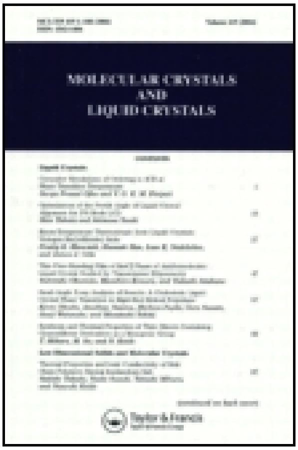

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Spiropyran-Merocyanine Equilibrium in Presence of Organic Acids and Bases

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Spiropyran-Merocyanine Equilibrium in Presence of Organic Acids and Bases

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Manipulation of the rate of thermal reversion of N-functionalized merocyanines (MC) to the corresponding spiropyran isomers in the dark, was demonstrated by using both organic acid and base additives. In the presence of organic bases, increase or decrease of the rate of reaction was dependent on the solvent used. When organic acids were used, in all cases the reaction rate decreased when compared with the system containing no acid. Similar behavior was also observed in polymer films. This approach is of interest for applications in the design of optical switches and memory with enhanced stability of the stored information.

Keywords: merocyanine; optical switch; spiropyran

Spiropyrans represent one of the most promising classes of materials for applications in molecular devices including sensors, optical switches, signal transducers and optical memories.

When aiming to design optical switches, one of the disadvantages of spiropyran materials is that the open state isomer (merocyanine; MC) does not persist for a long enough time. An optical memory device

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using these materials would keep the stored information only for a relatively short period of time.

Several approaches were previously investigated in order to achieve increased thermal stability of the merocyanine isomer. Notable results were obtained by incorporation of silica nanoparticles into spiropyran-containing Langmuir-Blodgett films [1], incorporation of spirobenzopyran into siloxan matrices [2], incorporation of spiropyrans with long alkyl chains into polymeric films [3], and by dissolution of spiropyrans in fluoroalcohols [4]. In our group we have demonstrated the stabilization of merocyanine isomer by using metal salts [5]. However, metal salts have limited solubility in common organic solvents. In addition, they also have limited compatibility with many organic polymers. Using organic acids and bases as additives instead of metal salts may provide a wider scope for optimization of optical switches, because of their superior miscibility with polymers in organic solvents.

We report here our preliminary results with respect to the investigation of the effect of organic acids and bases as additives in spiropyran solutions. Several spiropyrans were synthesized from the Fischer's base or its quaternary salt by reaction with 2-hydroxy-5-nitrobenzaldehyde in ethanol, in the presence of a base [6]. Chemical structures of spiropyran (SP) isomers are shown in Figure 1.

They are divided in series as a function of number of chelating groups. Series A yields monodentate MC, while series B and C yield bidentate and tridentate MC, respectively.

Merocyanine isomers are obtained from closed spiropyran isomers after illumination with UV light in solution.

EXPERIMENTAL RESULTS

Addition of Bases

Solutions of a concentration of 1×10^{-4} M of spiropyrans in the given solvent were prepared and to these various amounts of bases were added. Two solvents were used: methanol and acetone while two bases were investigated: tri-N-butylamine (TBA) and N,N-diisopropylethylamine (dIEA). The kinetics of the thermal reversion reaction of merocyanine isomer (MC) to the closed isomer (SP) were studied by measuring the decay of absorbance at λmax of MC by using UV-VIS absorption spectroscopy after irradiation for 90 s with UV light. Typical results are shown, for comparison, in Figure 2. Data shown are for the MC(4.x) series and for TBA as a base.

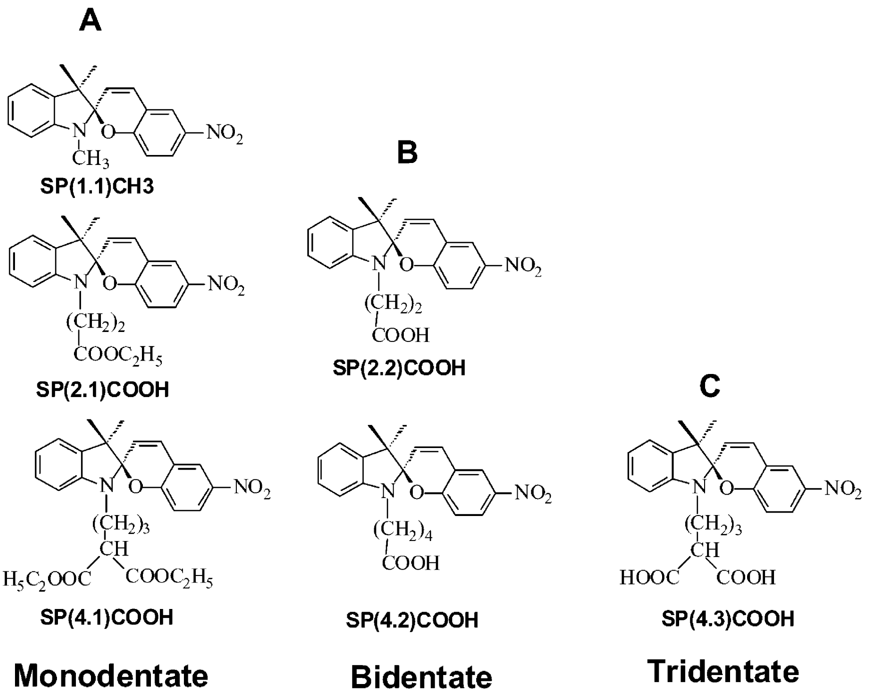

FIGURE 1 N-functionalized spiropyrans (SPs) investigated in this work. The SP series A, B and C on irradiation with UV light afford monodentate, bidentate and tridentate merocyanines (MCs), respectively.

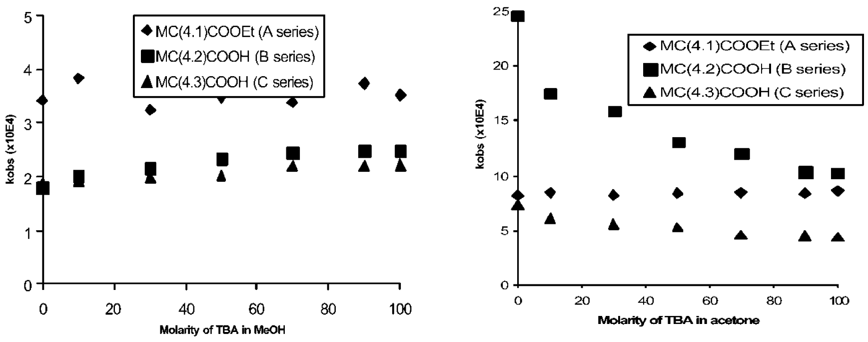

FIGURE 2 Decay of MC concentration as a function of base used in methanol (left side) and in acetone (right side). TBA was used as the base. Data are shown for selected MC(4.x) compounds, i.e., spacer is four methylene groups in length. x is 1, 2, 3 for mondentate (series A), bidentate (series B) and tridentate (series C) compounds, respectively.

The main observations when bases were added are as follows:

- –no spectral changes were observed when base was added;
- –series A shows no effect on rate of reversion with respect to solvent or addition of base;
- –for series B and C an effect on rate was observed and this depended on the solvent used;
- –in methanol, there is slight increase of the rate constant for decoloration reaction;
- –in acetone there is a significant decrease of the rate constant when large amount of base is added.

Addition of Acids

Trifluoro acetic acid was used in various amounts and in methanol as solvent. The main observations are as follows:

- –new peaks appeared in the UV-VIS spectra at 414 nm and 314 nm, while the peak of free merocyanine at 570 nm disappeared.
- –for all series (A, B and C) the rate constant for thermal reversion of the merocyanine isomer decreased, i.e., the fading reaction was slowed down when TFA was added.

Discussion

The key to understanding these various behaviors is the possibility of proton transfer from $N-(CH_2)_n-COOH$ to the p-nitrophenoxide group of the MC isomer. If proton transfer occurs, then it impedes thermal decoloration through ring closure to SP. By analyzing available pKa data on model compounds (acetic acid and p-nitrophenol) we concluded that in the protic solvent methanol $pKa(CH_3COOH) < pKa$(p-nitrophenol) and as a result, in methanol proton transfer from $R-COOH$ to ArO^- occurs thus impeding ring closure. On the contrary, in polar aprotic solvents (DMSO, DMF, acetone) $pKa(CH_3COOH) > pKa$ (p-nitrophenol) and as a result this proton transfer does not occur, leaving the rate of ring closure unaffected.

In presence of organic bases in methanol, we propose the mechanism shown in Figure 3.

In methanol, where the proton transfer occurs, the acceleration of thermal decoloration reaction is explained by the fact that the phenolic proton in III (Figure 3) is abstracted by the added base yielding the aryloxide IV, which undergoes reversion to the closed isomer.

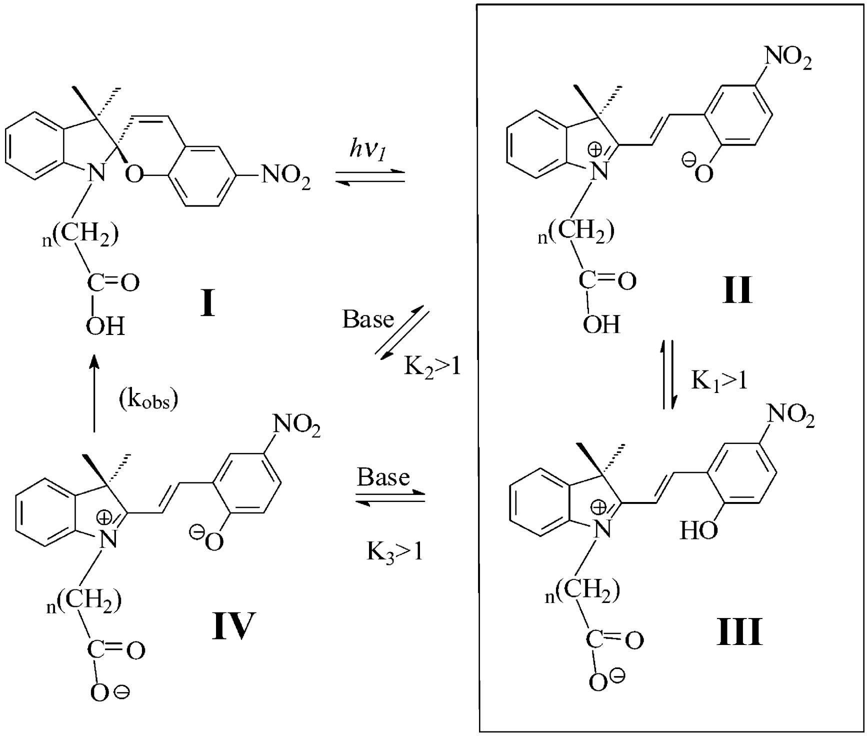

FIGURE 3 Proposed mechanism for acceleration of thermal reversion from MC to SP in methanol when bases are added.

On the other hand, in acetone where the proton transfer does not occur, the major isomer present is the phenoxide II (Fig. 4) which is expected to revert rapidly to the closed isomer. Addition of tertiary base yields the ammonium salt which forms an ion pair with the carboxylic acid and phenoxide anions IP-IV. The latter provides stabilization of the merocyanine (MC) isomer when base is added.

When organic acid (TFA) is added in methanol, the protonation of phenoxide anion V-VI (Fig. 5), slows down the thermal reversion of MC to SP in all cases. One uncertainty in experiments with TFA arises from the possibility of reaction of TFA with methanol which was reported previously in the literature [7]. To the extent that this occurs, the actual concentration of TFA will be lower than expected. However, the trend towards stabilization of the MC isomer due to protonation is still valid. On the other hand, TFA is not known to react with other organic solvents like THF or acetone. We are currently investigating the effect of TFA in such solvents.

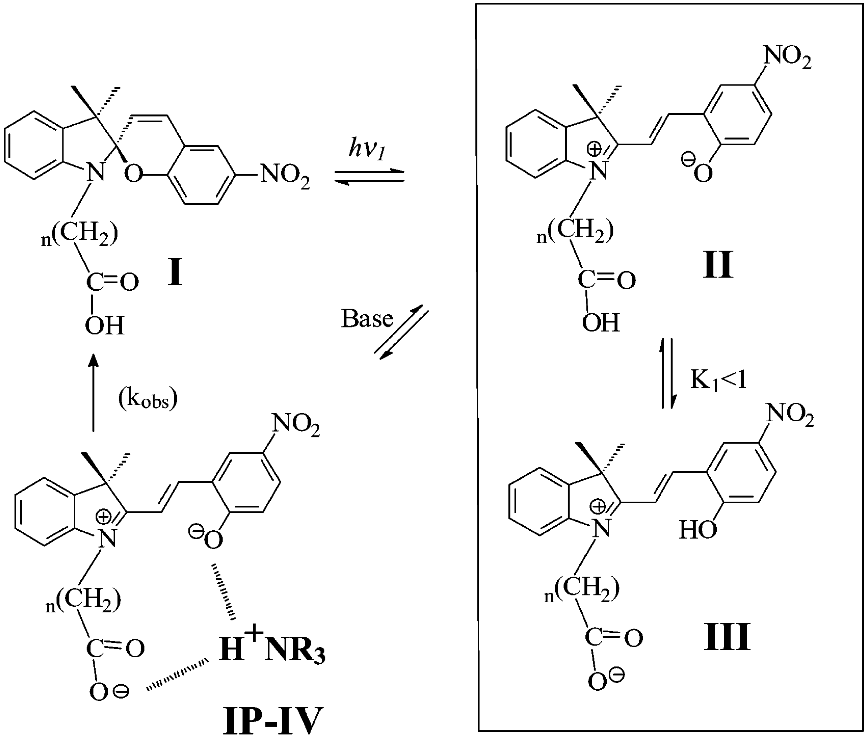

FIGURE 4 Proposed mechanism for slowing down of thermal reversion reaction in acetone when base is added.

Polymeric Films

The next step was to extend the stabilization mechanism by organic acids to polymer films. Polymer films were prepared on glass substrates by spin-coating solutions containing SP(1.1)CH3, poly-methyl-methacrylate (PMMA) and TFA in tetrahydrofuran as solvent. As seen from Figure 6 (left side), the addition of TFA resulted in a significant blue shift of the absorption maximum of MC isomer from 575 nm to about 415 nm. Decay tests after illumination with UV light showed significantly increased stability of the MC isomer in presence of TFA in the dark, when compared with the sample having no organic acid added. For example, after 90 min. the sample containing TFA is still showing an absorbance close to 100% of the initial value, while the reference sample (no TFA) decayed to about 20% of its initial value (Fig. 6 right side).

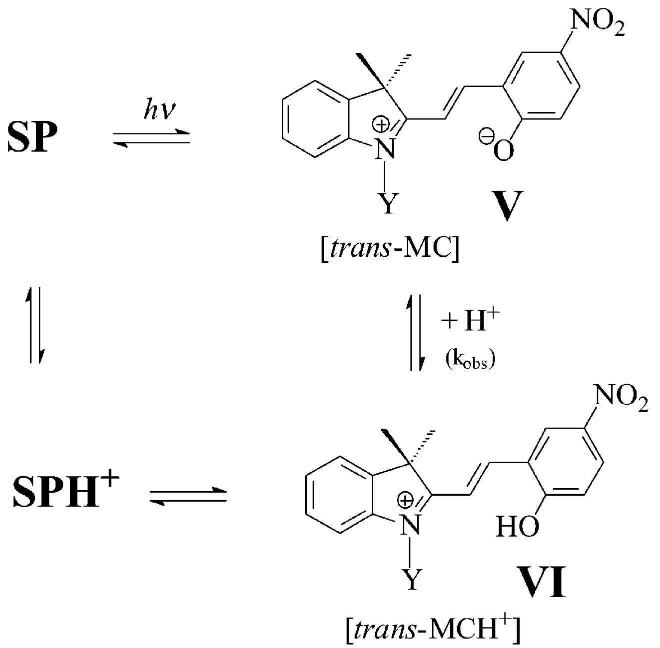

FIGURE 5 Mechanism in presence of acids.

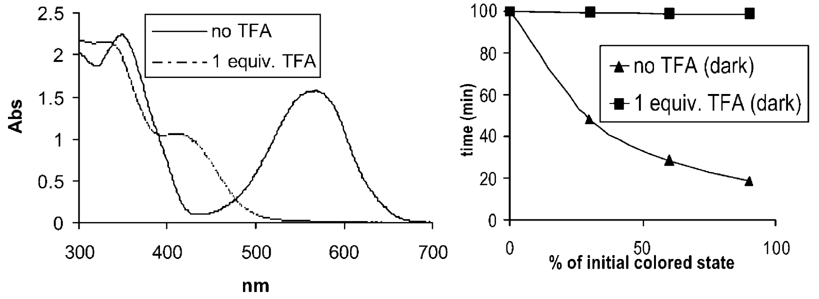

FIGURE 6 UV-VIS absorption spectra of MC and MCH$^+$ in PMMA film (left) and decay of colored state (MC) in PMMA films in presence of TFA and with no TFA (right).

Conclusions

The objective of this work was to investigate new approaches for stabilizing the MC isomer in solutions and in polymer films. We have found that depending on the type of MC used and of the nature of solvent, the addition of bases could slow down or accelerate the thermal reversion reaction. In contrast, addition of acids always slowed down the decay of MC isomer. Mechanisms explaining these different behaviors were proposed.

Stabilization of MC isomer in polymeric films by added organic acid was also demonstrated. This result is of interest for fabrication of optical switches with improved bistability. Next steps in this work involve extension this study by taking into account pKa of excited states of the species involved in these processes.

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