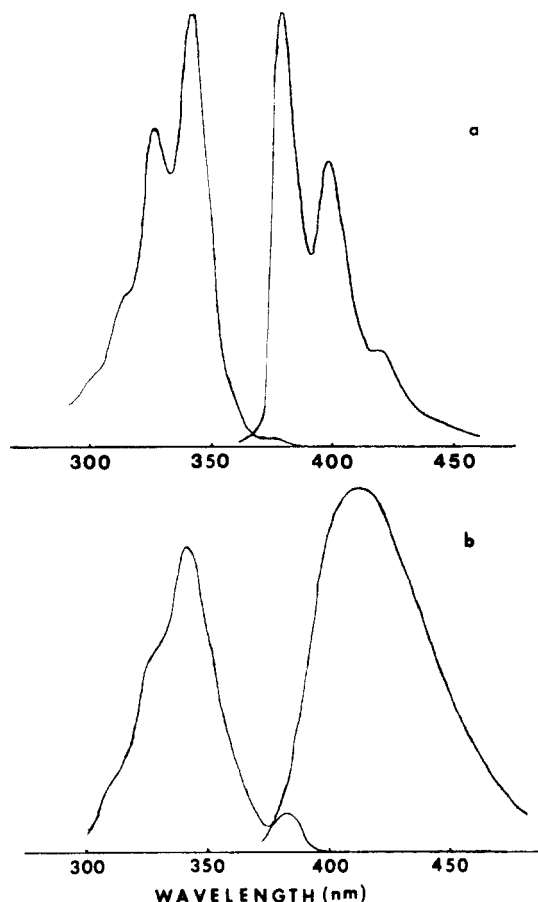
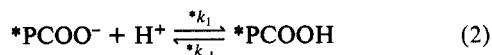
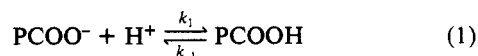


Figure 1. Absorption (left) and emission (right) spectra of PCA in aqueous solutions at 295 K: (a) pH 13; (b) pH 3.3.

consequence of the stronger mixing of the  $\pi\pi^*$  and  $n\pi^*$  states.

Previous studies of the protolytic equilibria in aqueous solutions of PCA resulted in the scheme



where eq 1 corresponds to the ground state, while eq 2 corresponds to the first singlet excited state. As there is a big discrepancy in the published values of the equilibrium constants in the ground state and excited state ( $\Delta \text{pK} = \text{pK} - ^*\text{pK}$ ), the measurements were repeated. The application of the Förster cycle led to two different values of the  $\Delta(\text{pK})$ , namely, if the energies of the  $0 \rightarrow 0$  transitions were determined by means of the wavenumbers, measured at half-intensities, of the bands, a  $\Delta(\text{pK}) = -4.2$  was obtained. On the other hand, if the energies of the  $0 \rightarrow 0$  transitions were determined as an intersection point of the absorption and excitation spectra,  $\Delta(\text{pK}) = -1.4$  was obtained. It is pertinent to note that the former value is in a good agreement with the value reported by Vander Donckt et al., while the latter is the same as that found by Perez and Fendler. Such a big difference in the  $\Delta(\text{pK})$  values, taken together with the lack of structure in the emission spectrum at pH 3.3, indicates a more complicated protolytic equilibrium than that proposed earlier. In order to gain further insight to the phenomena studied, transient emission experiments were performed.

The steady-state data indicated 380 nm to be a convenient wavelength to monitor kinetics of the anionic form of PCA, as this is the only emitting species at that particular wavelength. It was found, in a basic aqueous solution, that the excited anion of PCA decays with the rate constant of  $2.3 \times 10^7 \text{ s}^{-1}$ . Upon decreasing the pH, the emission decays faster maintaining first-order kinetics. From the slope of the plot of  $K$  vs  $[\text{H}^+]$  a rate constant of  $(1.0 \pm 0.1) \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  is obtained for the reaction

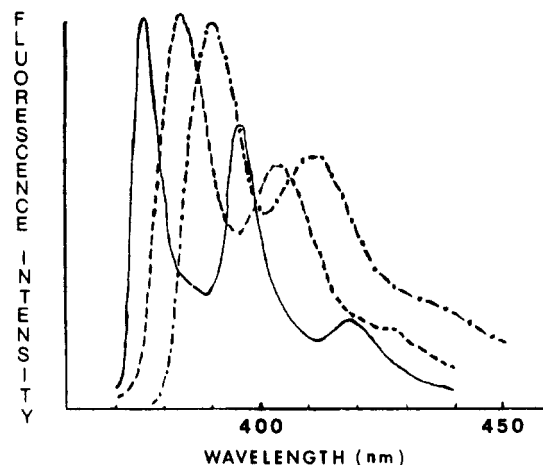
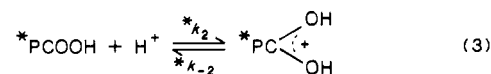


Figure 2. PCA emission spectra at 77 K; 20% glycerol-water, pH 13 (solid line); 20% glycerol-water, pH 2 (dashed line); 1:1  $\text{H}_2\text{SO}_4$ -water (dotted-dashed line).

TABLE I: Maxima of PCA Emission Spectra at 77 K Corresponding to Various Ionic Forms

vibronic transition	$^*\text{PCOO}^-$ , nm	$^*\text{PCOOH}$ , nm	$^*\text{PCOOH}_2^+$ , nm
0,0	376	384	391
0,1	397	404	411
0,2	416	425	

of  $\text{H}^+$  with the excited anion of PCA. However, it should be noted that in the region below pH 4, the decay is complex and does not obey pseudo-first-order kinetics. This is an additional indication that another equilibrium operates in the system at low pH. To elucidate the problem, PCA emission spectra were compared at 77 K and at room temperature. At 77 K, the solid matrix obtained prevents any motion of the reacting species, thus providing "pure spectra" without interference of the other emitting species that might be produced on illumination of the system. Figure 2 shows that in basic medium the spectra obtained at room temperature and 77 K are in good agreement. However, the spectra corresponding to the acid medium of pH 2 differ greatly. In contrast to the one obtained at room temperature (shown in Figure 1), the emission spectrum at 77 K is well structured and exhibits a much smaller Stokes shift. This can be rationalized in the following way: there is an additional protolytic equilibrium of the excited neutral form of PCA:



The photophysics of PCA in an acid medium can be understood in terms of an increasing electron-withdrawing ability of the acidic functionality  $\text{COO}^- < \text{COOH} < \text{COOH}_2^+$ . The protonated form very strongly affects the  $\pi$ -electron system of the pyrene ring. The lack of vibrational structure in the emission spectrum can be attributed to the free rotation around the C-C bond connecting the pyrene ring and the carboxylic group. In order to confirm the above statement, the emission spectrum of PCA was taken at 77 K in an extremely acid medium of 1:1 water- $\text{H}_2\text{SO}_4$ , where it is expected that PCA is protonated even in its ground state. Indeed, the spectrum shown in Figure 2 is shifted 7 nm with respect to that corresponding to the neutral form; the vibrational structure is retained as a frozen medium prevents the free rotation. The assignments of the vibrational bands are summarized in Table I.

To provide additional evidence for a two-step protolytic equilibrium of excited PCA, transient emission experiments were performed. In PCA solutions at pH 4 which are close to the  $\text{pK}_1$  value (3.8), all three species should be present on illumination. The acid functionality exhibits a marked influence on the  $\pi$  electrons of the pyrene ring, which should affect the photophysical properties, e.g., fluorescent lifetimes of the corresponding excited

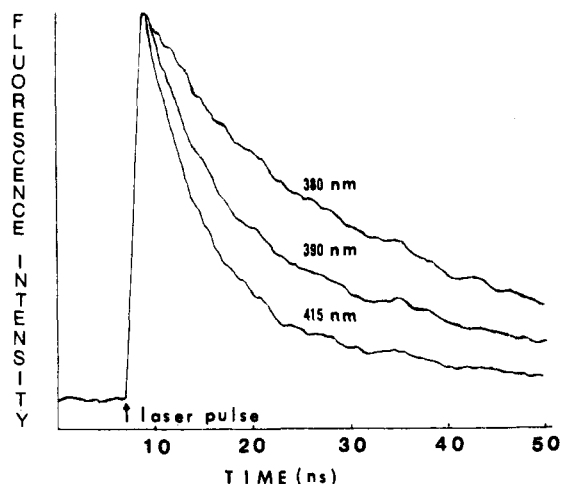


Figure 3. Fluorescence decays obtained at various wavelengths upon excitation of PCA in an aqueous solution of pH 3.9.

species. This effect can be used to identify the various species by kinetic analysis. The experimental results obtained with PCA solutions of pH 3.9 are shown in Figure 3. The decay of the  $\text{PCOO}^-$  species emitting at 380 nm is slower than the decay of the  $^*\text{PCOOH}$  species emitting at 390 nm, which is also slower than the emission decay at 415 nm, which corresponds to the  $^*\text{PCOOH}_2^+$  species. Studies performed with PCA solutions at pH < 2, i.e., a situation where  $^*\text{PCOO}^-$  does not exist, and where the protonation of  $^*\text{PCOOH}$  is very fast, showed that the  $^*\text{PCOOH}_2^+$  lifetime decreases on decreasing the  $\text{H}^+$  concentration. From the plot of  $K$  vs  $[\text{H}^+]$  a rate constant of  $(8 \pm 1) \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  was obtained for the quenching of  $^*\text{PCOOH}_2^+$  by a hydronium ion.

Further conformation of the photophysical scheme comes from the studies performed with moderately polar media.

**Methanol Solution.** Figure 4 shows the absorption and emission spectra of PCA in methanol. The upper spectra correspond to an alkaline solution of 1 g of NaOH/1000 mL. It can be observed that the spectra are nearly identical with those obtained in basic aqueous solution. The lower spectra correspond to a solution that has been acidified with HCl ( $5 \times 10^{-4} \text{ mol dm}^{-3}$ ). The absorption spectrum clearly shows that PCA is in a neutral form. However, in contrast to the situation in a moderately acid aqueous solution, the emission spectrum in methanol possesses vibrational structure. This was taken as evidence that the excited neutral form of PCA undergoes a protonation in acid aqueous solutions. The fact that this does not occur in the methanol solution could be attributed to the dielectric constant of methanol, which is lower than that of water; a less polar medium tends to destabilize charged species and the equilibrium moves more toward the neutral species. Figure 5 shows the spectra of PCA in a solution of 0.4 mol  $\text{dm}^{-3}$  HCl in methanol. It can be observed that a new broad emission band with a maximum at 465 nm appears. However, no such band exists in the spectrum taken at 77 K. Transient emission experiments showed that, in methanol-glycerol solutions, the rate of build-up of the species emitting at 465 nm decreases with increasing viscosity. Lowering the temperature has a similar effect, which also proves that some chemical reaction involving either HCl or  $\text{H}^+$  is required to bring about the new emission band. The possibility that the emission originates from a charge-transfer complex formed by PCA and HCl in their ground states can thus be ruled out.

By analogy with the behavior of PCA in aqueous solutions it may be concluded that the change in the spectrum is due to protonation of PCA; i.e., the emission centered around 465 nm originates from  $^*\text{PCOOH}_2^+$ . However, the emission maximum of the protonated form of PCA in aqueous solution is at 415 nm, and it is difficult to rationalize such a big difference in the Stokes shift in terms of a solvent effect. On the other hand, the emission maximum coincides with that of a pyrene excimer. Since all carboxylic acids exist in low-polar solvents in the form of dimers,

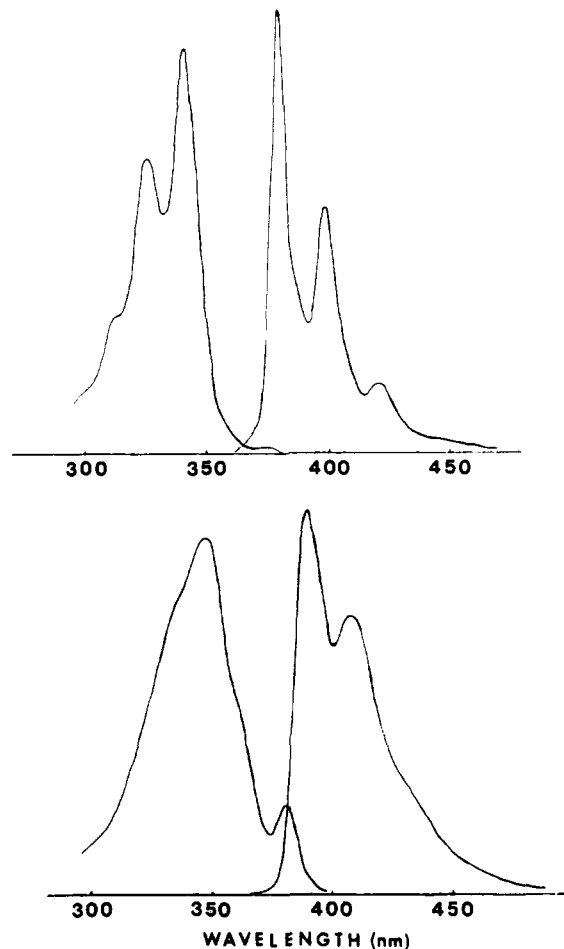


Figure 4. Absorption (left) and emission (right) spectra of PCA in methanol solutions at room temperature. Upper spectra correspond to 0.1% NaOH solution while lower spectra correspond to  $5 \times 10^{-4} \text{ mol dm}^{-3}$  HCl.

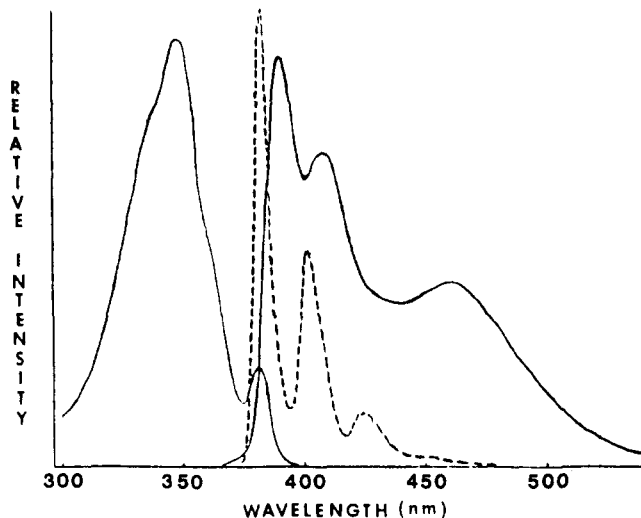
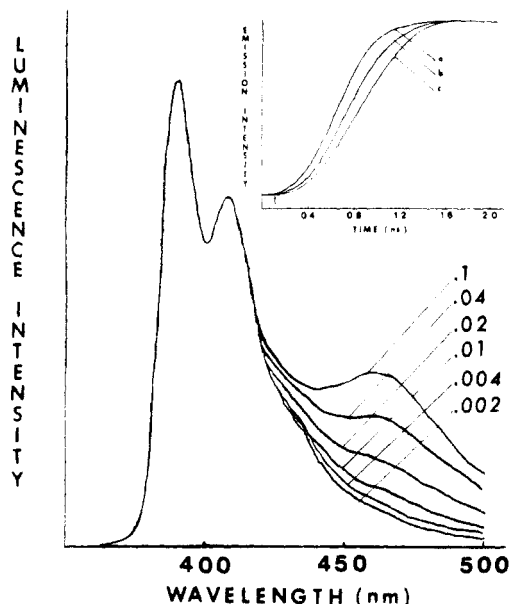


Figure 5. Absorption and emission spectra of PCA in acid-methanol solution (0.4 M HCl). The solid line corresponds to room temperature, while the dashed line corresponds to 77 K.

it is suggested that, on illumination, the hydrogen bond breaks, which is followed by excimer formation. The enhancement of the emission band centered around 465 nm on increasing the HCl concentration (Figure 6) can be interpreted as involvement of  $\text{H}^+$  in the hydrogen bond cleavage.

In order to resolve which mechanism is operative in the system, the transient emissions at 390 and 470 nm were monitored and shown in the insert of Figure 6. Two PCA-methanol solutions were prepared containing 0.01 and 0.1 mol  $\text{dm}^{-3}$  HCl. It was



**Figure 6.** Effects of HCl concentration ( $\text{mol dm}^{-3}$ ) on PCA emission spectra in methanol solutions. The insert shows the initial intensities of the PCA emission following the laser pulses. See text for details.

found that the initial emission intensity at 390 nm matches the profile of the laser pulse (curve a), while the emission at 465 nm exhibited intricate kinetics. The maximum intensity of the emission in a solution of  $0.1 \text{ mol dm}^{-3}$  HCl (curve c) was about 3 times larger than that of a solution containing  $0.01 \text{ mol dm}^{-3}$  (curve b). Normalization of the decay curves shows that it takes longer to reach the maximum emission intensity at the higher HCl concentration. The  $\text{PCOOH}_2^+$  formation should follow simple pseudo-first-order kinetics; i.e., the build-up should be faster upon increasing the  $\text{H}^+$  concentration. Therefore, it is concluded that the emission at 465 nm is due to excimer formation.

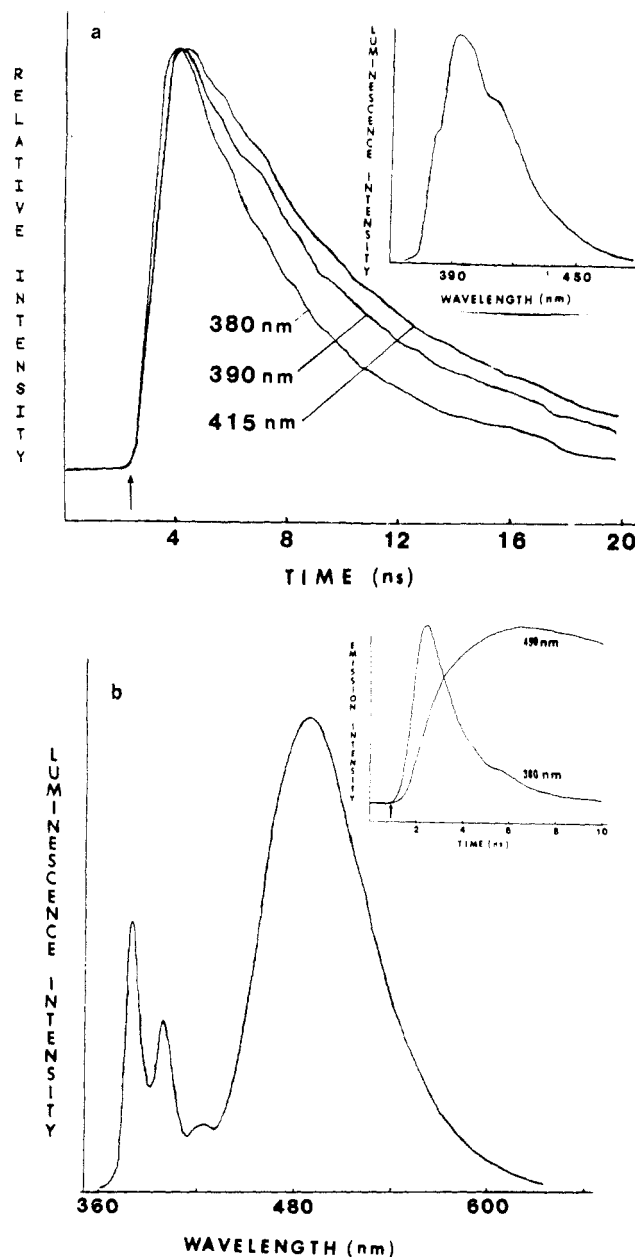
**Low-Polarity Solvents.** The absorption and emission spectra of PCA in benzene, *n*-hexane, and cyclohexane solutions are not reported as all of them correspond to spectra in weakly acid-methanol solution. The absorption spectra show that PCA is in a neutral form in all the solutions. The emission spectra are well-structured and resemble spectra observed with methanol as a solvent. No emission maximum was observed around 465 nm, indicating that no excimer is formed although the short lifetime ( $\sim 5 \text{ ns}$ ) of the excited state indicates that the acid is in the form of a dimer. This can be attributed to a strong hydrogen bonding in solvents of low polarity which prevents excimer formation.

**PCA in CTAC Micellar Solutions.** PCA ( $2.0 \times 10^{-5} \text{ M}$ ) in micellar cetyltrimethylammonium chloride (CTAC,  $10^{-2} \text{ M}$ ) at neutral pH exhibits absorption and emission spectra indicative of the anionic form of PCA (Figure 7a). This is confirmed by identical decay rates for emission at 380 and 380 nm with a lifetime of 2.3 ns. This lifetime is shorter than that found in water (30 ns) and is attributed to quenching of the excited state by the quaternary ammonium group.

Increasing the bulk pH of the medium to 3.4 leads to a slight increase in the absorption spectrum at 350 nm. This is due to 5% of PCA in the free acid form, the rest being in the anionic form. This shows, not unexpectedly that the pH at the CTAC micelle surface is not 3.4, or that of the bulk.

The emission spectrum of this system shows that all excited states of three forms are present,  $\text{PCOO}^-$ ,  $\text{PCOOH}$ , and  $\text{PCOOH}_2^+$ . The micelle surface now affects the rate of formation of the protonated species and produces data that are contrary to those found in water (Figure 3). In the micellar system the decay rates of the various species are  $\text{PCOOH}_2^+$  ( $\lambda = 415 \text{ nm}$ )  $<$   $\text{PCOOH}$  ( $\lambda = 390 \text{ nm}$ )  $<$   $\text{PCOO}^-$  ( $\lambda = 380 \text{ nm}$ ) (Figure 7a).

Decreasing the CTAC concentration to a system of  $2 \times 10^{-5} \text{ M}$  PCA and  $2 \times 10^{-3} \text{ CTAC}$  leads to further modification of the photophysics. The PCA absorption spectrum exhibits a weak absorbance at 380 nm and a pronounced peak at 333 nm, indi-

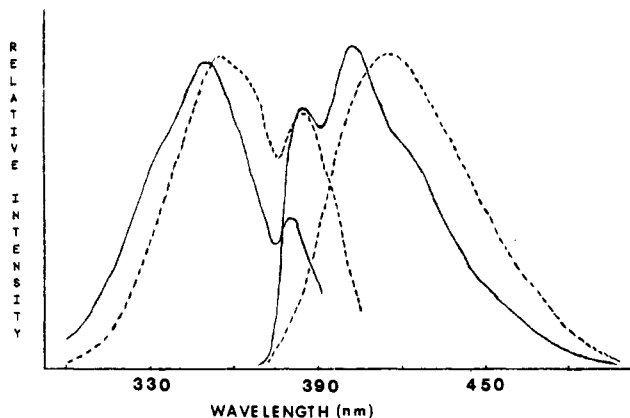


**Figure 7.** (a) Fluorescence spectrum of PCA in micellar CTAC solution. Decay of emission of various excited forms of PCA in micellar CTAC solution: 415 nm,  $\text{PCOOH}_2^+$ ; 390 nm,  $\text{PCOOH}$ ; and 380 nm  $\text{PCOO}^-$ . (b) Emission spectrum of PCA in CTAC micellar solution. The insert shows the time-resolved emission intensities corresponding to the monomer (lower curve) and excimer (upper curve).

cative of the anionic form of the acid (Figure 7b). The emission spectrum indicates that  $\text{PCOO}^-$  ( $\lambda = 380 \text{ nm}$ ) and the excimer ( $\lambda = 490 \text{ nm}$ ) are present. This is due to the enhanced PCA content of each micelle. The excimer is formed dynamically via decay of  $\text{PCOO}^-$ . It is interesting to note that the carboxylic acid group on the pyrene ring does not inhibit excimer formation.

**PCA in Solid Silica Surfaces.** Earlier work<sup>6</sup> with aminopyrene showed that the photophysics of this molecule could be used to distinguish vicinal and geminal OH groups on silica surfaces. PCA can be used in a similar manner, and relevant data are shown in Figure 8.

**Vicinal OH Groups.** The Fisher Scientific Co. silica, which contains vicinal OH groups, exhibits a PCA excitation spectrum which contains 25% in a neutral form and 75% in an anionic form. The emission spectrum also shows that both PCA forms are present on the silica surface. The data indicate that the "microenvironment" of PCA on this surface corresponds to an aqueous solution of pH 4.1. The rate of decay of the  $\text{PCOO}^-$  anion of  $3.8 \times 10^7 \text{ s}^{-1}$  also corresponds to a pH of 4.1. However,



**Figure 8.** Emission and excitation spectra of  $1 \times 10^{-7}$  mol/g of PCA adsorbed on silica surfaces. The solid line corresponds to the MCB silica gel/cyclohexane matrix, while the dashed line corresponds to the Fisher silica/cyclohexane matrix.

it is not possible to place a meaningful pH to the whole silica surface as local interactions of the PCA with the OH site control the photophysics.

**Geminal OH Groups.** The Matheson Coleman Bell Co. silica, which contains geminal OH groups, exhibits photophysical properties of PCA which indicate that the acid is entirely in the neutral form, i.e., an extremely acidic surface.

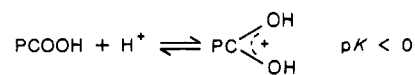
The emission spectrum of PCA on this surface indicates that only  $^*\text{PCOOH}_2^+$  is present. Transient experiments show that the proton uptake by  $^*\text{PCOOH}$  is very rapid and well short of  $10^{-9}$  s.

The emission of  $^*\text{PCOOH}_2^+$  at 415 nm decays with a rate constant of  $1.9 \times 10^8 \text{ s}^{-1}$ , indicating that quenching of  $^*\text{PCOOH}_2^+$  by  $\text{H}^+$  takes place on the surface. The data indicate that the "microenvironment" of PCA on the surface corresponds to a pH of 1.6 in an aqueous solution. The same caution used in pH studies of vicinal OH also apply here.

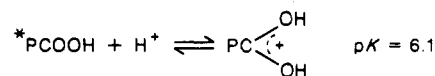
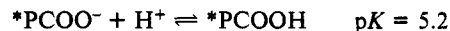
### Conclusions

The photophysics of PCA is strongly affected by medium polarity:

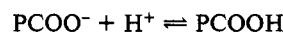
1. In polar solvents, such as water, the ground state of PCA is involved in a two-step equilibrium:



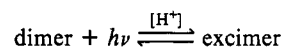
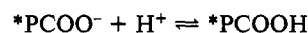
The first singlet excited state exhibits similar behavior, but the  $\text{p}K$ 's differ significantly from those corresponding to the ground state:



2. In moderately polar media, such as methanol, due to hydrogen bonding the ground-state equilibria are altered compared with those in water:



Consequently, the excited-state equilibria are



The excimer formation is controlled by the  $\text{H}^+$  concentration as the first reaction step is a hydrogen bond cleavage involving  $\text{H}^+$ .

3. In media of low-polarity PCA exists as a dimer in its ground state. However, no excimer was found on excitation which can be attributed to strong hydrogen bonding.

4. The photophysical properties of PCA respond in an acknowledged way to the environment of a cationic micelle, in particular pH.

5. PCA may be used to distinguish between geminal and vicinal OH groups on silica surfaces.

**Registry No.** PCA, 19694-02-1;  $\text{PCOO}^-$ , 93638-12-1;  $\text{PCOOH}_2^+$ , 113748-27-9; CTAC, 112-02-7; HCl, 7647-01-0; glycerol, 56-81-5; water, 7732-18-5; methanol, 67-56-1; cyclohexane, 110-82-7.

## Dielectric Relaxation with Kinetic Irreversible Transition

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A model of dielectric relaxation accompanied by an irreversible transformation of relaxing moieties is presented. Calculations show that for a heating with constant rate there are some maxima on the  $\epsilon'$  vs  $T$  plots. The heights of the peaks decrease when the frequency of electrical field increases. That result is qualitatively consistent with some experimental data published elsewhere. In addition, the model predicts an influence of the heating rate on the heights and positions of the  $\epsilon'(T)$  peaks. Unfortunately, that conclusion has not been confirmed yet experimentally.

### Introduction

Recently, two papers have appeared (ref 1 and 2) in which the pronounced maxima of dielectric permittivity  $\epsilon'$  as a function of temperature  $T$  have been observed. In the first reference some cured polyimides have been investigated, and in the second reference the polyepichlorohydrin-nitrobenzene system was treated.

It was shown there that at nearly constant rate heating the heights of the maxima decrease when frequency of the electric field increases. The observed behavior, i.e., appearing of the maxima, have been suggested to be either a kinetic transformation leading to a new conformation of the epichlorohydrin polymer chains<sup>2</sup> or a reordering of molecular movements connected with an irre-

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