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RESEARCH ARTICLE

Stability of merocyanine-type photoacids in aqueous solutions

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Abstract

Over the past years, protonated merocyanines (MEHs) have been used as photoacids to control various chemical, material, and biological processes using visible light. For the applications under aqueous conditions, stability of this type of photoacid has been a concern. While hydrolysis of merocyanines is well known, this work showed that deprotonation of MEH to form merocyanine is not necessary for the hydrolysis of MEH. The decomposition products were identified by ultraviolet-visible spectroscopy and liquid chromatography–mass spectrometry. Comparing the behaviors of different MEHs under different conditions indicates that the hydrolysis is catalyzed by OH^- and thus MEHs are more stable at a lower pH. Modifying an MEH with an electron-donating group conjugated to the double bond significantly improved its stability. Photostability of an MEH was tested by conducting 100 irradiating/recovering cycles, and the photoacid showed good photostability.

KEYWORDS

hydrolysis, merocyanine, photoacid, photostability

1 | INTRODUCTION

Over the past few years, protonated merocyanines (MEHs) have been used as photoacids for reversible control of proton concentration using light. Because of their ability of creating a large pH change, visible-light sensitivity, and good reversibility, this type of photoacid has been used to control acid-catalyzed reactions, volume-change of hydrogels, polymer conductivity, bacteria killing, odorant release, and color change of materials.[1–5] Other applications including control of supramolecular assemblies,[6] molecular switches,[7] microbial fuel cells[8] cationic sensors,[9,10] and nanoparticle assemblies[11] have also been demonstrated recently.

This type of photoacid is related to the photochromic spiropyran (SP), which has been extensively studied[12] (Figure 1). An SP undergoes a ring-opening reaction under ultraviolet (UV) light and transforms to a phenolate merocyanine (ME). An ME-type photoacid has an MEH structure. Under visible light, the MEH undergoes a cyclization reaction to form, formally, a protonated spiropyran, which is acidic and can release a proton. The acidic protonated spiropyran is metastable and thermally relaxes back to MEH in the dark (Figure 1). Given that many of the applications mentioned above are under aqueous conditions, the stability of MEH in aqueous condition has been a major concern. Stafforst and Hilvert reported that MEs generated by irradiating SPs were hydrolyzed in aqueous solutions, but the reaction rate became very slow in 0.1% trifluoroacetic acid solution.[13] Andréasson and coworkers studied the decomposition reaction both experimentally and theoretically using quantum mechanical calculations.[14] Their results suggested that the hydrolysis reaction was catalyzed by the phenolate anion of ME and thus MEH should be stable. In this work, we studied the decomposition of MEH photoacids in aqueous solution and demonstrated an approach for improving their stability. In addition, the photostability of this type of photoacid was also studied.

2 | RESULTS AND DISCUSSION

PAH1 in Figure 1 is the most studied metastable-state photoacid and has been used in many applications.[1–10] Therefore, its decomposition in aqueous solutions was studied in this work. Previous work by Stafforst and Hilvert showed that the decomposition products of an ME, which was generated by irradiating an SP, were a salicylaldhyde and an indolinium.[13] However, ME-type photoacid such as PAH1 has a predominant MEH rather than ME form in water. Therefore, the decomposition products need to be

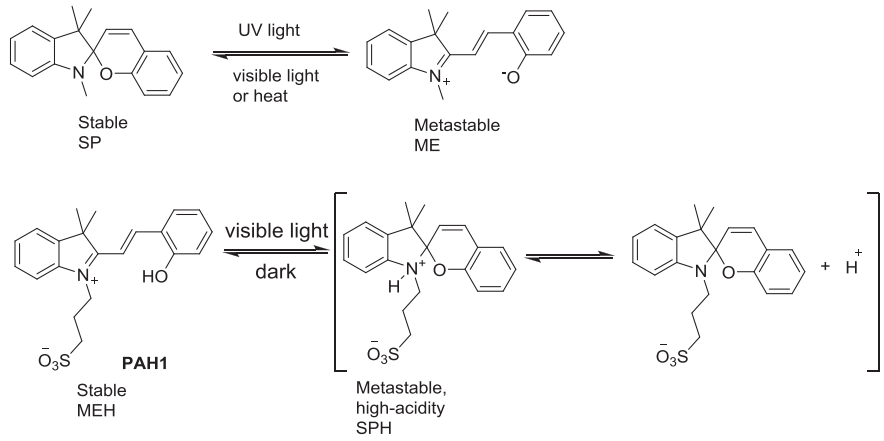

FIGURE 1 Photoreactions of a common spiropyran (top) and a merocyanine-type photoacid (bottom). ME indicates merocyanine; MEH, protonated merocyanine; SP, spiropyran; SPH, protonated spiropyran; UV, ultraviolet

investigated. In this work, an aqueous solution of PAH1 was kept in the dark for a month. Yellowish white precipitates were observed indicating that PAH1 decomposed. If PAH1 decomposed in a similar way as that of an ME, a salicylaldehyde and a indolinium would form as shown in Figure 2. Ultraviolet-visible (UV-Vis) spectrum of the solution showed substantial decrease of absorption at 426 nm comparing to the spectrum of the freshly prepared solution (Figure 3). The absorbance peaks matched that of salicylaldehyde and the indolinium (**2** in Figure 2). To further confirm the existence of salicylaldehyde, the solution was added a drop of concentrated sodium hydroxide solution to convert salicylaldehyde to its anion. As expected, a strong absorption peak at 376 nm appeared, which was consistent with a standard solution of deprotonated salicylaldehyde. The yellowish white precipitate was collected and examined using liquid chromatography–mass spectrometry (LCMS). Liquid chromatography–mass spectrometry spectrum showed that the precipitate was mostly the indolinium (**2** in Figure 2) together with small amount of PAH1. These results show that the decomposition reaction of MEH in water is also hydrolysis and the products of MEH are the corresponding salicylaldehyde and indolinium.

Previous studies showed that the rate of the hydrolysis reaction depends on the pH of the solution.[13,14] Therefore, hydrolysis of PAH1 in different pH buffers was studied. We first studied the hydrolysis in a buffer with a pH of 5.4, which is chosen based on properties of PAH1. PAH1 has a pKa of approximately 7.5 in the dark and a maximum concentration of approximately 0.5mM in water. The pH of a PAH1 solution at this concentration is about 5.4. A photoacid solution with maximum concentration would theoretically result in maximum pH drop upon irradiation and thus is of special interest. A buffer with a pH of 5.4 mimics the condition of a PAH1 solution at the maximum concentration. The decomposition rate of PAH1 was studied by monitoring the decrease of the UV-Vis absorbance at 424 nm over 3 hours. The concentrations were obtained by dividing the absorbance with the molar absorptivity of PAH1 (3.2×10^4 L mol^{-1} cm^{-1}) and fitted to a first order kinetic equation (Figure 4). The rate constant was calculated to be $1.223 \pm 0.004 \times 10^{-5}$ s^{-1}, and the half-life is about 16 hours. This value is in the same order of magnitude as that of some MEs previously reported,[13,14] which indicates that the decomposition must not mainly due to the small amount of ME generated from the equilibrium between ME and MEH (Figure 2). As further confirmed in the latter sections, MEH does not need to change to ME to be hydrolyzed. When a buffer with a pH of 4 was used, the decomposition rate was substantially decreased to $7.16 \pm 0.05 \times 10^{-7}$ s^{-1} indicating that OH^- involves in the reaction. Given that the hydrolysis reaction occurs at low pH and the rate is not proportional to the concentration of OH^-, the role of OH^- is likely to be a catalyst but not a reactant.

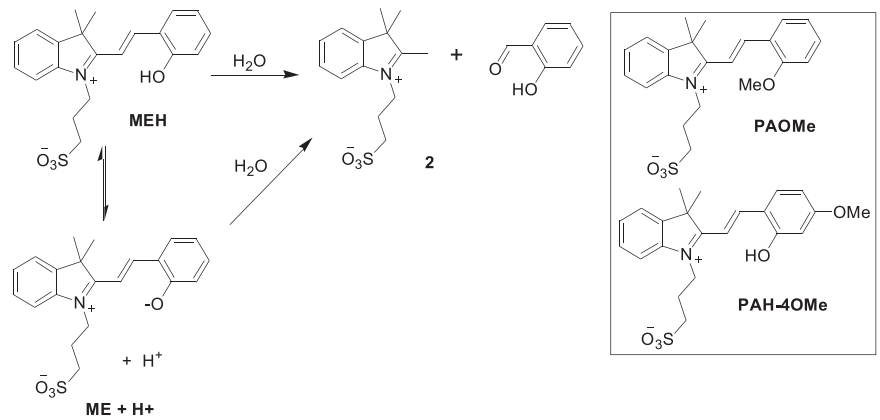

FIGURE 2 Decomposition reaction of PAH1 and structures of PAOMe and PAH-4OMe. ME indicates merocyanine; MEH, protonated merocyanine

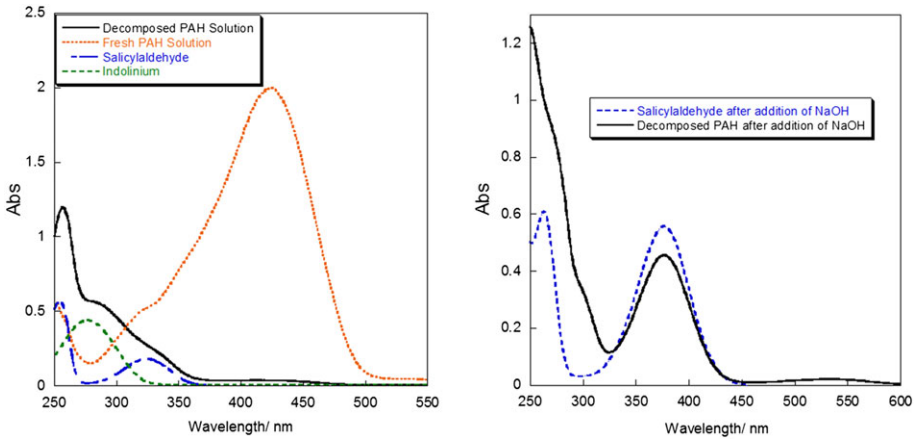

FIGURE 3 UV-Vis spectra of freshly prepared and decomposed solution of PAH1 compared to that of salicylaldehyde and the indolinium (left), and the spectra of the decomposed solution after addition of a drop of NaOH solution and that of a salicylaldehyde solution after addition of a drop of NaOH solution

As described above, decomposition of MEH is complicated by the involvement of ME. Previous work by Andréasson and coworkers suggested that the hydrolysis reaction was catalyzed by the phenolate anion of ME and thus MEH should be stable.[14] Therefore, it is important to know whether MEH is directly hydrolyzed or MEH must change to ME before hydrolysis. To solve this problem, PAOMe (Figure 2) was designed and synthesized. PAOMe has the same structure as PAH1 except that the OH group in PAH1 is substituted by an methoxy (OMe) group, which prevents the formation of ME. Decomposition of PAOMe was also tested in a pH 5.4 buffer, and the rate constant was obtained using the same method for PAH1 (Figure 4). The rate constant is $9.51 \pm 0.05 \times 10^{-6}$ s^{-1}, which is close to that of PAH1 ($1.223 \pm 0.004 \times 10^{-5}$ s^{-1}). This result confirms that ME is not necessary for the hydrolysis of ME-type photoacids.

PAOMe, which neither dissociates to ME nor cyclizes to SP, allows us to study the hydrolysis at a high pH. For comparison, PAH1 cannot be tested even at a pH close to 7 because it exists as an equilibrium of MEH, ME, and SP with only approximately 20% MEH at this pH.[15] Prior work by Andréasson and coworkers shows that mechanism of the hydrolysis of ME changes when pH is higher than 9. The reactant changed from water for the pH below 9 to OH^- for the pH above 9. So 9 is the highest pH value allowed for comparison with the test conducted at pH 5.4. Therefore, decomposition of PAOMe was tested at pH 9. The rate constant obtained was $1.17 \pm 0.01 \times 10^{-5}$ s^{-1}, which was only marginally higher than that of pH 5.4, although the concentration of OH^- was more than a thousand times higher. This result confirms that OH^- functions as a catalyst but not a reactant. Based on the experimental results described above, the mechanism of the hydrolysis is proposed as in Figure 5.

Understanding the mechanism of the decomposition makes it possible to improve the stability of ME-type photoacids. Given that hydrolysis occurs at the double bond and it is a nucleophilic reaction, increasing electron density on the double bond by introducing electron-donating groups conjugated to it could improve the stability. To test this hypothesis, PAH-4OMe (Figure 2) was studied. PAH-4OMe was previously used in a fragrant releasing material because

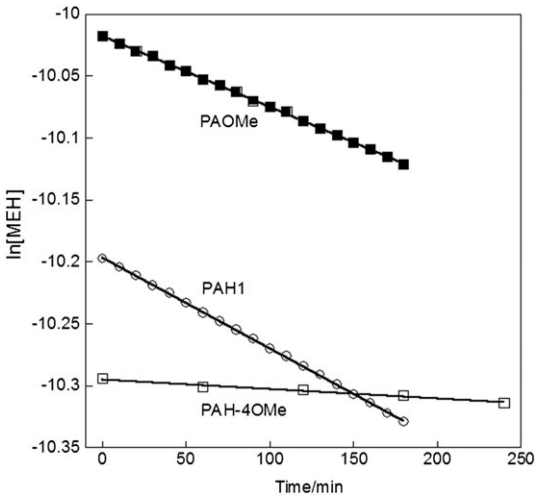

FIGURE 4 First-order decomposition of PAH1, PAOMe, and PAH-4OMe at pH 5.4. MEH indicates protonated merocyanine

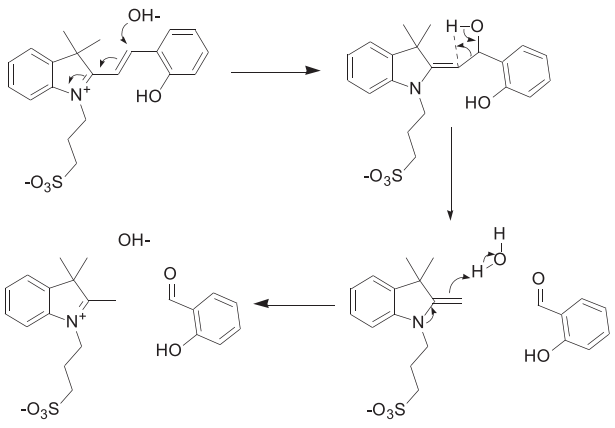

FIGURE 5 Proposed mechanism of the hydrolysis of a merocyanine-type photoacid

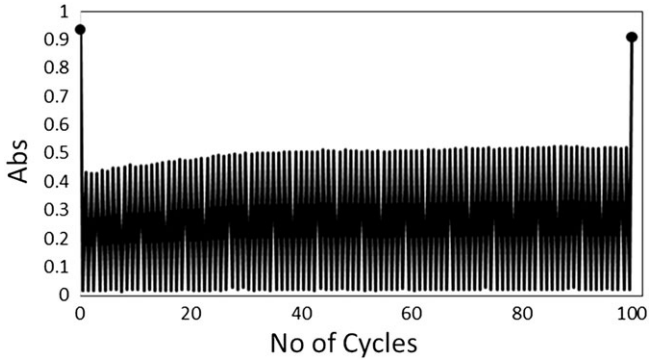

FIGURE 6 Absorbance of a PAH1 solution at 424 nm during 100 cycles of 1 min irradiation (lower points) followed by 2 min in the dark (upper points)

of its fast reverse reaction rate.[5] The OMe group is at the para-position of the double bond and thus is electron-donating to it. As shown in Figure 4, the hydrolysis rate of PAH-4OMe is $1.86 \pm 0.03 \times 10^{-6}$ s^{-1} in a pH 5.4 buffer, which is significantly lower than both PAH1 and PAOMe. The half-life is increased to 4.2 days comparing to 16 hours for PAH1.

High photostability is required for reversible photoacids. It is known that SPs do not have high photostability partially because short-wavelength UV light is required for the reaction[16] (Figure 1). Merocyanine-type photoacids function under visible light and thus are expected to have better stability than SPs. The photostability of PAH1 was tested using a buffer solution with a pH of 4. As described above, at pH 4, hydrolysis reaction is slow ($k = 7.16 \pm 0.05 \times 10^{-7}$ s^{-1}), and the half-life is more than 11 days. So the thermal decomposition can be ignored if the photostability test is conducted in a day. The photostability was tested by irradiating a solution of PAH1 at a pH of 4 using a 470 nm light-emitting diode (LED) light. The power of the light source was about 25 mw/cm^2. The solution was irradiated for 1 minute then kept in the dark for 2 minutes. The UV-Vis spectra of the solution, before irradiation, immediately after irradiation, and 2 minutes after irradiation, were collected and the concentration of the PAH1 was calculated from the absorbance at 424 nm. As shown in Figure 6, approximately 98% of PAH1 reacted after 1 minute irradiation. After 2 minutes in the dark, approximately 45% of PAH1 recovered because of the reverse reaction (Figure 1). The cycle was conducted for 100 times with good reproducibility. After the last irradiation, the solution was kept in the dark for a day, which resulted in 95% recovery. This experiment showed that PAH1 has good photostability.

3 | CONCLUSION

Merocyanine-type photoacid slowly decomposes to an indolinium and a salicylaldehyde in aqueous solutions because of hydrolysis. The hydrolysis reaction is catalyzed by OH^-, and thus, the photoacid is more stable at a lower pH. Protonated merocyanine can be hydrolyzed directly without changing to ME. Modifying PAH1 with an electron-donating methoxy group conjugated to the double bond improves its stability. Photostability of PAH1 was tested by conducting 100 irradiating/recovering cycles, and the photoacid showed good photostability in the test.

4 | EXPERIMENTAL SECTION

Unless otherwise noted, reagents and solvents were commercially available and used as received without any further purification. PAH1 and PAH-4OMe were synthesized following literature methods.[1,2] Ultraviolet-visible spectra were obtained from a Varian Cary 60 Scan UV-Vis spectrophotometer. ^{1}H NMR spectra were determined in deuterated dimethyl sulfoxide on a Bruker AV400 NMR spectrometer. Chemical shifts were reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane. High resolution mass spectra were recorded on an Accu TOF mass spectrometer by positive ion electrospray ionization mode with Direct Analysis in Real Time (DART) as an ion source. The light sources for irradiation were 470 nm LED arrays with 120 LEDs purchased from www.theledman.com.

4.1 | LCMS analysis of the decomposition products

A solution (2.6mM) of PAH1 was prepared by dissolving 10 mg of PAH1 in 10 mL water containing 20% ethanol, which was added to increase the solubility of the photoacid. The solution was purged with nitrogen and sealed in a valve. The sample was kept at room temperature for a month. A yellowish white precipitate was observed at the bottom of the valve, and it was collected by filtration. The decomposition product was subjected to LCMS analysis as described below.

Samples were analyzed by a 1260 Infinity LC system (Agilent Technologies) with a Zorbax rapid resolution HTSB C18 2.1 × 50 mm-1.8 μm reversed phase column (Agilent technologies) at 40°C using a 0.550 mL/min flow rate. Samples were eluted with a linear gradient from 100% water to 100% methanol over the course of 5 minutes. Scanning range was 190 to 400 nm. Mass spectra was performed using an attached 6120 Qadrupole LCMS (Agilent Technologies) in atmospheric pressure ionization-positive electron spray (APCI-ES positive) model at 100-V fragment voltage, scanning masses between 100 and 1000 Da.

Peaks corresponding to PAH1; m/z 386.1 $[M+H]^+$, R_t = 2.7 minutes and 2,3,3-trimethyl-1-(3-sulfonatepropyl)-3H-indolium; m/z 282.3 $[M+H]^+$, R_t = 6.0 minutes were observed.

4.2 | Buffer preparation

The pH 4.0 buffer solution (55.6 mL) was prepared by mixing 0.2 M sodium acetate (10 mL) and 0.2 M acetic acid (45.6 mL) in 18:82 V/V ratio; pH 5.4 buffer solution

(71.4 mL) was prepared by mixing 0.2 M sodium acetate (61.4 mL) and 0.2 M acetic acid (10 mL) in 86:14 V/V ratio.

4.3 | Synthesis of PAOMe

A mixture of 2,3,3-trimethyl-1-(3-sulfonatepropyl)-3H-indolium (0.479 g, 1.8 mmol) and 2-methoxybenzaldehyde (0.417 g, 1.7 mmol) was refluxed at 60°C in absolute ethanol (1 mL) over night. An orange color solid was obtained by filtration, washed with ice-cold ethanol, and dried in vacuo (0.658 g, 92% yield). The product was pure enough for NMR and UV-Vis analysis. ^{1}H NMR (400 MHz, d6-dimethyl sulfoxide): δ = 8.56 (d, 1H, J = 16.4), 8.34 (d, 1H, J = 7.2), 8.06 (dd, 1H, J = 8.4), 7.93 (d, 1H, J = 16.4), 7.88 (dd, 1H, J = 8.5), 7.67-7.63 (m, 3H), 7.25 (d, 1H, J = 8.4), 7.15 (t, 1H, J = 7.5), 4.84 (t, 2H, J = 7.8), 4.02 (s, 3H), 2.68 (t, 2H, J = 6.1), 2.19 (m, 2H), 1.79 (s, 6H). HRMS (electrospray ionization): m/z [M+1] calcd for C22H25NO4S +H, 400.1583; found, 400.1973.

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