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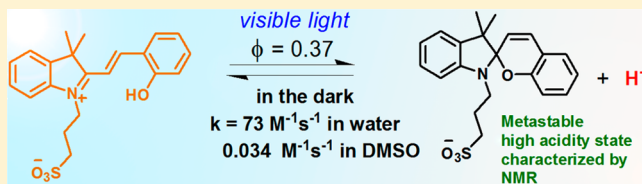
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## Physicochemical Study of a Metastable-State Photoacid

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**ABSTRACT:** A photoacid that possesses a metastable acidic state induced by visible light is studied. Previous work showed that this photoacid can reversibly produce a large pH change capable of controlling chemical reactions, altering material properties, and killing bacteria. In this work, we studied the relaxation kinetics of the metastable acidic state in different solvents including water, ethanol, and DMSO. In all of these solvents, the kinetic data can be fitted well to a second-order rate equation, which indicates that protonation is involved in the rate-limiting step. The rate constants in water, ethanol, and DMSO are 73, 1.6, and 0.034 M<sup>-1</sup> s<sup>-1</sup>, respectively. The slow relaxation in DMSO allowed us to fully characterize the structure of the metastable acidic state using proton NMR. We also measured the quantum yield of the photoreaction, which is as high as 0.37.



## ■ INTRODUCTION

A photoacid is a molecule that transforms to a strong acid upon photoirradiation. Irreversible photoacids, which are usually called photoacid generators (PAGs), have been extensively studied as photoinitiators for cationic polymerization and been applied to photolithography.<sup>1–7</sup> In the literature, photoacids often refer to those molecules that have high-acidity excited states, for example, derivatives of naphthol. These excited-state photoacids have been studied since the 1970s<sup>8–12</sup> and have been used in the studies of fast proton-transfer events.<sup>13–16</sup> Another type of photoacid is characterized by a metastable high-acidity state generated from a reversible photoreaction. It has been reported that a metastable-state photoacid (**1** in Scheme 1) can reversibly change the pH of an aqueous solution by more than 2 units under visible light with moderate intensity<sup>17</sup> (Scheme 1). This photoacid has been applied to

control acid-catalyzed reactions, change the volume of a hydrogel, change the conductivity of a polymer, and kill bacteria.<sup>17–19</sup>

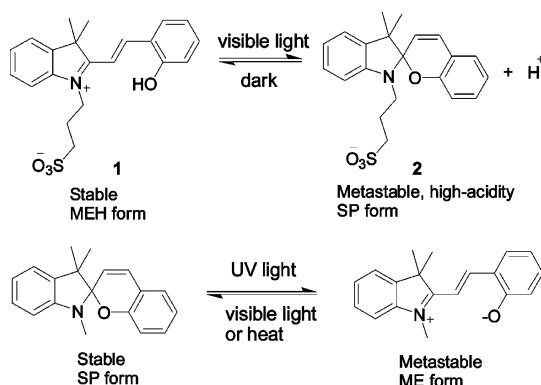
While the function of **1** as a powerful photoacid has been demonstrated, the photoreaction has not been well-studied, which hinders it from widespread applications. For example, the structure of the acidic metastable state has not been fully characterized; the quantum yield of the photoreaction has not been reported due to the fast reverse reaction; and the kinetics of the reverse reaction, which allows prediction of the pH change with time after irradiation, has not been well-studied. Herein, we report a physicochemical study of the photoinduced metastable state of **1** including structure, relaxation kinetics, quantum yield, and media effects.

## ■ RESULTS AND DISCUSSION

Photoacid **1** has a protonated merocyanine (MEH) structure with an absorption band ( $\lambda_{\text{max}} = 424$  nm in water) in the visible-light range. Irradiation with a wavelength in the absorption band induces a trans–cis isomerization to form *cis*-MEH, which undergoes a nucleophilic reaction to form the cyclic spiropyran (SP) **2** after releasing a proton.<sup>17</sup> The SP **2** is a strong acid, which has a predominant proton-dissociation state in water. It is a metastable structure and reverts back to **1** in the dark. Consequently, the photoinduced pH drop can also revert back to the original level. This reaction is similar to but different from the photochromic reaction of SP (Scheme 1), which has been extensively studied.<sup>20</sup>

The stability of the metastable state **2** was previously studied by fitting the kinetic data of the reverse reaction into a first-

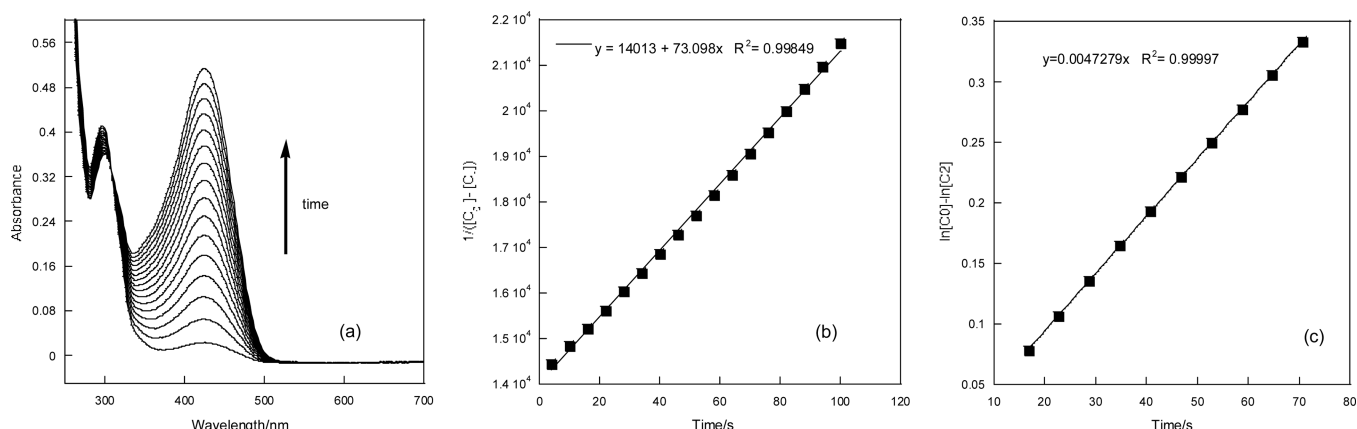
**Scheme 1. Reversible Photoreaction of the Photoacid 1 (top) and a Well-Known Photoreaction of a Common Spiropyran (SP) (bottom)**



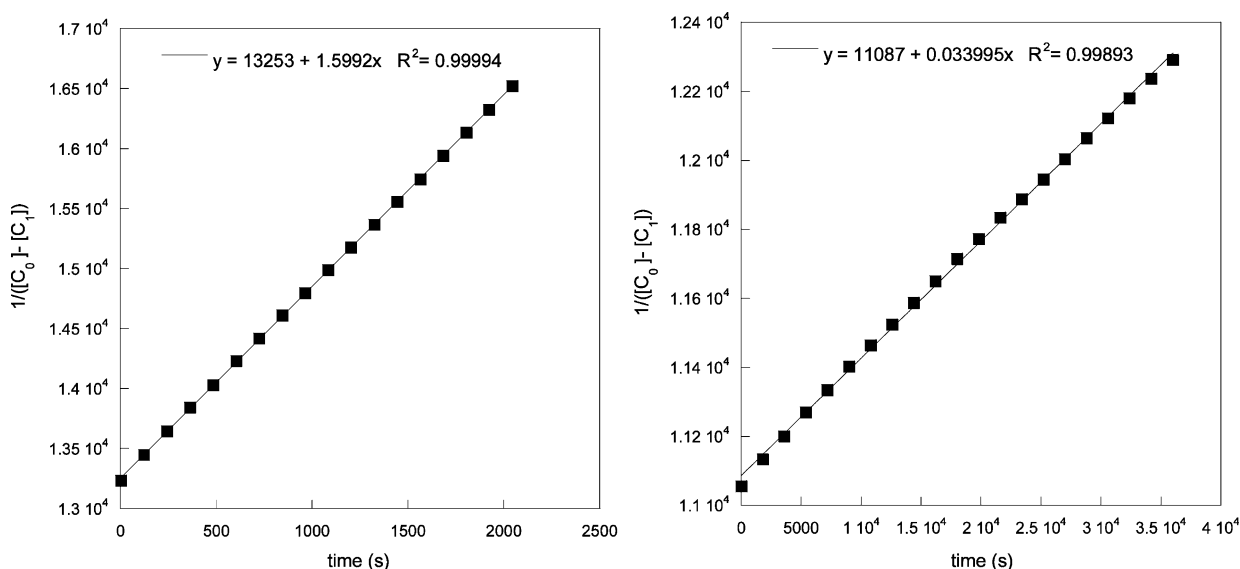
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**Figure 1.** (a) UV-vis absorption of an aqueous solution of **1** ( $7.03 \times 10^{-5}$  M) with time after irradiation (the irradiation time was 5 min, and spectra were collected every 6 s after irradiation). (b) A plot of the data for this relaxation fitted into eq 2, and (c) a plot of relaxation data in a solution ( $7.26 \times 10^{-5}$  M) of pH equal to 3.04 fitted into a first-order rate equation.



**Figure 2.** Kinetic data of relaxation of **2** in ethanol (left) and DMSO (right) fitted into eq 2

order rate equation.<sup>17</sup> However, only the data collected at a very early stage of the reaction can fit well to the equation. Understanding the kinetics of this process is important because it allows us to estimate the pH change with time after irradiation and to obtain information of the relaxation mechanism. If the rate-limiting step of the reverse reaction ( $2 + \text{H}^+ \rightarrow 1$ ) involves protonation of **2** and the majority of the protons in the solution come from the high-acidity state (i.e.,  $[\text{H}^+] = [\text{C}_2]$ ), then the kinetics follows a second-order rate equation

$$\frac{d[\text{C}_1]}{dt} = k[\text{C}_2][\text{H}^+] = k[\text{C}_2]^2 \quad (1)$$

If no other long-lived species is involved,  $[\text{C}_2] = [\text{C}_0] - [\text{C}_1]$  (where  $[\text{C}_0]$  is the total concentration), and eq 1 can be integrated to give eq 2.

$$\frac{1}{([\text{C}_0] - [\text{C}_1])} = kt + \frac{1}{[\text{C}_0]} \quad (2)$$

Experimentally, the kinetics was studied by monitoring the reformation of **1** after irradiation using UV-vis spectroscopy (Figure 1). UV-vis spectra were collected every 6 s after 5 min

of irradiation, and the data were fit into eq 2. As shown in Figure 1, the kinetics fits well with the second-order rate equation, and the rate constant was calculated to be  $73 \text{ M}^{-1} \text{ s}^{-1}$  with a confidence interval  $R^2$  of 0.9985. The fact that the kinetic data fit well into eq 2 indicates that protonation is involved in the rate-limiting step of the reverse reaction.

The relationship between the relaxation kinetics and  $[\text{H}^+]$  were further studied by conducting the reaction in buffer solutions with different pHs. Because the  $[\text{H}^+]$  is constant in buffer solutions, eq 1 becomes a first-order rate equation with  $k' = k[\text{H}^+]$ . Citric acid/ $\text{Na}_2\text{HPO}_4$  buffers (suitable pH range: 2.6–7.6) with pHs of 3.04, 4.00, 4.99, and 6.05 were prepared, and the photoacid was dissolved in the buffers. The solution of pH equal to 6.05 showed a small amount of deprotonated MEH (ME) in its UV-vis spectrum, which means that the concentration of SP is no longer equal to  $[\text{C}_0] - [\text{MEH}]$ . Therefore, we cannot use this solution because the molar absorptivity of ME is difficult to determine due to its equilibrium with SP and MEH. For the solutions with pHs of 3.04, 4.00, and 4.99, the data can indeed be fitted to a first-order rate equation (Figure 1c) with  $k'$  equal to  $4.7 \times 10^{-3}$ ,  $4.1 \times 10^{-3}$ , and  $3.3 \times 10^{-3} \text{ s}^{-1}$ , respectively. The value of  $k'$  increases

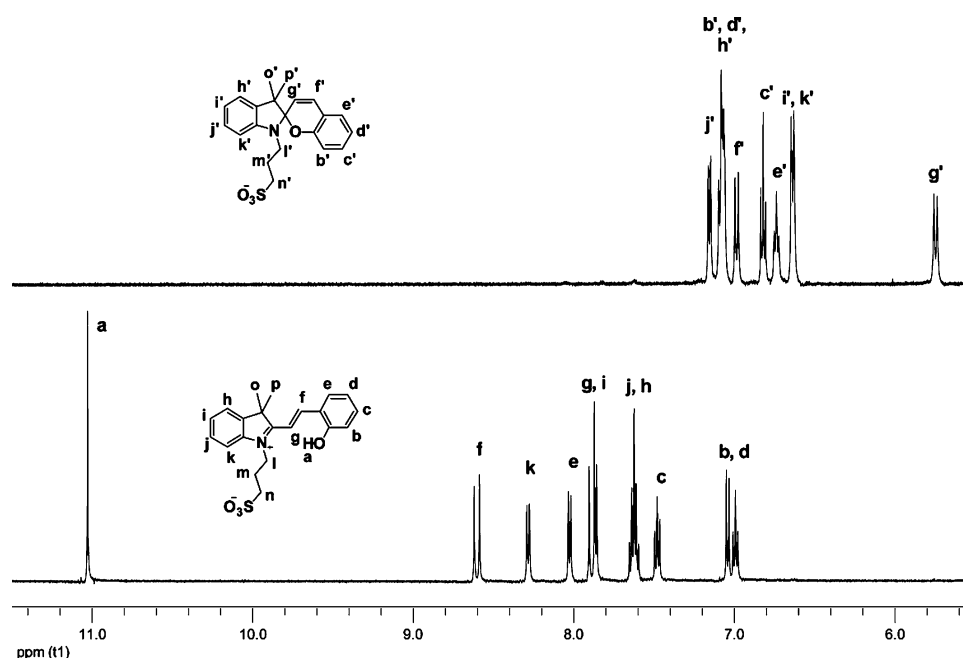


Figure 3. NMR of the photoacid **1** before (lower) and after (upper) irradiation.

with  $[H^+]$  as expected, but the magnitude is much less than the increase of  $[H^+]$ . A study by Wojtyk and co-workers showed that a significant amount of SP-NH<sup>+</sup> (SP structure protonated at the indolinium nitrogen) forms in a millimolar solution of trifluoroacetic acid, which slows down the acid catalyzed ring-opening reaction of as SP molecule.<sup>21</sup> A similar mechanism may be involved in the relaxation process of the photoacid in the acidic buffers.

The kinetics in ethanol and DMSO were also studied. The data for both solutions can be fitted well to eq 2 (Figure 2). The rate constants of ethanol and DMSO solutions are 1.6 and 0.034 M<sup>-1</sup> s<sup>-1</sup> respectively, both significantly lower than that of water (73 M<sup>-1</sup> s<sup>-1</sup>). The fact that **2** changes back to **1** slower in ethanol than in water may be explained by the lower polarity of ethanol (dielectric constant = 24) than that of water (dielectric constant = 80). Previous studies showed that the stability of SPs relative to corresponding merocyanines is increased in less polar media.<sup>20</sup> The increased stability of **2** in ethanol results in a slower reverse reaction than that in water. However, this cannot explain the very low rate constant in DMSO, which has a higher dielectric constant (47) than ethanol. The trend can better be explained by the hydrogen bond donor (HBD) acidity (Taft–Kamlet  $\alpha$  scale), which is related to the ability of the solvents to transfer the proton to SP.<sup>22</sup> The  $\alpha$  scales of water, ethanol, and DMSO are 1.10, 0.76, and 0.25, respectively, based on a calculation by Leggett.<sup>23</sup> The trend is consistent with that of the rate constants in the three solvents. In addition, previous work by Bordwell shows that the  $pK_a$  of many acids is significantly higher in DMSO than that in water.<sup>24</sup> The slow reaction in DMSO may also be partially due to less acidity of **2** and consequently fewer protons available in DMSO than in water for the rate-limiting step.

As shown in Scheme 1, although the reaction is similar to the well-known photochromic reaction of SPs, it is actually a new reaction. The structure of the metastable product **2** has not been well characterized due to the fast reverse reaction in water. The slow reverse reaction in DMSO allowed us to fully characterize the structure of **2** by NMR. Thus, a solution of **1**

was prepared in deuterated DMSO and subjected to a <sup>1</sup>H NMR study (Figure 3). Comparison of the spectra before and after irradiation showed that the reaction went to completion to give **2** quantitatively as the only photoproduct. The chemical shifts of the two hydrogens on the double bond (f and g) changed from 8.60 and 7.88 to 6.97 and 5.73 (f' and g'), and the coupling constants changed from 16.4 to 10.2 Hz, both indicating a trans to cis transformation. The peaks corresponding to the aromatic hydrogens on the indolinium moiety of **1** all shifted upfield after irradiation due to the absence of the positive charge in **2**. For the same reason, peaks for the methylene group adjacent to the nitrogen (l/l') shifted from 4.80 to 3.23. In addition, the absence of the phenolic proton (a) in the spectrum after irradiation further confirms the occurrence of the cyclization reaction. Detailed information about chemical shifts and coupling constants are given in the Experimental Section.

Quantum yield is important for characterization and application of a photoreaction. The quantum yield of the photoacid **1** has not previously been reported due to the fast reverse reaction. The slow reverse reaction in DMSO allows us to measure the quantum yield. Solutions of **1** with concentrations near  $5 \times 10^{-5}$  M (absorbance >1.5) were irradiated at intervals of 5 s with a 470 nm LED. The photon flux was adjusted to be  $\sim 28 \mu\text{mol m}^{-2} \text{s}^{-1}$ . The progress of the photoreaction was monitored by UV–vis absorption spectroscopy. The reverse reaction was ignored because even at the maximum concentration of the samples tested ( $6.40 \times 10^{-5}$  M), the half-life ( $1/k[C]$ ) of **2** is as long as 128 h. A multisample average of the quantum yield was calculated to be 0.37. Although the quantum yield in other solvents may be different, this measurement at least provides a value for estimating the efficiency of the photoreaction of **1**.

## CONCLUSION

The photoinduced high-acidity state of photoacid **1** has been studied. The relaxation kinetics of the metastable state in water, ethanol, and DMSO can be fitted well to second-order rate

equations, indicating the involvement of protonation in the rate-limiting step. The rate constants in water, ethanol, and DMSO are 73, 1.6, and  $0.034 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. The slow relaxation in DMSO allowed us to fully characterize the structure of the metastable acidic state with NMR and measure the quantum yield of the photoreaction, which is as high as 0.37. The high quantum yield, good reversibility, and well-defined kinetics make this photoacid a useful tool for macroscopic control of proton concentration with light.

## ■ EXPERIMENTAL SECTION

Photoacid **1** was synthesized following a literature procedure.<sup>12</sup> UV–vis spectra were obtained from a Varian Cary 50 Scan UV–vis spectrophotometer. The light source for the photoreaction was a 470 nm LED array with 56 LEDs (Elixa, Ltd.). The intensity of the light was adjusted by changing the distance between the light source and the sample and/or blocking some of the bulbs on the array. Photon flux was measured by an Apogee MQ-200 quantum sensor. Quantitative details of the experiments are given in the Results and Discussion section.

**Proton NMR of 1.** <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta/\text{ppm}$  = 11.05 (s, 1H), 8.60 (d, 1H,  $J$  = 16.4 Hz), 8.28 (m, 1H), 8.02 (m, 1H), 7.88 (m, 2H, one is a clear doublet with  $J$  = 16.4 Hz), 7.66–7.58 (m, 2H), 7.48 (m, 1H), 7.04–6.97 (m, 2H), 4.80 (broad triplet, 2H), 2.65 (t, 2H), 2.18 (m, 2H), 1.77 (s, 6H).

**Proton NMR of 2.** <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta/\text{ppm}$  = 7.14 (dd, 1H,  $J^1$  = 1.6 Hz,  $J_2$  = 7.5 Hz), 7.09–7.05 (m, 3H), 6.97 (d, 1H,  $J$  = 10.2 Hz), 6.80 (td, 1H,  $J_1$  = 1.1 Hz,  $J_2$  = 7.4 Hz), 6.73 (m, 1H), 6.62 (d, 2H,  $J$  = 7.9 Hz), 5.73 (d, 1H,  $J$  = 10.2 Hz), 3.23–3.13 (m, 2H), 2.43 (m, 2H), 1.89–1.79 (m, 2H), 1.18 (s, 3H), 1.07 (s, 3H).

## ■ AUTHOR INFORMATION

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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