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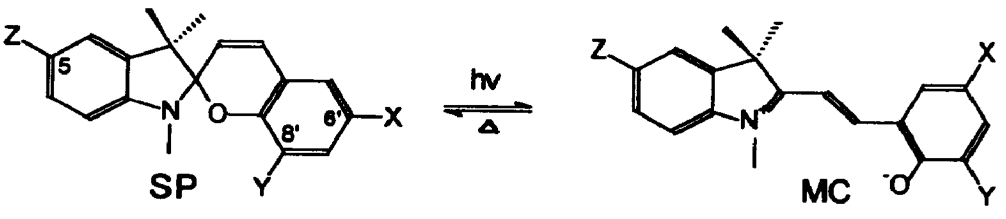
A NOVEL METHOD FOR MEASUREMENT OF THE MEROCYANINE-SPIROPYRAN INTERCONVERSION IN NON-ACTIVATED 1,3,3-TRIMETHYLSPIRO-(2H-1-BENZOPYRAN-2,2'-INDOLINE) DERIVATIVES

Sam-Rok Keum[*a], **Ki-Bong Lee**[a], **Peter M. Kazmaier**[b] and **Erwin Buncel**[*c]
Departments of Chemistry, [a]Korea University, Chung-Nam, South Korea 339-700;
[b]Xerox Research Centre of Canada, Mississauga, Ont., Canada, L5K 2L1;
[c]Queen's University, Kingston, Ont., Canada K7L 3N6.

Summary: A novel method for studying the merocyanine ⇄ spiropyran (MC ⇄ SP) interconversion is proposed, consisting of an acid-induced ring opening of the spiropyran followed by neutralization and stopped-flow measurement of ring closure of the resulting merocyanine; the obtained solvatokinetic data indicated a duality of mechanistic pathways depending on the nature of the dye and solvent polarity.

Spiropyran-merocyanine transformations[1] have been studied extensively since their discovery in 1952, owing to the potential applications of these dyes in copying, recording, display materials and non-linear optics. A basic requirement of these systems is[2,3] that the ring-closed spiropyran (SP) and the opened merocyanine (MC) forms should both be accessible near ambient temperature through photochemical or thermal interconversion, eq. 1.



(1)

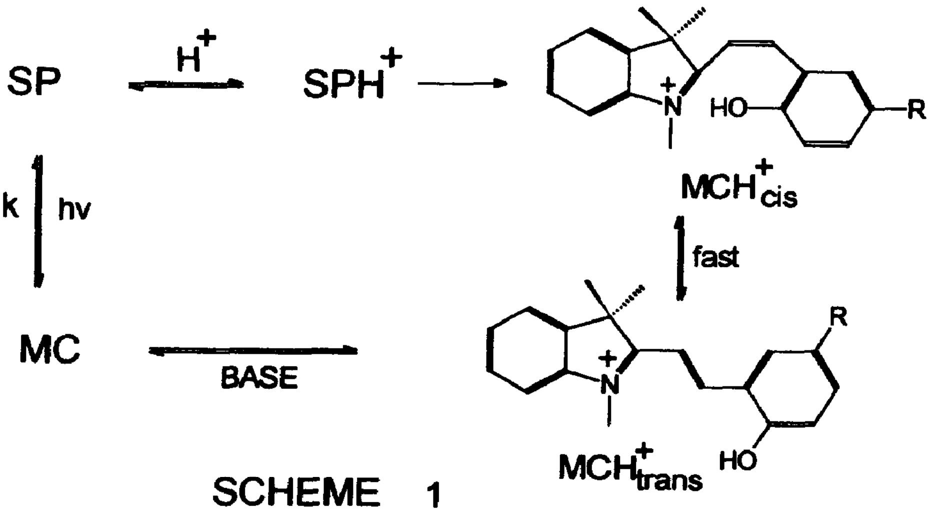
1 X= N=N-Ph, Y= H, Z= H

2 X= Ph, Y= H, Z= H

3 X= NO_2, Y= OMe, Z= Cl

In practice, most such studies of photo- and thermochromism have utilized activated systems with a nitro group in the 6' position to stabilize the MC form, coupled with the large extinction coefficients of the species in the visible region. Non-activated systems have hitherto not been accessible to ready measurement of the SP ⇄ MC interconversion by UV-VIS spectroscopy, since UV-irradiation of the SP form does not give a detectable concentration of the MC form in these systems. Through laser or flash photolysis, or at very low temperatures, the SP ⇄ MC equilibrium could, however, be studied with the non-activated systems.[4] In contrast we,[3] and others,[1] could obtain a wealth of information with the strongly chromotropic nitro-activated substrates, by UV irradiation of the SP forms and subsequent following the rate of the thermal MC → SP process as a function of solvent medium and substituent changes.

We report herein a simple, readily available method for following these processes with non-activated compounds showing no chromotropism at ambient temperature. The method involves treatment of the SP form in an organic solvent with HCl which within a few hours at room temperature causes the protonated spiro form to ring open to give the protonated merocyanine (MCH^+). Treatment of the latter with a tri-n-butylamine solution as base in a stopped-flow apparatus results in ring closure to SP (Scheme 1).



SCHEME 1

We have applied this method to the non-activated compounds 1 and 2 in different solvents by monitoring the disappearance of the MC absorption at 570-620 nm by stopped-flow. Excellent first-order kinetics were obtained (r = 0.999). Compound 3 with NO_2 at the 6' position and OMe and Cl at the 8'- and 5- positions could be used as a borderline model system to calibrate the results. This compound with the electron withdrawing chlorine substituent is sufficiently activated so that UV irradiation of the SP form gave a readily measurable concentration of the MC form; the rate of the MC → SP transformation could then be measured at 25°C by following the disappearance of the MC absorption maximum, as previously.[3] The results compared favourably with those obtained by the novel method.

Data for the MC → SP conversion in representative solvents (alcohols → → ethers) obtained via stopped-flow measurement using the novel method for 1 and 2, and by both the novel and traditional methods for 3, are displayed in Figure 1 in the form of plots of log (rate) vs the $E_T(30)$ solvent polarity parameter.[5] The biphasic plots derived from the solvatokinetic studies of 1 and 3 are indicative of dual mechanistic processes,[6,7] i.e., a transition state with increased zwitterionic character in more polar solvents[8] and an electrocyclic process with an isopolar transition state in less polar solvents.[9] The single linear plot with zero slope in the case of 2 is indicative of a transition state with isopolar character throughout the range of solvents studied.

The present study represents the first report of thermo- and photochromism of non-activated spiropyrans at ambient temperature. Further studies of the SP ⇄ MC interconversion with non-activated substrates, including obtention of kinetic data for the acid catalyzed ring opening of the spiropyrans, and thermodynamic parameters for the SP ⇄ MC equilibrium are in progress and will be reported in due course.

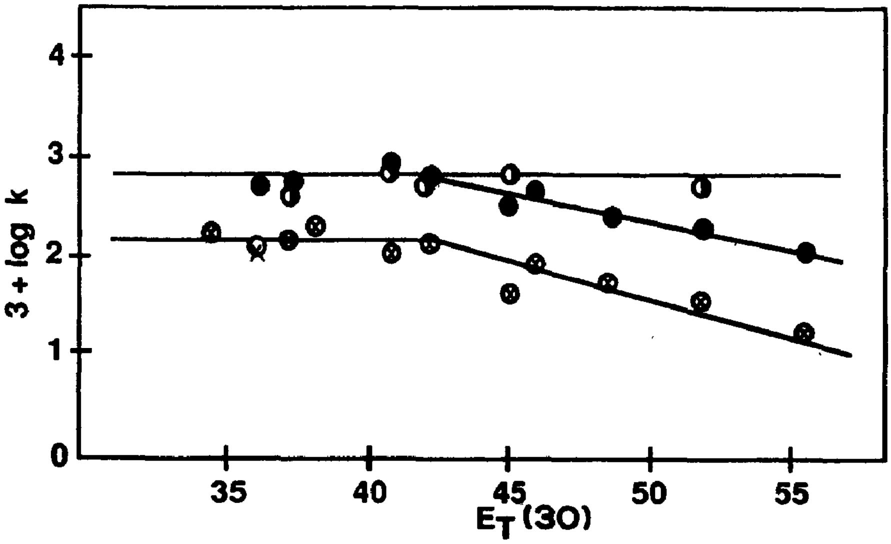


Figure 1. Plots of log k versus solvent polarity parameter, $E_T(30)$, for dyes 1 (●), 2 (⊗), and 3 (O) in various solvents; the symbol (X) represents data for 3 obtained by the UV-VIS irradiation method.

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