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Photolysis of 1-pyrenemethylamine ion-exchanged into a zirconium phosphate framework

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Abstract

The photolysis of the luminescence probe 1-pyremethylamine (PYMA) ion-exchanged into a layered zirconium phosphate (ZrP) framework has been studied. The ZrP used was an hydrated form of α-ZrP with six water molecules per formula unit and with an interlayer distance of 10.3 Å. The luminescence spectrum for a PYMA ion-exchanged in ZrP (PYMA-exchanged ZrP) colloidal suspension in aqueous solution, after irradiation, shows a rapid decrease of the most intense peak at 376 nm and an increase of the peak at 383 nm of the PYMA molecule. The photolysis of a PYMA aqueous solution proceeds slowly to give a luminescence spectrum similar to that observed upon photolysis of PYMA-exchanged ZrP. We have identified pyrene, 1-hydroxypyrene, 1,6-pyrenedione, and 1,8-pyrenedione as stable photoproducts using steady-state luminescence spectroscopy, high performance liquid chromatography, and UV–vis spectrophotometry. The XRPD pattern for PYMA-exchanged ZrP, after photolysis, shows that the photoproducts remain entrapped between the layers. The influence of polarity of the solvent and the presence of air, nitrogen, or oxygen on the formation of the photoproducts have been investigated. Based on the photoproduct identification a reaction mechanism is proposed involving the formation of radicals.

Keywords: Zirconium phosphate; 1-Pyrenemethylamine; Intercalation; Photolysis; Luminescence

1. Introduction

The photolysis of polynuclear aromatic hydrocarbons (PAHs), such as pyrene (PY) and its derivatives, absorbed on heterogeneous microenvironments such as alumina, carbon black, fly ash, silica gel and micelles have been studied [1–3]. The PAHs photodegradation depends on the physical and chemical nature of the substrate to which the PAHs are absorbed. There are substrates that absorb most of the light, stabilizing the reactive PAHs by preventing the light from reaching the PAHs [1]. The photolysis of PY in water and in micellar media leads to the formation of 1,6-pyrenedione and 1,8-pyrenedione as stable photoproducts and 1-hydroxypyrene (PYOH) as a product of the initial photochemical oxidation [2]. The irradiation of PY at the air/solid interface of unactivated and activated silica gel produces PYOH, 1,6-pyrenedione and 1,8-pyrenedione, among the main reaction photoproducts [3]. The zirconium phosphate layered materials offer a unique chemical microenvironment suitable to establish comparisons of PAHs photolysis with other microheterogeneous environments.

The zirconium phosphate layered materials are very attractive because they exhibit behavior as ion-exchangers, catalysts, photocatalysts and hosts for intercalation of a broad spectrum of guests [4,5]. Zirconium bis(monohydrogen orthophosphate) monohydrate ($Zr(HPO_4)_2 \cdot H_2O$), also called α-zirconium phosphate (α-ZrP), is the most studied zirconium phosphate. The zirconium atoms lie nearly in a plane and are joined by phosphate groups above and below the plane [4,5]. Three phosphate oxygens are bonded to each zirconium atom and the fourth is bonded to a hydrogen atom and points into the interlayer space [4,5]. The α-ZrP interlayer distance is 7.6 Å.

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La Ginestra et al. studied the photo-oxidation of alkylbenzenes and naphthalenes in the presence of the layered zirconium phosphate as photocatalyst [6,7]. These authors showed that the catalysis is a surface phenomenon, without any intercalation of organic molecules between the layers. The Brønsted acidic phosphate groups and the Zr^{4+} Lewis acid sites on the surface of the zirconium phosphate material play an important role in the behavior of this material as catalyst. In the absence of the catalyst, the layered zirconium phosphate, no reaction or very slow conversion reaction rates were reported. The authors suggested that zirconium phosphate is photoexcited and then an electron transfer occurs from the absorbed organic substrate to the excited inorganic phase, generating an organic radical cation.

Recently, we have reported the direct ion exchange of a cationic derivative of pyrene, 1-pyrenemethylamine (PYMA), into the 10.3 Å phase of ZrP (10.3 Å ZrP), and studied the nature of PYMA excimer formation in this phase through photophysical studies [8]. The 10.3 Å ZrP is a hexahydrated phase of ZrP that can easily exchange large cations, which are not exchanged into the monohydrated phase [9]. The luminescence spectrum of PYMA in aqueous solution shows a fine structured monomer region with four major peaks located at 376, 387, 396, and 417 nm; the peak at 376 nm is the most intense. We observed that to produce a PYMA-exchanged ZrP phase, PYMA must be at a high intercalation loading level in the reaction mixture (PYMA/ZrP solution molar ratios of 10:1, 5:1, and 1:1) to ion exchange into the interlayers of zirconium phosphate, instead of just exchanging on its surface (which occurred for PYMA/ZrP solution molar ratios of 1:50, 1:100, and 1:1000). In addition, a PYMA excimer band was observed at 458 nm for all loading levels except for the one prepared with a 1:1000 PYMA/ZrP solution molar ratio. This excimer band is absent in the luminescence spectrum of a 0.1 mM PYMA aqueous solution. The intensity of the PYMA excimer band increases at low PYMA loading levels, where PYMA is surface bound and not intercalated.

In this paper, we present the results of our investigation on the photolysis of PYMA-exchanged ZrP. Characterization techniques like steady-state luminescence spectroscopy, high performance liquid chromatography (HPLC), and ultraviolet-visible (UV–vis) spectrophotometry were employed in the identification of the photoproducts. The effect of solvent polarity and the presence of air, nitrogen, and oxygen were investigated to propose a reaction mechanism for the formation of the photoproducts.

2. Experimental

2.1. Materials

1-Pyrenemethylamine hydrochloride (PYMA, 95%), 1-pyrene (PY, 99%), 1-hydroxypyrene (PYOH, 98%), and zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, 98%) were obtained from Aldrich and used as received. All other chemicals were reagent grade and were obtained from commercial sources.

2.2. Samples preparation

The synthesis of 10.3 Å ZrP is reported elsewhere [10]. The direct ion exchange in a aqueous solution of PYMA into ZrP at different PYMA:ZrP solution molar concentration ratios was conducted as previously reported [8]. The PYMA-exchanged ZrP materials were prepared at the PYMA:ZrP solution molar concentration ratios of 1:1, 1:50, and 1:100; and referred to as 1:1 PYMA:ZrP, 1:50 PYMA:ZrP, and1:100 PYMA:ZrP.

2.3. Photolysis procedure

The photolysis experiments were conducted on colloidal suspensions of PYMA-exchanged ZrP (0.008%, w/v) and on PYMA-exchanged ZrP powder. The photolysis was carried out using a Xe–Hg 1000 W Oriel light source equipped with a 10 cm long cylindrical tube for water circulation to absorb the IR radiation. A Corning 7–54 band-pass filter was used to isolate the 230–450 nm wavelength region that overlaps well with the absorption band of PYMA. The cells were placed on an optical bench at a distance of 35 cm from the lamp housing. The effect of nitrogen or oxygen on the photolysis was studied by purging solutions with the respective gas for 30 min prior and during irradiations.

2.4. Photophysical measurements

Steady state luminescence measurements were obtained with a SE-900 spectrofluorometer (Photon Technology International, PTI) using a 150 W xenon lamp as the excitation source and a PTI Model 710 photon counting detector with a Hamamatsu R1527P photomultiplier. The excitation wavelength was 340 nm and the emission scans were recorded between 360 and 600 nm. The emission band-pass was set to 2.5 nm, unless otherwise specified. UV–vis absorption measurements in solution were obtained on a HP-8453 diode array spectrophotometer. Diffuse reflectance spectra were obtained using a Cary 1E spectrophotometer. Photoproducts were identified by high performance liquid chromatography (HPLC) using a C18 reverse phase column on a Waters system (501 and 600 A pumps, 994 diode array and 470 fluorescence detectors), matching retention time and UV–vis spectra with those of authentic samples. The product separation for a 50 μL injection was obtained using a gradient mode starting with methanol/water (70:30, v/v) at a flow rate of 1 mL/min changing the methanol/water ratio linearly to 100:0 in 15 min, and returning to 85:15 after an additional 15 min for a total of 30 min.

2.5. X-ray powder diffraction

X-ray powder diffraction (XRPD) measurements were obtained using a Siemens D5000 powder diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) with a filtered flat LiF secondary beam monochromator. The XRPD patterns were run on a 2θ range of 1.2–45°.

3. Results and discussion

Fig. 1 shows the luminescence spectra for an aqueous colloidal suspension of 1:1 PYMA:ZrP under an atmosphere of air taken at different times after irradiation. The luminescence spectra show a decrease in the most intense peak at 376 nm and an increase of the peak at 383 nm upon photolysis. The intensity changes observed in these bands suggest the formation of photoproducts, with no further spectral changes observed after 60 min. The PYMA emission band at 396 nm and the emission intensity at the excimer band region at 458 nm for the PYMA-exchanged ZrP samples do not show change after photolysis. Similar results were observed for the 1:50 and 1:100 PYMA:ZrP samples. The luminescence spectrum of a 0.1 mM PYMA aqueous solution does not shows any emission intensity at the excimer band region at 458 nm [8] (as is shown in Fig. 2 at 0 min). The presence of the emission intensity at the excimer band region upon photolysis of the PYMA:ZrP samples indicates that the ground state pre-associated PYMA dimers do not dissociate into PYMA monomers. Similar results have been reported previously by Dabestani et al. for other PAHs adsorbed on silica gel [11].

Dabestani et al. studied the spectroscopy and photochemistry of fluorene (FL) at a silica gel/air interface [11]. These authors reported monomer and excimer-like emissions of FL on silica surface. Dabestani et al. showed that the photolysis does not lead to FL dimers dissociation into constituent monomers and proposed that the surface provides a barrier to FL pair dissociation. The ZrP framework restricts the PYMA dimers mobility forming a barrier that avoids their dissociation.

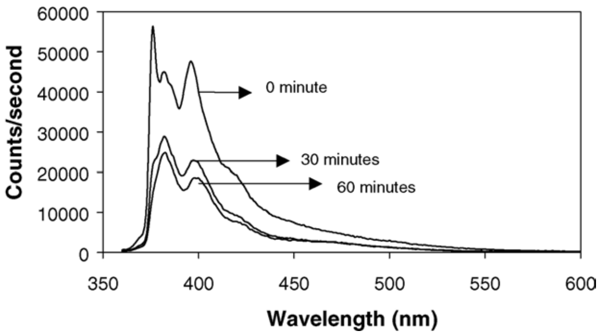


Fig. 1. Luminescence spectra of 1:1 PYMA-exchanged zirconium phosphate under an atmosphere of air taken at different times after irradiation, $\lambda_{exc} = 340$ nm.

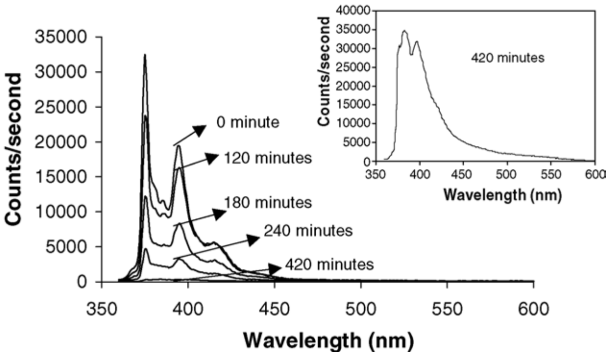


Fig. 2. Luminescence spectra of a 0.1 mM PYMA aqueous solution under an atmosphere of air at different times after irradiation, $\lambda_{exc} = 340$ nm. The inset shows the spectrum at 420 min with the emission band-pass set to 5.00 nm.

The photolysis of a 0.1 mM PYMA aqueous solution was studied to help identify the photoproducts obtained from the PYMA-exchanged ZrP samples after photolysis. Fig. 2 shows the luminescence spectrum of a 0.1 mM PYMA aqueous solution under an atmosphere of air after irradiation at different times. In contrast to the PYMA/ZrP result, the intensity of the bands in aqueous solution change more slowly, but the luminescence spectrum after 60 min irradiation is similar to the luminescence spectrum after 420 min irradiation observed for the colloidal suspension in aqueous solution of PYMA-exchanged ZrP sample (Fig. 1). The band at 396 nm remains present upon photolysis. However, the formation of the photoproducts takes longer in aqueous solution than in the PYMA:ZrP samples, being completed in 420 min. This result suggests that the presence of ZrP catalyzes the photolysis of PYMA. Similar results have been reported previously by La Ginestra et al. [6,7] (vida supra) but are contrary to those reported by Dabestani et al. [3].

Dabestani et al. reported that the photolysis of PY at the solid/air interface of unactivated and activated silica gel proceeds slowly [3]. The photodegradation rate of PY on unactivated silica containing residual solvent proceeded slowly. Solvent molecules can replace loosely held PY molecules from the surface to cover the sites, which results in an increase in the collisional deactivation rate of excited PYs and leads to less photoproduct formation. The extremely slow photodegradation rate of PY on activated silica was attributed to the presence of ground state pairs and/or aggregates which can act as a light sink to absorb the incident light without inducing any photochemistry.

Luminescence spectra, HPLC retention times, and absorption spectra were used to identify the photoproducts by matching their spectral features with those of authentic samples. Fig. 3 shows the luminescence spectrum of a 0.1 mM PY aqueous solution obtained at an excitation wavelength of 340 nm. The spectrum in solution shows two main peaks at 383 and 397 nm and a small shoulder at 376 nm. This spectrum is similar to that obtained for the irradiated PYMA-exchanged ZrP colloidal suspension in aqueous solution and for the 0.1 mM PYMA aqueous solution after photolysis,

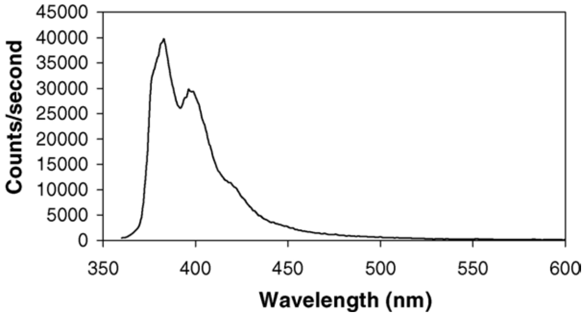


Fig. 3. Luminescence spectrum of a 0.1 mM PY aqueous solution, $\lambda_{exc} = 340$ nm.

suggesting that PY is their principal decomposition photoproduct.

This result was corroborated by obtaining the chromatogram of a 0.1 mM PYMA aqueous solution sample after photolysis. The chromatogram (not shown) shows the presence of PY, PYOH, 1,6-pyrenedione, and 1,8-pyrenedione. The chromatogram peaks were identified by matching the retention times and the characteristic absorption bands with those of authentic samples. Table 1 shows the wavelengths of the absorption bands from the absorption spectrum of the photoproducts and the authentic samples. Similar photoproducts have been reported previously for the photolysis of PY by Dabestani et al. (vida supra) [2,3].

We have previously reported that the XRPD pattern for the 1:1 PYMA:ZrP molar ratio sample shows an interlayer distance of 23.2 Å [8]. Fig. 4 shows the XRPD pattern for the 1:1 PYMA:ZrP molar ratio sample before and after photolysis. Both XRPD patterns show an interlayer distance of 23.2 Å, which suggests that after photolysis the photoproducts remain intercalated between the layers of ZrP. Since PY is the main photoproduct, direct intercalation of PY into 10.3 Å ZrP was attempted at 5:1 and 1:1 PY/ZrP molar ratios. However, the XRPD patterns (not shown) for the PY-exchanged ZrP samples show an interlayer distance of 7.6 Å. This interlayer distance is that of unintercalated α-ZrP. The α-ZrP is formed upon dehydratation of 10.3 Å ZrP without any intercalated species present [12]. This result indicates that photolysis permits the formation of photoproducts entrapped in ZrP, which cannot be directly exchanged into the ZrP framework.

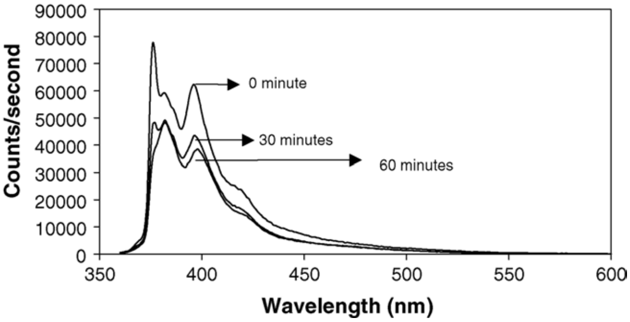


Fig. 5. Luminescence spectra of 1:1 PYMA-exchanged zirconium phosphate under an atmosphere of nitrogen at different times after irradiation, $\lambda_{exc} = 340$ nm.

Fig. 5 shows the luminescence spectra for an aqueous colloidal suspension of 1:1 PYMA:ZrP under an atmosphere of

Table 1
Characteristic wavelengths of the absorption bands from the absorption spectrum of the photoproducts and the authentic samples

Sample	Photoproduct sample λ (nm)	Authentic sample λ (nm)
Pyrene	230, 240, 276, 340	230, 240, 260, 272, 318, 333
1-Hydroxypyrene	240, 266, 276, 346	241, 267, 277, 346, 363, 383
1,6-Pyrenedione	208, 238, 265, 277, 334, 350	208, 238, 265, 277, 335, 351, 402
1,8-Pyrenedione	238, 276, 296, 310, 350	238, 277, 295, 308, 353, 396, 460

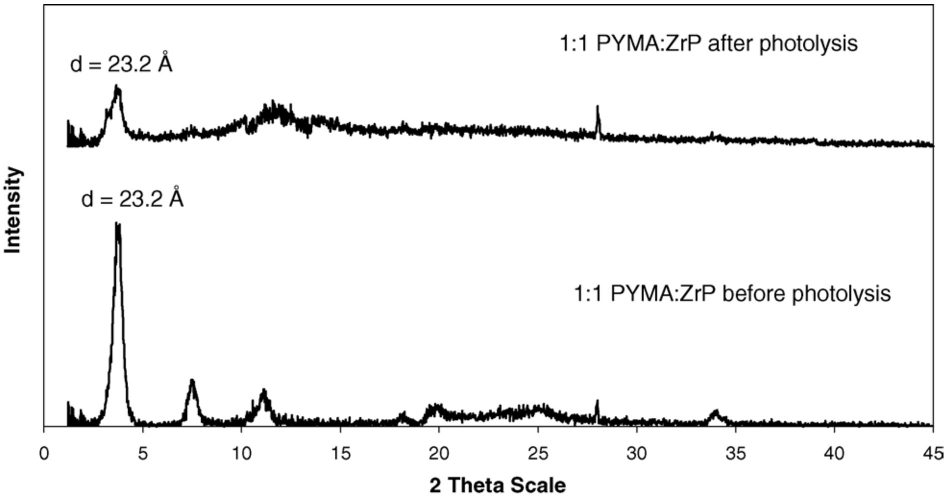


Fig. 4. XRPD pattern of 1:1 PYMA-exchanged zirconium phosphate before and after photolysis.

nitrogen taken at different irradiation times. Upon photolysis, spectral changes are observed at 30 and 60 min after irradiation; no further changes are observed at 90 min after irradiation (spectrum not shown). This result indicates that the photolysis is completed at 60 min. The luminescence spectrum of 1:1 PYMA:ZrP under an atmosphere of nitrogen after irradiation shows a small shoulder corresponding to the peak at 376 nm which disappeared when the photolysis is carried out under an atmosphere of air. To probe if the presence of oxygen is required for the disappearance of the 376 nm shoulder, the experiments were repeated under an atmosphere of oxygen and compared to the results obtained under an atmosphere of air (Fig. 1) or nitrogen (Fig. 5).

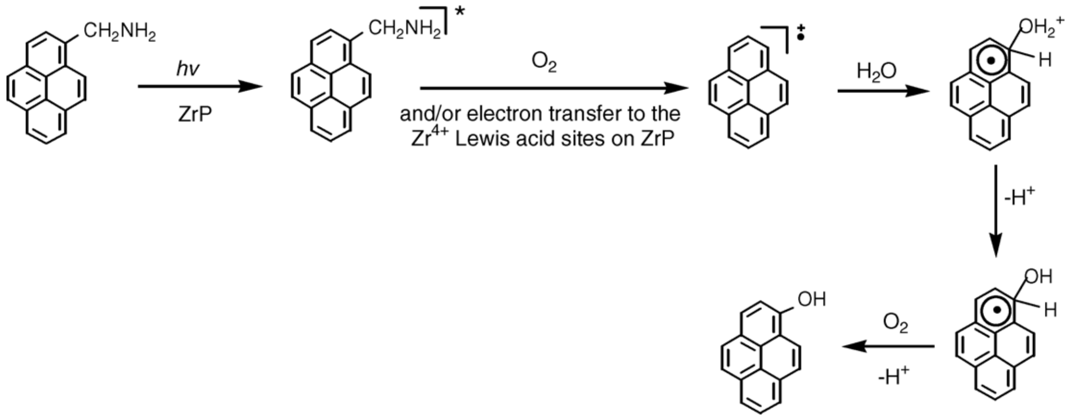
The photolysis of an aqueous colloidal suspension of 1:1 PYMA:ZrP in the presence of oxygen is completed in just 30 min and the luminescence spectrum after 30 min (not shown) is identical to the spectrum obtained in the presence of air; no band at 376 nm is observed. Similarly, the luminescence spectrum of a 0.1 mM PYOH aqueous solution in the presence of air, obtained at an excitation wavelength of 340 nm (not shown), shows three main peaks at 387, 408 and 430 nm. The spectrum does not show a band at 376 nm. These results suggest that upon photolysis the formation of PYOH is preferred in the presence of air or oxygen.

Contrary to the results obtained in a aqueous solution under an atmosphere of air, nitrogen, and oxygen, the luminescence spectra after photolysis of both, a 1:1 PYMA:ZrP colloidal suspension in methanol solution and a 0.1 mM PYMA methanol solution (not shown) show differences to those obtained in aqueous solution. The band at 376 nm decrease while that the bands at 388 and 395 nm increase. The luminescence spectra results indicate that the formation of the photoproducts during photolysis depends on the nature of the solvent. Further experiments will be needed to identify the photoproducts in methanol solution. Meanwhile, spectra for these materials were obtained in the solid state (i.e. powder form).

The luminescence spectra of 1:1, 1:50, and 1:100 PYMA:ZrP obtained for these samples in powder form show photodegradation of PYMA (not shown). The luminescence spectrum of 1:1 PYMA:ZrP in powder form shows only the excimer band which decreases after photolysis. The luminescence spectra of 1:50 and 1:100 PYMA:ZrP in powder form are similar to those obtained for an aqueous colloidal suspension. After photolysis, their luminescence spectra show a decrease of all the bands. The photolysis for the PYMA-exchanged ZrP powder samples is completed in 120 min.

The results obtained in this study indicate that oxygen and the presence of water play an important role in the formation of the photoproducts. Based on these results we can conclude that the irradiation of PYMA in aqueous solution produces PY as a photoproduct of the initial photolysis. Then, PY is photolyzed to produce PYOH, 1,6-pyrenedione, and 1,8-pyrenedione. The photodegradation of pyrene in water occurs via electron transfer from pyrene in its excited state to oxygen, which produces the pyrene cation radical [2,3]. The pyrene cation radical in the presence of water produces PYOH which is then photolyzed to produce 1,6-pyrenedione and 1,8-pyrenedione as final products.

Similar results were obtained for PYMA:ZrP samples. For these samples, we propose a mechanism (Scheme 1) where PY photoproduct formation is initiated through an electron transfer reaction from PYMA molecules in the excited state to oxygen and/or to the Zr^{4+} Lewis acid sites on the surface of the zirconium phosphate material, to produce the pyrene cation radical. A similar mechanism was proposed by La Ginestra et al. for cation radical formation from photolysis experiments of naphthalenes and alkylbenzenes in the presence of ZrP [6,7]. However, these authors proposed that the substrate cation radical was produced by electron transfer from the substrate in the ground state to ZrP in the excited state. That proposal was based on the observation of differences in the photoproducts obtained upon photolysis of samples in the presence or absence of ZrP under conditions permitting direct irradiation of the substrate and ZrP. Contrary to La Ginestra results, we observed in our samples the same photoproducts in the presence or absence of ZrP, but in the presence of ZrP the photoproduct formation rate is faster. The pyrene cation radical produces PYOH by subsequence reaction with water in the presence of oxygen [2,3]. The



Scheme 1.

photolysis rate of PYMA increases in the presence of ZrP, which indicates that the characteristic microheterogeneous environment of ZrP plays an important role as catalyst.

4. Conclusion

We have studied the photolysis of the luminescence probe PYMA ion-exchanged into a ZrP framework, the formation of the photoproducts, and the effect of the presence of air, nitrogen, and oxygen; and solvent polarity. We have observed that the formation of the photoproducts proceeds more rapidly for PYMA ion-exchanged into ZrP than for PYMA in aqueous solution, suggesting that the presence of ZrP catalyzes the photolysis of PYMA. We have identified PY, PYOH, 1,6-pyrenedione, and 1,8-pyrenedione as stable photoproducts in both water and ZrP. The photolysis of PYMA-exchanged ZrP permits the formation of photoproducts entrapped in ZrP, which cannot be directly exchanged into the ZrP framework by any other means. The photolysis of PYMA-exchanged ZrP under an atmosphere of nitrogen produced PY as the main photoproduct, while photolysis under an atmosphere of air or oxygen produces PYOH as the main photoproduct. Differences were observed for the photolysis results in methanol solution, compared to aqueous solution, indicating that the formation of the photoproducts depends on the nature of the solvent. Further experiments will be conducted to identify the photoproducts obtained in methanol solution and in other organic solvents; and compare the results obtained with those in aqueous solution. The results of these experiments will be reported in the future.

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