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ACID CATALYSIS IN A THERMOCHROMIC SYSTEM

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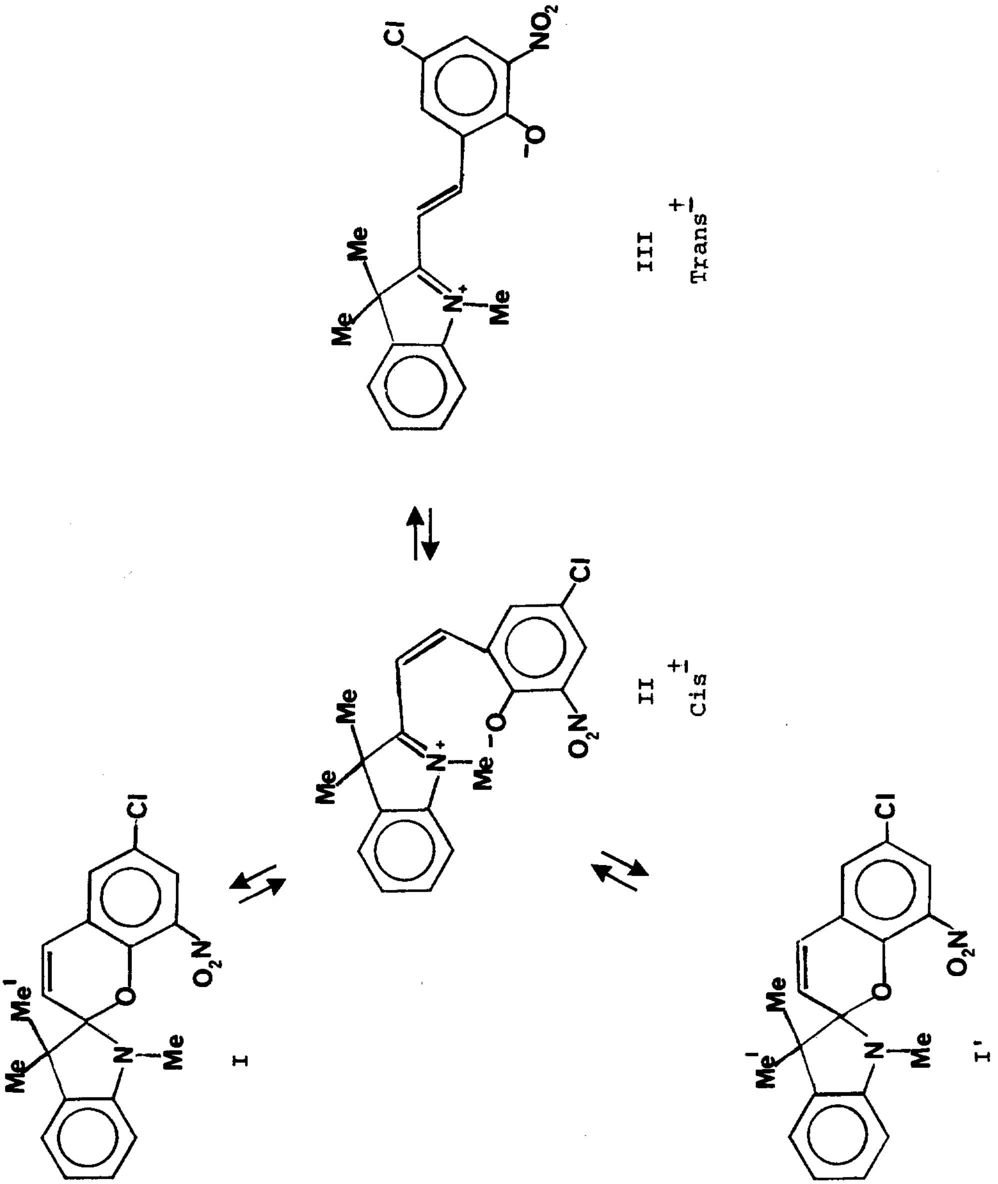
Color formation in thermochromic spiropyrans results from reversible ring-opening (colorless I $\rightleftarrows$ colored III in Figure 1)[1,2]. The forward direction is favored by polar solvents and by electron-withdrawing substituents[3,4,5]. Since the trans configuration (III) is much more stable than the cis (II), the latter exists in concentrations too low to observe by simple means. The magnetically non-equivalent gem-dimethyl groups in I become equivalent at elevated temperatures where ring opening and closure (I $\rightleftarrows$ II $\rightleftarrows$ I') is rapid relative to the NMR time scale[6,7].

We have found that acid affects both rates and equilibria in Figure 1, thus providing a means controlling photochromic and thermochromic processes not fully utilized in the past[8]. The gem-dimethyl peaks of I[9] in DMSO[10] (δ = 1.08 and 1.24 ppm) broaden, approach one another, and eventually coalesce into a single peak as p-nitrobenzenesulfonic acid[11] is added to the solution. Observed rate constants for methyl exchange at 40° (secured by a standard NMR line-shape analysis[12]) are linearly related to the sulfonic acid concentration (0.023-0.16 M) and give a second-order rate constant of 490 $M^{-1}sec^{-1}$ [13]. If no acid is added to the DMSO, then one must heat the substrate to 140° to secure coalescence. A linear plot of ln k vs. 1/T extrapolated to 40° for the uncatalyzed exchange shows that 1.0 M p-nitrobenzenesulfonic acid induces a 250-fold rate acceleration.

Catalyzed methyl exchange is not the only reaction that occurs when I is dissolved in acidic DMSO. A time-dependent process was detected as well; it is

Figure 1



III Trans$^{\pm}$

II Cis$^{\pm}$

I

I'

followed most readily by the appearance of a new downfield C-methyl signal at $\delta = 1.72$ ppm. The amplitude of this singlet increases while, concommitantly, the original *gem*-dimethyl doublet or singlet (depending on the acid concentration) decreases in size. Although the amplitude of the upfield *gem*-dimethyl signal changes with time, its line-shape does not, thus indicating no direct interrelationship between the time-dependent and the time-independent reactions. Observed rate constants for formation of the new species were obtained by plotting $\log (A_\infty - A_t)$ *vs.* time (where A's are peak areas). Disappearance of the upfield peak and the appearance of the downfield peak give the same rate constants. Moreover, the rate constants are *independent* of the acid concentration within experimental error ($k_{obs} = 1.1 \pm 0.3 \times 10^{-3} sec^{-1}$ from 0.060 to 0.22 M *p*-nitrobenzenesulfonic acid in DMSO at 40°).

The simplest mechanism consistent with our results is given in Eq. 1 (see also Fig. 1). Interconversion of I and I' involves two intermediates both having open rings and *cis* configurations. Acid, which promotes the heterolysis of the labile C-O bond in I, enables the *gem*-dimethyls to become magnetically equivalent at temperatures 100° less than in the absence of acid. Interestingly, acid-catalyzed methyl exchange seems insensitive to the substituents on the benzopyran moiety[14]; electron-withdrawing substituents improve the leaving ability of the oxygen but also diminish its affinity for the catalyst, and the effects cancel[15]. The *cis* double bond slowly isomerizes to *trans* as manifested by the appearance of the C-methyl peak at $\delta = 1.72$ ppm. Ring-opening destroys the chiral center so that the peak is a singlet at all acid concentrations. Ring-opening also generates a quaternary nitrogen which explains why the *gem*-dimethyls are deshielded relative to those of I. The rate of *cis*/*trans* isomerization is unaffected by acid, indicating that $[\text{cis}]^\pm$ (not $[\text{cis-OH}]^+$) gives rise to the *trans* material. This is reasonable since resonance arguments sug-

$$\begin{tikzcd}
 & \text{I} \arrow[dr, shift left] \arrow[dl, shift left] & & & \\
{[\text{Cis-OH}]^+} \arrow[ur, shift left, "H^+"] \arrow[dr, shift left, "H^+"] & & {[\text{Cis}]^\pm} \arrow[ul, shift left] \arrow[dl, shift left] \arrow[r, shift left, "\text{Slow}"] & \text{Trans}^\pm \arrow[l, shift left] \arrow[r, shift left, "H^+"] & \text{Trans-OH}^+ \arrow[l, shift left] \\
 & \text{I'} \arrow[ul, shift left] \arrow[ur, shift left] & & &
\end{tikzcd} \qquad (1)$$

gest that the olefinic linkage in zwitterionic [cis]$^{\pm}$ possesses a smaller bond order than that in cationic [cis-OH]$^{+}$. Although acid does not catalyze the *cis* to *trans* reaction, it does serve to drive Eq. 1 to the right. When the isomerizations reach equilibrium, the ratio of open-to-closed spiropyran is 0.42, 3.7, and 6 at *p*-nitrobenzenesulfonic acid concentrations of 0.025, 0.11 and 0.22 M, respectively. In the absence of acid, no *trans* at all is observable by NMR. *Trans*-OH^{+} is not highly colored; hence, solutions of I in DMSO (which are dark blue owing to low levels of *trans*$^{\pm}$) turn yellow if sufficient acid is added.

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References and Notes

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(10) Deuterated dimethylsulfoxide (DMSO-d_6) from Aldrich or Baker was used in all runs. Neither addition of 0.56 *M* water to the DMSO-d_6 nor drying the solvent with molecular sieve changed the rate constants.

(11) Water was removed from the acid by azeotropically distilling it from a benzene solution of I using a Dean-Stark trap. This was followed by crystallization from dry benzene.

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(13) The substrate concentration was 0.10 M in these runs. Doubling the concentration reduced k_2 by 20% (barely larger than our experimental error).

(14) This is a tentative conclusion based on three spiropyran derivatives.

(15) No N-protonation of I under the experimental conditions was detectable by NMR.

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