The Photo- and Thermochromic Transients from Substituted 1′,3′,3′-Trimethylindolinobenzospiropyrans[1]

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Abstract: The absorption spectra, thermal equilibria, and dark reactions of photoinduced transients in 1′,3′,3′-trimethyl-6-nitrospiro[2H-benzopyran-2,2′-indoline] (I) and, in part, 1′,3′,3′-trimethyl-6-nitro-8-bromospiro[2H-benzopyran-2,2′-indoline] (II) and 1′,3′,3′-trimethyl-6-nitro-8-methoxyspiro[2H-benzopyran-2,2′-indoline] (III) have been examined in a wide range of solvents. The visible absorption spectra of transients in nonpolar solvents indicate the dominant species to be an all-*trans* monomeric isomer of the cyanine type. At high concentrations of I, $>10^{-1}$ *M*, the formation of dimers and higher polymers is observed. In polar solvents the preferred formation of a dimeric species and/or a monomer–solvent complex is observed over a wide range of concentration of I. The equilibrium thermodynamics and reaction energetics of the transformations between I, II, and III and their colored transients are analyzed relative to solvent properties, particularly solvent dielectric constant and cohesive energy. These data are consistent with the spectral assignments and show that the colored species are zwitterionic. It is found that the transient form I in polar solvents, *e.g.*, ethanol, is more stable than that in nonpolar, *e.g.*, benzene, by 3–4 kcal mol^{-1}. This stabilization results from an exothermic dimerization and/or solvation of the polar transient.

The nature of the colored form of spiropyrans in solution has been discussed[2] widely. The spectroscopic identity of the thermochromic and photochromic transients was first noted by Hirshberg and Fisher.[3] It is generally assumed that a photo- and thermosensitive equilibrium exists between the spiropyran and a planar, colored transient resulting from scission of the bond between spiro carbon and pyran oxygen. That a change in molecular configuration must accompany rupture of the pyran ring was inferred from the absence of thermochromism in the sterically blocked 3′-substituted compounds.[4] Thus the formation of the highly colored transient by ring opening is probably the result of rehybridization of the spiro carbon from sp^3 to sp^2 to give coplanar rings; this is in contrast to the noncoplanarity of rings in the spiropyran. The most compelling support for this view lies in the very recent discovery of a similar mobile equilibrium between *cis*-β-ionone and the corresponding α-pyran,[5] as well as the benzopyran quinoid photochromism of chromenes.[6] Various structures have been proposed for the colored form of spiropyrans, including biradical or ionic radical, quinoid, and zwitterionic species. While the existence of the first of these was inferred earlier[7] from signals observed in epr measurements on the crystalline colored species (isolated by photolysis of a number of indolinobenzospiropyrans), it now appears that this observation is an artifact, resulting from interaction between atmospheric oxygen and the dye species.[8] In fact, such effects are now well known[9] for dyes in general. Attempts in this laboratory and elsewhere[10] to detect epr signals from solutions of indolinospiropyrans during photolysis yielded negative results. Since no signals were observed $>10^{13}$ unpaired electrons/cm^3, the probability of biradical or ionic radical structures in solution appears small and will not be considered further. Of the remaining structures, an illustration is given in part for 1′,3′,3′-trimethylindolino-6-nitrobenzospiropyran[11] (I) in Figure 1. There is evidence available favoring all of these structures and their various mesomers. In particular, the adsorption of spiropyrans on polar surfaces as colored adsorbates,[12] solvent effects on the stability of colored transients,[3,13] substituent effects,[14] and salt-forming ability[15] are cited[2,16] as supporting the mesoionic species (Figure 1a,b) as dominant. The similarity in visible absorption spectra to that of the nonionic merocyanine dyes[17] suggests possible resonance contributions from the quinoid structures[3,18] (Figure 1c).

The present study of solvent effects on the optical absorption spectra, equilibria, and thermochromic reactions of photoinduced transients in I, II, and III was undertaken with particular attention to those details of the structure and steroisomerism of the colored transients which may be inferred therefrom. The absence of any systematic investigation of the effect of solvent on photochromic processes in solution was

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[1] Presented, in part, at the Informal Symposium on Reversible Photochemical Processes, University of Dayton, Dayton, Ohio, May 1967, and the 154th National Meeting of the American Chemical Society, Division of Physical Chemistry, Chicago, Ill., Sept 1967.

[2] J. H. Day, *Chem. Rev.*, 63, 65 (1963); R. Dessauer and J. P. Paris, *Advan. Photochem.*, **1**, 275 (1963).

[3] Y. Hirshberg and E. Fisher, *J. Chem. Soc.*, 297 (1954); 3129 (1954).

[4] A. Mustafa, *ibid.*, 2295 (1959); C. F. Koelsch, *J. Org. Chem.*, 16, 1362 (1951).

[5] (a) E. N. Marvel, G. Cople, T. A. Gosink, and G. Zimmer, *J. Amer. Chem. Soc.*, 88, 619 (1966); (b) unpublished data, this laboratory.

[6] R. S. Becker and J. Michl, *J. Amer. Chem. Soc.*, 88, 5931 (1966).

[7] C. A. Heller, D. A. Fine, and R. A. Henry, *J. Phys. Chem.*, **65**, 1908 (1961).

[8] E. Berman, *ibid.*, 66, 2275 (1962).

[9] *Cf.*, *e.g.*, J. M. Assour and S. E. Harrison, *ibid.*, 68, 872 (1964).

[10] Y. Hirshberg and S. I. Weissman, *J. Chem. Phys.*, 28, 739 (1958).

[11] The less cumbersome common names are used wherever appropriate in the remainder of this paper.

[12] A. Schonberg, A. Mustafa, and W. Asker, *J. Amer. Chem. Soc.*, **74**, 5640 (1952).

[13] O. Chaudé and P. Rumpf, *C. R. Acad. Sci., Paris*, **233**, 405 (1951); O. Chaudé, *Cahiers Phys.*, 50, 17 (1954); **51**, 6 (1954); **52**, 3 (1954).

[14] (a) E. B. Knott, *J. Chem. Soc.*, 3038 (1951); (b) C. F. Koelsch and W. R. Workman, *J. Amer. Chem. Soc.*, **74**, 6288 (1952).

[15] W. Dilthey and H. Wubken, *Ber.*, **61**, 963 (1928).

[16] R. Exelby and R. Grinter, *Chem. Rev.*, **65**, 247 (1965).

[17] R. Heiligman-Rim, Y. Hirshberg, and E. Fisher, *J. Chem. Soc.*, 156 (1961).

[18] Y. Hirshberg, *J. Amer. Chem. Soc.*, 78, 2304 (1956).

noted by Brown and Schaw.[19] While limited thermodynamic kinetic and spectral data have been reported by Chaudé,[13] these data on the effects of selected hydroxylic and polar aprotic solvents were analyzed in an empirical and approximate fashion.

It is the intent of this study to extend the thermodynamic and kinetic data and to include nonpolar solvents as well. By application of the appropriate electrostatic models, it should be possible to determine if the colored transients are truly zwitterionic species.

While the similarity in absorption spectra of merocyanines and colored species from spiropyrans have been cited[2,8,16–18] as evidence for the quinoid structure of I and similar compounds, one cannot overlook the equally similar character of the spectra of ionic cyanines, and the tendency of such dye structures to isomerize and aggregate under appropriate conditions.[20] Furthermore, the existence of isomers of the colored forms of I and II has been inferred by Lashkov and Shablya[21] from luminescence measurements, and for similar compounds by other workers.[22] Thus the concentration dependence of the absorption spectra of colored transients, as well as the possibility of photoinduced interconversion of various stereoisomers of transient species, are explored to provide an explanation for the solvatochromism of indolinospiropyrans. The profound effects of solvent properties on the absorption spectra and reaction kinetics of these indolinospiropyrans, as well as their photo- and thermochromic behavior in a conveniently accessible temperature range, make them ideal candidates for such a study.

Experimental Section

A. Materials. All indolinospiropyrans were prepared by condensation in refluxing ethanol of equimolar amounts of 1,3,3-trimethyl-2-methyleneindoline (Chemicals Procurement Labs) and the appropriately substituted salicylaldehyde. Compounds were multiply recrystallized, vacuum dried, and stored in the dark. Analyses (C, H, N) were satisfactory, and melting points agreed with those reported.[14b,23]

All solvents, unless otherwise stated, were Baker Reagent spectrophotometric grade, or Reagent grade when the former was unavailable. Ethanol was U.S.I. Absolute Reagent Quality. N,N-Dimethylformamide was alternately distilled at low pressure from P_2O_5 and KOH. The material so obtained was distilled twice more at low pressure, with center fractions retained and used within a few hours of preparation.

B. Equipment. All spectrophotometric measurements were made using a Beckman DK-2A spectrophotometer modified to allow irradiation of cells within the sample compartment. Cells of paths 0.1, 1.0, 5.0, and 10 cm were used. For kinetic and equilibrium measurements, standard 1-cm cells were housed in a thermostated metal block, the temperature of which was controlled ($\pm 0.1°$) by circulation of water from an external thermostat.

The light source for ultraviolet ($\sim$365 mμ) excitation was a GE S-4 100-W mercury arc. According to manufacturer's specifications, about 5.7 W output from this lamp occurs below 380 mμ. Suitable spectral regions were isolated by use of Corning filters CS7-51 and CS7-60, or Bausch and Lomb interference filters for 365, 380, and 390 mμ. Excitation in the visible spectrum was accomplished with a Sylvania Type DWY tungsten–iodine lamp, using a water filter, and Corning sharp cut filters CS7-30 for $\lambda >$ 480 mμ, or CS2-60 for $\lambda >$ 610 mμ

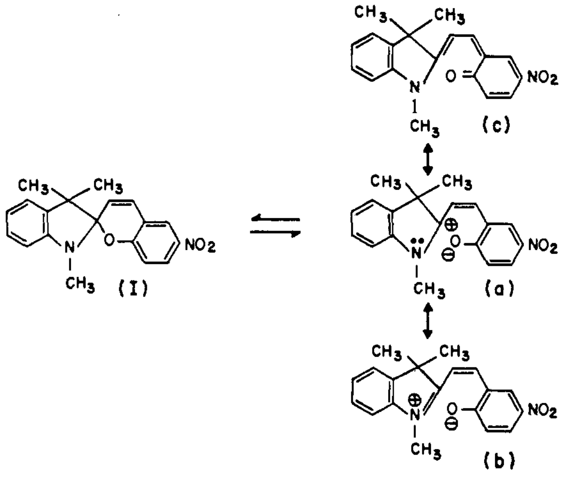

Figure 1. Proposed reaction paths and selected mesomeric structures for the colored transient of 1′,3′,3′-trimethylindolino-6-nitrobenzospiropyran (I).

C. Equilibrium Measurements. Thermodynamic constants, K_e, for the equilibrium between the colorless and colored species of I in solution were determined as follows. Solutions of spiropyran were prepared quantitatively in various solvents in sufficient concentration to give a measurable intensity of absorption in the visible after equilibration at room temperature. The concentration ranges were dependent on solvent, about 10^{-2} to 10^{-1} M in nonpolar solvents and 10^{-4} to 10^{-2} M in ethanol and acetone. Solutions were monitored at various temperatures in the range 0–54° until the visible absorption maximum was constant for several hours. All systems were completely reversible with temperature.

For a visible absorbing species (B) which obeys Beer's law in the concentration range of interest, at equilibrium

$$K_e = (B)/S_e \qquad (1)$$

with $S_T = S_e + (B)$ where S_e = equilibrium concentration of colorless spiropyran, and S_T = concentration of spiropyran based on initial amount dissolved before equilibration. Substitution and rearrangement gives

$$S_T = A_e\left[\frac{1}{\epsilon}\left(1 + \frac{1}{K_e}\right)\right] \qquad (2)$$

where ϵ = molar extinction coefficient for visible absorbing species at the absorption maximum and A_e = equilibrium absorbance at the visible absorption maximum. In all cases, over the ranges of concentration and temperature studied, the relationship between S_T and A_e was linear within experimental error, as required by eq 2. Application of this equation and derivation of thermodynamic quantities related thereto is presented below. All results are based on duplicate determinations. Concentrations were corrected for variation of solvent density with temperature.

D. Kinetic measurements on the spiropyrans I, II, and III (10^{-5} to 10^{-3} M) were made spectrophotometrically by monitoring the changes in the visible absorption band, at the absorption maximum and at various positions within the band in a wide range of solvent systems. Measurements were made of the decay rates of photoinduced (ultraviolet) colored transients as well as the growth rates of color after bleaching of equilibrated solutions with visible light. In all cases, approach to equilibrium from either direction, *i.e.*, decay or growth of color, obeyed first-order kinetics over several half-lives. Average deviations in calculated rate constants for I (*vide infra*) over the temperature range of 4–50° did not exceed 10% in the worst case.

Results

A. Spectra of Colored Transients. Both the wavelength of maximum absorption and the shape of the absorption band of the colored transient from I, II, and III change significantly as solvent properties are varied. The spectra of benzene and ethanol solutions

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[19] G. H. Brown and W. G. Shaw, *Rev. Pure Appl. Chem.*, **11**, 2 (1961).

[20] W. West and S. Pearce, *J. Phys. Chem.*, **69**, 1894 (1965); W. West, S. Pearce, and F. Grum, *ibid.*, **71**, 1316 (1967).

[21] G. I. Lashkov and A. V. Shablya, *Opt. Spektrosk.*, **19**, 455 (1965).

[22] R. Heiligman-Rim, Y. Hirshberg, and E. Fisher, *J. Phys. Chem.*, 66, 2465, 2470 (1962).

[23] E. Berman, R. E. Fox, and F. D. Thomson, *J. Amer. Chem. Soc.*, 81, 5605 (1959).

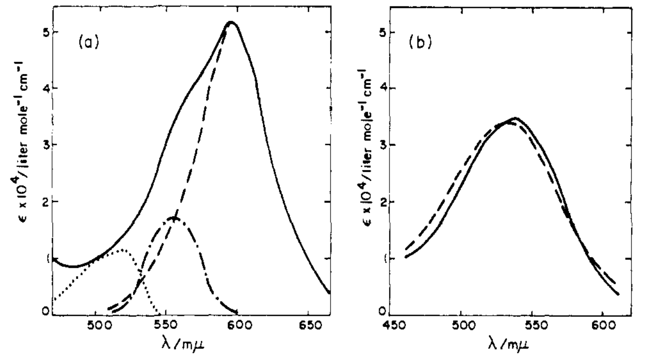

Figure 2. (a) Absorption spectrum of I in benzene at 25°, 0.44 *M*: ——, measured absorption; – – – –, *trans*-monomeric transient; –·–·–, second monomeric transient; ····, dimeric transient with "polymeric" absorption superimposed. (b) Absorption spectrum of I in ethanol at 25°: ——, 3.6 × 10^{-5} *M*; – – –, 1.2 × 10^{-2} *M*,

of I shown in Figure 2 are illustrative of the magnitude of these effects.

The visible absorption spectrum for I in benzene is not measurable (1.0 cm) below a concentration of *ca.* 5 × 10^{-2} *M* I. Above this concentration, the spectrum of a thermally equilibrated solution is reconstructed as shown in Figure 2a for 0.44 *M* I (~1.8 × 10^{-5} *M* "dye"). It is assumed here that optical densities are additive, that bands are symmetrical around their maxima, and that the longest wavelength maximum is not overlapped significantly by the shorter wavelength bands. The structured long wavelength absorption consists of two bands, at 596 and 555 mμ. That this band structure does not correspond simply to a vibronic progression in this compound was determined by irradiation in the longest wavelength band. A sharp cut filter was used which overlapped the long wavelength tail of this band. This experiment resulted in a decrease of the long wavelength band (596 mμ), relative to that at 555 mμ. Reequilibration of these bands was complete in a few seconds at room temperature. Thus the existence of at least two interconvertible species in benzene at room temperature is evident.

The absorption spectrum of I in benzene in the range 10^{-2} to 10^{-1} *M* was essentially the same as that produced by irradiation (365 mμ) of solutions less than 10^{-2} *M* I, as shown in Figure 3. However, at concentrations greater than 10^{-1} *M* a new band appeared at 490 mμ. This is partially resolved in Figure 2a and shown as a solid curve in Figure 3. An increase of total spiropyran concentration resulted, after thermal equilibration, in a simultaneous increase of the optical density at 490 mμ, with concomitant diminution of those bands at longer wavelength. The absorption spectrum of I in ethanol (Figure 2b) is distinctly different, with a single structureless band at 540 mμ (4 × 10^{-5} *M* I), shifting with increasing concentration to 532 mμ (1 × 10^{-2} *M* I).

In general, the equilibrium (>10^{-1} *M*) and photoinduced visible absorption spectra for indolinospiropyrans in hydrocarbon and other nonpolar solvents are similar, with structured absorption at long wavelength (~600 mμ). As solvent polarity is increased the band structure disappears and the absorption maximum gradually shifts to shorter wavelength, approaching the spectrum in ethanol.

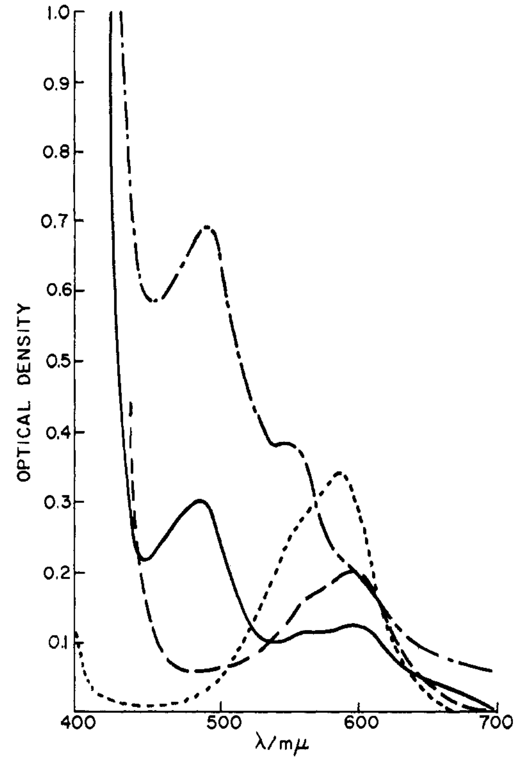

Figure 3. Absorption spectra of I in benzene at 25°: ····, photoinduced transient, 1.2 × 10^{-4} *M*, 1.0 cm; – – –, thermal transient, 1.2 × 10^{-1} *M*, 1.0 cm; ——, thermal transients ~1 *M*, 10.0 cm; –·–·–, products isolated from ethanol, >10^{-1} *M*, 10.0 cm.

The nmr spectra of I and its colored modification were measured; the pertinent results[24] are in Table I. The colored crystalline species was obtained by photolytic precipitation from hexane[7] and dried in air. The visible absorption spectra of this colored material when it was redissolved in various solvents corresponded to the transient spectra which resulted from photolysis of I in the respective solvents.

Table I. Nmr Spectra[a] for I and Its Colored Transient

Compd	δ,[b] ppm	Relative intensity	Assignment
I	1.15	3	$(CH_3)_2C<$
	1.25	3	
	2.69	3	$CH_3N<$
Colored transient of I	1.22	6	$(CH_3)_2C<$

[a] Solvent CD$_3$OD; 30°; Varian HA-100 nmr spectrometer. [b] Relative to TMS.

B. Equilibria. The results of application of eq 2 for I in benzene are illustrated graphically in Figure 4. The required linear relationship between total spiropyran concentration S_T and optical density of the visible absorption maximum is apparent for the concentration range 10^{-2} to 10^{-1} *M* spiropyran. Calculation of K_e at a given temperature from the slopes of these plots demands knowledge of the molar extinction coefficient, ε. This is known for a limited number of

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(24) These data were provided by Dr. William L. Budde, Midwest Research Institute, Kansas City, Mo. 64110.

Table II. Equilibrium Data for I at 25°[a]

Solvent	10^5K_e	ΔH, kcal mol^{-1}	ΔG, kcal mol^{-1}	ΔS, cal (mol deg)$^{-1}$
C_2H_5OH	843 ± 271	2.1 ± 0.4 (2.1)	2.8 ± 0.2 (2.6)	−2.4 ± 2.0 (−1.9)
$(CH_3)_2CO$	134 ± 43	1.8 ± 0.3 (3.0)	3.9 ± 0.2 (3.8)	−7.1 ± 1.6 (−3.1)
$CHCl_3$	9.76 ± 3.15	0.52 ± 0.22	5.4 ± 0.2	−16 ± 3
C_6H_6	4.10 ± 1.31	4.4 ± 0.4	6.0 ± 0.2	−5.4 ± 2.0

[a] Values in parentheses from ref 13.

solvents and spiropyrans, but is generally in the range 3.6–6.0 × 10^4 l. mol^{-1} cm^{-1},[25] the higher values occurring in nonpolar solvents.

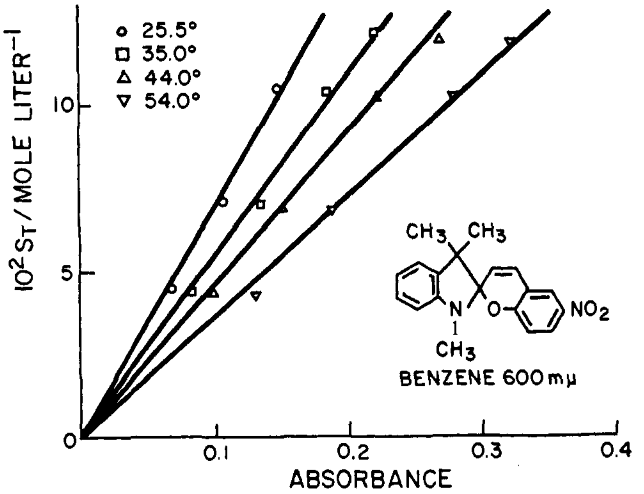

Figure 4. Initial concentration of I *vs.* equilibrum absorbance in benzene at 600 mμ: concentration range, 10^{-2} to 10^{-1} *M*.

While the magnitude of K_e depends on ϵ, it can be shown that thermodynamic data derived therefrom are relatively unaffected. Hence, for the colored transient from I, the value 3.5 × 10^4 l. mol^{-1} cm^{-1} in ethanol[7,25] was used for polar solvents, and 5.2 × 10^4 l. mol^{-1} cm^{-1} [25] for nonpolar solvents. Allowance was made for a 50% variation in these numbers. The temperature variation of K_e for four solvents is shown in the van't Hoff isochores of Figure 5, where each point represents duplicate determinations of K_e. The limits of error for K_e at 25° and the derived thermodynamic data given in Table II largely reflect the uncertainty in ϵ.

C. Kinetic and Energetics. The kinetic equation describing approach to equilibrium *via* opposing first-order reactions, *i.e.*, in the present cases

$$S_e \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B \tag{3}$$

is given by

$$\frac{\partial A}{\partial t} = k_f(A_0 - A_t) - k_r(A_t) \tag{4}$$

where $\partial A/\partial t$ = rate of change of visible absorbance (sec^{-1}), k_f = first-order coloration rate constant (sec^{-1}), k_r = first-order decoloration rate constant (sec^{-1}), A_0 = visible absorbance if all spiropyran existed in the colored form, and A_t = visible absorbance at any time t. The solutions of this equation are

$$(k_f + k_r) = \frac{1}{t}\ln\left|\frac{A_t - A_e}{A_0 - A_e}\right| \tag{5}$$

for decoloration after exposure to ultraviolet, and

$$(k_f + k_r) = \frac{1}{t}\ln\left|\frac{A_e - A_t}{A_e - A_i}\right| \tag{6}$$

for coloration after bleaching with visible light, where A_i = visible absorbance after bleaching.

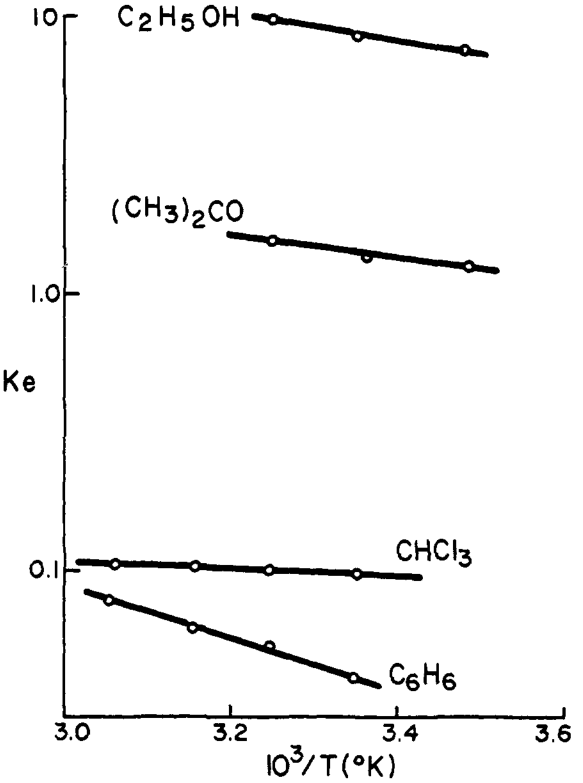

Figure 5. van't Hoff isochores for I in selected solvents.

In either case, for these reversible systems, the kinetic analysis predicts the logarithm of the difference between equilibrium absorbance and absorbance at time t to be linear with time, the slope giving the sum of the forward and reverse rate constants ($k_f + k_r$). When the magnitudes of these constants are sufficiently different, a measurement of *either* the decoloration or the coloration rate will yield the value of the larger, *i.e.*, k_f or k_r. In the present scheme, for I, the ratio k_f/k_r, given by K_e, is no greater than 10^{-2}, as seen in Table II. Thus

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[25] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 487.

Table III. Kinetics and Energetics of Thermal Decay of Visible Band from I at 25° [a]

Solvent	$10^4 k_r$, sec^{-1}	A_r, sec^{-1}	$\Delta S_r^{\ddagger}$, cal (mol deg)$^{-1}$	E_r, kcal mol^{-1}
C_2H_5OH	3.76	5.8×10^{14} (2.1×10^{15})	9.0	24.7 (25.7)
$(CH_3)_2CO$	47.3	2.0×10^{15} (3.3×10^{15})	11.4	23.9 (24.3)
$CHCl_3$	133	1.9×10^{15}	11.3	23.3
CCl_4	211	1.7×10^{10}	−11.7	16.2
C_6H_6	1120	1.6×10^{11}	−7.2	16.5

[a] Values in parentheses from ref 13.

the kinetic data for either decoloration or coloration give a direct measure of the reverse rate constant k_r. In fact, this is verified in all systems studied, insofar as the measured rate constant ($k_f + k_r$) is independent of the direction of approach to equilibrium. A typical kinetic rate plot for I is shown in Figure 6, for equilibration from either direction in ethanol. The equivalence of the gradients of these curves is evident over several half-lives ($\tau \sim$700 sec). A similar situation prevails for II and III. The rates of disappearance of the colored transient from I after ultraviolet exposure were measured at 25° in a wide range of solvents, including hydrocarbons, polar aprotic solvents, and alcohols. These results are shown for I in Figures 7–9 plotted against selected solvent parameters. Plots for I of log ($k_f + k_r$) are shown *vs.* solvent cohesive energy or internal pressure in Figure 7. The latter was calculated as the ratio of energy of vaporization E_v to solvent molar volume V_m.[26] Figure 8 shows the relationship between log ($k_f + k_r$) and the reciprocal of solvent dielectric constant, ϵ. The dependence of log ($k_f + k_r$) on the reciprocal of the dielectric constant–viscosity product, $\eta\epsilon$, is in Figure 9. Figure 10 shows the kinetic data for I, II, and III in dioxane-water mixtures. Included in this plot for comparison are the ionic association constants of Atkinson and Mori for LiI,[27] The percentages refer to weight per cent dioxane. Solvent properties were were taken from the data of Akerlöf and Short.[28]

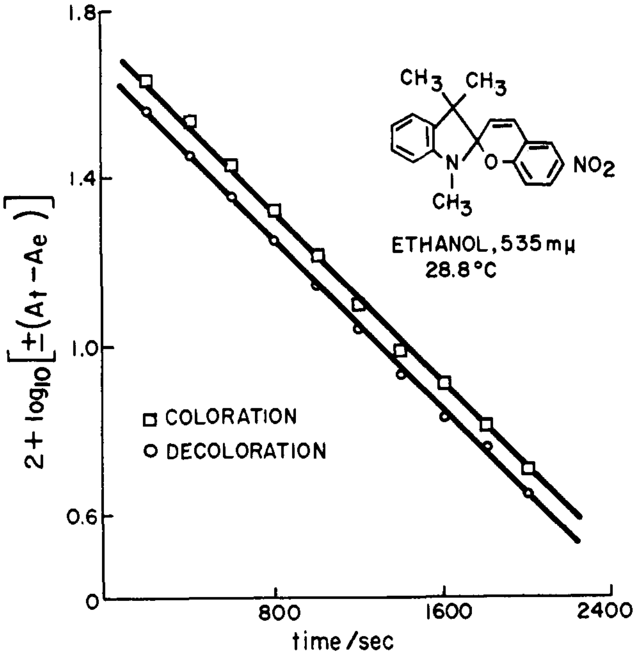

Figure 6. Kinetic rate plot for first-order coloration and decoloration reactions of I in ethanol at 28.8°, λ 535 mμ; ($k_f + k_r$): □, 6.3×10^{-4} sec^{-1}; ○, 5.9×10^{-4} sec^{-1}.

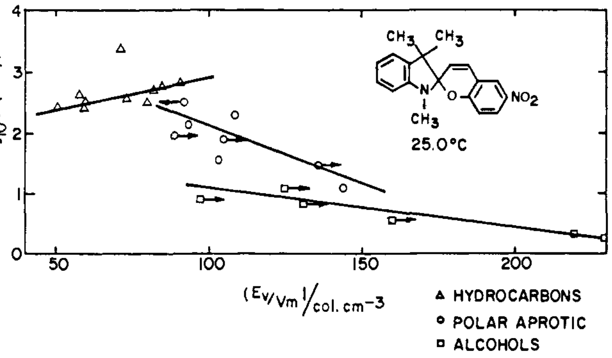

Figure 7. Relation of log ($k_f + k_r$) for I to cohesive energy of selected solvents at 25°.

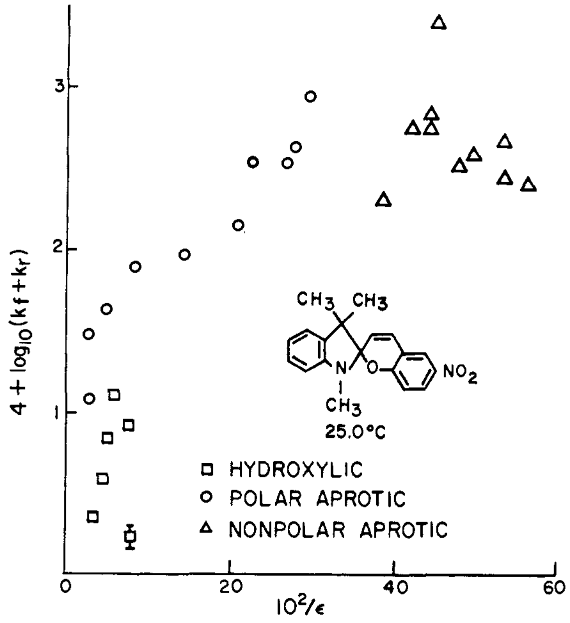

Figure 8. Dependence of log ($k_f + k_r$) for I on $10^2/\epsilon$ in selected solvents at 25°.

The variation with temperature (4–50°) of ($k_f + k_r$) was determined for thermal reactions of the colored transient from I in five different solvents. The results

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(26) Heats of vaporization from N. A. Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1956, p 1550. Points marked with arrows correspond to solvents for which E_v at 25° is not reported. For all but one of these, the E_v corresponds to the normal boiling point of the solvent. Hence the points so denoted should be shifted in the indicated directions.

(27) G. Atkinson and Y. Mori, *J. Chem. Phys.*, **45**, 4716 (1966).

(28) G. Akerlöf and O. A. Short, *J. Amer. Chem. Soc.*, **58**, 1241 (1936).

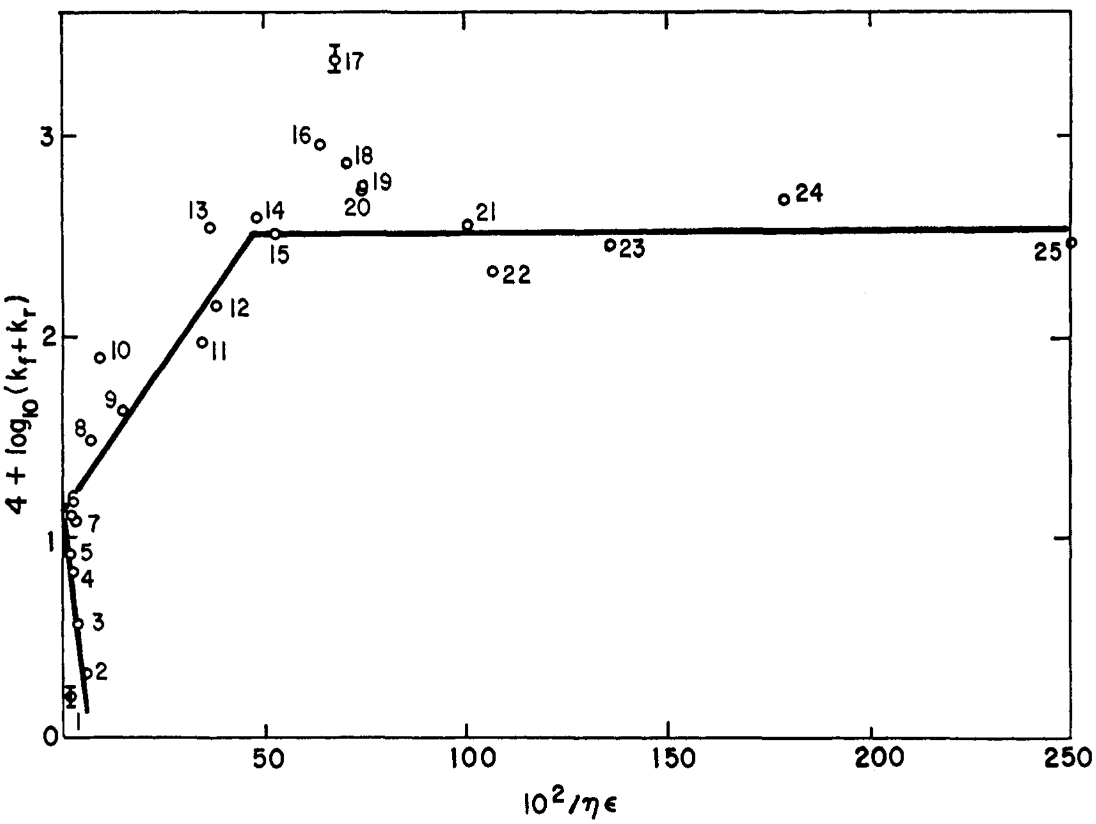

Figure 9. Log $(k_f + k_r)$ *vs.* $10^2/\eta\epsilon$ for I at 25°; solvents: 1, benzyl alcohol; 2, methanol; 3, ethanol; 4, 1-propanol; 5, 1-pentanol; 6, 2-propanol; 7, N,N-dimethylformamide; 8, acetonitrile; 9, acetone; 10, pyridine; 11, ethyl formate; 12, chloroform; 13, ethyl acetate; 14, cyclohexane; 15, carbon tetrachloride; 16, propyl ether; 17, cyclohexene; 18, benzene; 19, toluene; 20, *p*-xylene; 21, ethyl ether; 22, carbon disulfide; 23, heptane; 24, hexane; 25, 2-methylbutane.

are shown graphically in Figure 11 as an Arrhenius plot. Table III summarizes the pertinent kinetic rate constants and derived quantities $\Delta S_r^{\ddagger}$ and E_r, the entropy and energy of activation, respectively, for the reverse reaction or decoloration.

While a direct measure of k_f at a given temperature is not possible in the present systems, it is attainable through the relationship $K_e = k_f/k_r$. Likewise, $\Delta S_f^{\ddagger} = \Delta S + \Delta S_r^{\ddagger}$, and $E_f = \Delta H + E_r$. These derived quantities for I are in Table IV.

Table IV. Kinetics and Energetics for Thermal Coloration of I at 25° [a]

Solvent	$10^6 k_f$, sec^{-1}	A_f, sec^{-1}	$\Delta S_f^{\ddagger}$, cal (mol deg)$^{-1}$	E_f, kcal mol^{-1}
C_2H_5OH	3.2	1.7×10^{14} (8.4×10^{14})	6.6	26.8 (27.8)
$(CH_3)_2CO$	6.3	5.6×10^{13} (6.6×10^{14})	4.4	25.7 (27.3)
$CHCl_3$	1.3	4.4×10^{11}	−5.2	23.8
C_6H_6	4.6	1.14×10^{10}	−12.5	20.9

[a] Values in parentheses from ref 13.

Discussion

A. Spectra of Colored Transients. The existence of different stereoisomers of the colored transients from spiropyrans was inferred earlier from low-temperature optical absorption[18,22] and luminescence measurements,[21] but structural assignments have not yet been made, and the individual species have defied attempts at isolation. However, it appears necessary to consider in detail the multiplicity of transient species possible, and the various decay mechanisms of each, in order to arrive at a satisfactory explanation of the solvatochromism of the transients from indolinospiropyrans.

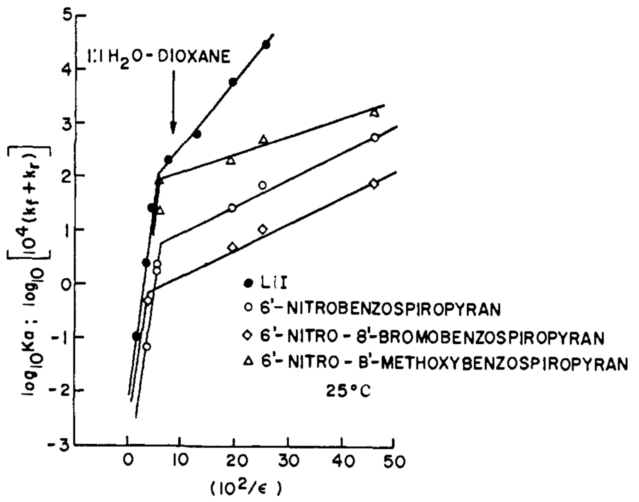

Figure 10. Dependence of log $(k_f + k_r)$ on $10^2/\epsilon$ for I, II, and III in dioxane–water mixtures. Dependence of log K_a on $10^2/\epsilon$ for LiI ion-pair association.[27] Weight per cent dioxane is indicated.

The visible absorption spectrum of the photoinduced colored transient of I (Figure 3) in benzene is resolved into two bands. That these bands cannot be attributed to normal vibrational structure is evidenced by the photochemical experiment demonstrating the existence of at least two independent molecular species. These

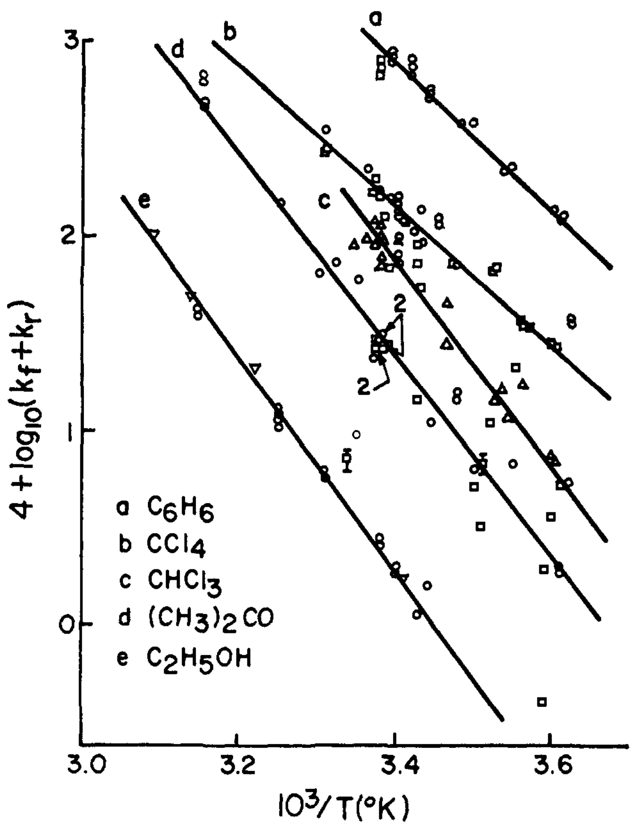

Figure 11. Arrhenius plot for thermal reactions of I. (a) C_6H_6: ○, 600 mμ; □, 615 mμ; decoloration; (b) CCl_4: ○, 617 mμ; □, 570 mμ; decoloration; (c) $CHCl_3$: □, 610 mμ; △, 580 mμ; ○, 540 mμ; coloration and decoloration; (d) $(CH_3)_2CO$: □, 565 mμ; ○, 545 mμ; coloration and decoloration; (e) C_2H_5OH: ○, 530 mμ; coloration and decoloration; ▽, decoloration, data from ref 8; □, decoloration, data from ref 14 and 18.

independent species are likely to be stereoisomers which rapidly interconvert at room temperature. The appearance of an additional band at 490 mμ and deviation of the long wavelength bands from Beer's law at high ($>10^{-1}$ *M*) spiropyran concentration indicate dimerization of the dye species. A shoulder toward short wavelength on the 490-mμ band in Figure 3 (solid curve) is support for the presence of higher aggregates.

The very recent studies by West and coworkers[20] on the solution absorption spectra of *meso*-substituted thiacarbocyanine dyes are of interest for comparison. These dyes are ionic and structurally quite similar to the postulated zwitterionic colored forms of spiropyrans. The existence of *cis* and *trans* monomeric isomers and, in polar solvents, *trans* dimers and higher "polymers" has been shown for these dye systems. Also demonstrated were the low-temperature interconvertibility of the isomers by visible light, and the subsequent rapid thermal equilibration of the isomers on warming to room temperature. A further example is found in the work of McCartin,[29] who demonstrated the existence of metastable isomeric cyanines under flash excitation. While other studies[30] of solvent effects on the spectra of merocyanines indicate the existence of isomeric species of these dyes, the authors did not interpret their findings from this viewpoint.

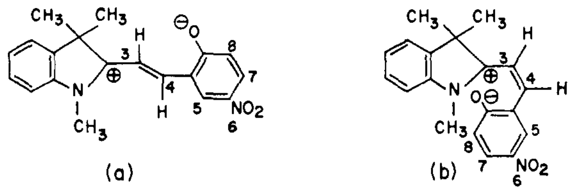

Figure 12. (a) *trans*-Monomeric transient of I; (b) *cis*-monomeric transient of I.

The shorter wavelength visible absorption in cyanines is ascribed[20] to a dimer, probably of an all-*trans* species. A shoulder at yet shorter wavelength corresponds to higher aggregates, or H polymers. To date, there are no reports of similar studies on nonionic merocyanine dyes.

Of the possible monomeric isomers of the colored transient of I, two are illustrated in Figure 12. In addition to the *trans* structure shown in Figure 12a, three other configurations are formally realized by 180° rotation of either or both of the substituent nuclei around the respective bonds to the 3 or 4 carbons. Such a rotation of the benzenoid nucleus leads to interactions between the 3 and 5 H atoms, the repulsive nature of which would raise the energy of such a conformation, relative to that of Figure 12a, which has an attractive interaction between the 3 H and 9 O. Such a repulsive interaction would act to destroy the coplanarity of atoms in the colored chromophore. Thus, two *trans* conformers are possibly energetically unfavorable; of the remaining two, corresponding to two orientations of the indolino nucleus, neither can be discarded on steric considerations, since chromophore planarity is conserved by both. On the other hand, if a *trans* isomer with positive charge on nitrogen is considered, a structure analogous to that of Figure 12a may be rendered unfavorable by the large charge separation in such a conformation. Thus it is clear that the relative stability of *trans* isomers is determined by a complex and subtle interplay of steric and coulombic factors. This situation makes *a priori* assignment of absolute configuration to a *trans* isomer a difficult task. Of the four possible *cis* conformers formally derived from Figure 12b, none is capable of achieving a completely planar configuration, because of steric interference between the two substituent nuclei joined by the spiro carbon. Thus any *cis* configuration attained is most likely of higher energy than the planar *trans* isomers and contributes to a lesser degree in equilibrium mixtures at room temperature.

On the basis of the preceding considerations, and the corresponding spectral behavior in cyanines, it is reasonable to assign the more intense long wavelength band at 596 mμ in benzene to a *trans* monomer from I. Such an assignment is consistent with the preferred formation of a *trans* isomer on energetic grounds and with the criterion advanced[31] to distinguish between extended *trans* and *cis* configurations of polymethine dyes; *i.e.*, a *trans* isomer exhibts greater extinction in the longest wavelength electronic absorption because of the enhanced transition moment associated with the

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(29) R. J. McCartin, *J. Chem. Phys.*, **42**, 2480 (1965).

(30) S. Hunig, *et al.*, *Ann.*, **690**, 9 (1965); Y. Hirshberg and E. Fisher, *J. Chem. Phys.*, 22, 57 (1954).

(31) R. S. Mulliken, *J. Chem. Phys.*, 7, 364, 570 (1939); H. Kuhn, *Helv. Chim. Acta*, 34, 1308 (1951); L. Zeichmeister, A. L. LeRosen, W. A. Schroeder, A. Polgár, and L. Pauling, *J. Amer. Chem. Soc.*, 65, 1940 (1943).

longer chromophoric chain. In fact, extinction coefficients for the dominant transient species from indolinospiropyrans in nonpolar solvents are generally two to three times greater than those for transients in polar solvents.[25] The shorter wavelength shoulder at 555 mμ then represents one of the less energetically favored *trans* isomers, or a *cis* isomer.

The parallel between the spectral behavior of the colored species from I and cyanine dyes suggests assigning the 596- and 555-mμ bands in benzene to monomeric species; the concentration-dependent bands at 490 mμ are probably those of a dimer and/or higher aggregates.

The presence of dimeric species of the transient dye from I should be confirmed by examining the respective concentrations of monomer, (M), and dimer, (D), as total concentration of spiropyran is changed. These concentrations should adjust according to the law of mass action, *i.e.*

$$(\mathrm{D}) = (\mathrm{M})^2 K_\mathrm{d} \tag{7}$$

where K_d is the dimeric dissociation constant. Thus a plot of log (D) *vs.* log (M) should be linear with slope of 2. In the present case for the spiropyran I, an attempt was made to confirm this relationship for the 596- and 490-mμ absorption bands in benzene and toluene. These solvents were chosen because I is readily soluble up to concentrations of *ca.* 1 *M*. Unfortunately, in these solvents the total concentration of "dye" species in equilibrium with I at its limit of solubility is of the order of 4×10^{-5} *M*. Thus over the range 0.1–1 *M* I, concentration studies were unsatisfactory because of low total absorption and the overlap of the respective absorption bands of species assigned as monomer and dimer. While a precise determination of the slope of a log (D) *vs.* log (M) plot was not possible, it was found that this slope lies between 1 and 3, bracketing the value required by eq 7. Since the direct experimental confirmation of the dimerization hypothesis is not attainable for the present system,[32,33] indirect approaches must be taken to gain support for this hypothesis. This is attempted in the analysis of spectral, kinetic, and thermodynamic data which follows.

Reconstruction of the absorption spectrum of the colored species from I in ethanol to obtain the contributions from each is not possible at room temperature. As shown in Figure 2b the spectrum is structureless over a wide range of concentration of I. However, it is likely that the relative amount of *trans* monomer is vanishingly small, since absorption is low in the region of 590–600 mμ. Two other possibilities exist, *i.e.*, a solvent-stabilized (*via* hydrogen bonding) *cis* monomer ($\sim$555 mμ) and/or a dimeric or polymeric species at 490 mμ. The shift of the absorption maximum in ethanol to shorter wavelength with increasing concentrations of I is probably the result of increasing dimer and/or polymer concentration. While the bands for these three species are not resolvable in the present case, it appears that there are contributions from each.

The dimer assignment, particularly for I in ethanol, is supported by the fact[20] that preferential dimerization of cyanines occurs in polar solvents, as well as by the following observations. When an ethanolic solution of I was allowed to evaporate slowly to dryness, the residue consisted of red and yellow crystalline material. When this material was dissolved in benzene at high concentration ($>10^{-1}$ *M*), the initial visible absorption spectrum was different from that normally found for solutions of I at high concentration in benzene or ethanol. This spectrum is shown in Figure 3. A strong band occurred at 490 mμ and a weaker band at 553 mμ. A shoulder at $\sim$600 mμ persisted to 700 mμ. These bands changed slowly, leaving after several hours the spectrum also shown in Figure 3 (dashed curve). An isosbestic point occurred in the region of 540 mμ. These observations are interpreted as the result of a gradual concentration of dimeric (or polymeric) species in ethanol, as solvent slowly evaporated. The residue, when dissolved at high concentration in benzene, was rich in the dimeric or polymeric colored species. The preferred stabilization of a *cis* isomer by ethanol is suggested by the band at 553 mμ in benzene solution of the residue from ethanol. The long tail to 700 mμ may represent *trans* monomeric isomers, or perhaps the "forbidden" N band of a dimer.[34]

The observed continuous variation in spectral wavelength maxima for the visible absorption of transients from I in polar aprotic solvents between the extremes just discussed is understood as representing differing extents of the "monomer–dimer" equilibria. Additional support for this is found in the examination of kinetic and thermodynamic results which follows.

B. Kinetic Solvent Effects. It is evident on inspection of Figures 7–9 that the kinetic behavior of the transients of I is strikingly different in the three classes of solvents. This result complements the spectral evidence for different transient species in the respective solvents.

The relationship between log $(k_\mathrm{f} + k_\mathrm{r})$ and solvent cohesive energy in Figure 7 shows the kinetic behavior in hydrocarbons to be distinct from that in alcohols. The slopes of lines connecting points for the solvents in these classes are opposite in sign. Furthermore, the absolute value of $(k_\mathrm{f} + k_\mathrm{r})$ varies between these solvents by as much as three orders of magnitude. The correlation for polar aprotic solvents is less reliable than that for the other two classes but, on the basis of the negative slope, places these solvents as intermediate, or closer to the alcohols. Stated otherwise, the reacting species in polar aprotic solvents is apparently more similar to that in alcohols than that in hydrocarbons.

A useful analysis of the relationships of the kinetic rate constants $(k_\mathrm{f} + k_\mathrm{r})$ for the first-order decoloration of the transient of I to the internal pressure or cohesive energy of solvent is possible in terms of the Hildebrand equation[35] for solute activity. If electrostatic forces are neglected, it can be shown that ln $(k_\mathrm{f} + k_\mathrm{r})$ is given by[36]

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[32] The spectrum in Figure 2a corresponds to an equilibrium "dye" concentration of $\sim 1.8 \times 10^{-5}$ *M*. Assuming a dimeric dissociation constant of 10^{-5} mol l.$^{-1}$,[20] and ϵ dimer $\sim 10^4$ l. mol^{-1} cm^{-1},[20] the absorbance of dimer is calculated as $\sim 10^{-1}$ or slightly greater. The agreement with the absorbance of the resolved dimer band in Figure 2a is more than satisfactory, in view of the approximate nature of this estimate.

[33] A similar situation was reported by S. E. Sheppard and A. L. Geddes, *J. Amer. Chem. Soc.*, 66, 2003 (1944).

[34] T. Förster, "Fluoreszenz Organisher Verbindungen," Vandenhoeck and Ruprecht, Göttingen, 1951, p 254.

[35] J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1950.

[36] For a different form of this equation, see A. A. Frost and R. G.

$$\ln (k_f + k_r) = \ln k_0 + \frac{V_B}{RT}\delta_B{}^2 - \frac{V_{\ddagger}}{RT}\delta_{\ddagger}{}^2 - \delta_1\left[\frac{2(V_B\delta_B - V_{\ddagger}\delta_{\ddagger})}{RT}\right] + \delta_1{}^2\left[\frac{(V_B - V_{\ddagger})}{RT}\right] \quad (8)$$

with $\delta = (E_V/V_m)^{1/2}$ and k_0 = specific first-order rate constant at infinite dilution (sec^{-1}). The subscripts B, $\ddagger$, and 1 refer, respectively, to the colored transient, to the transition state for decoloration, and to the solvent. Only the latter two terms on the right side of this equation refer to solvent, and of these the first is much smaller; *i.e.*, the term $(V_B\delta_B - V_{\ddagger}\delta_{\ddagger}) \ll (V_B - V_{\ddagger})$. Thus the relationship between log $(k_f + k_r)$ and $\delta_1{}^2 = (E_{V_1}/V_{m_1})$ is predicted to be linear for a range of solvents, with slope given by

$$(V_B - V_{\ddagger})/2.3RT \quad (9)$$

The results of the application of eq 8 to the data for I, shown in Figure 7, can then be discussed in terms of the relative molar volumes of colored dye species and the transition state for decoloration. The positive slope observed for hydrocarbon solvents leads to the result that $V_B > V_{\ddagger}$ in these systems. On the other hand, the negative slope for alcohols and polar aprotic solvents implies the reverse is true, *i.e.*, $V_{\ddagger} > V_B$. Both conclusions are understood in light of the foregoing analysis of spectroscopic data, where the predominant species in alcoholic and polar solvents is dimeric, or a solvent stabilized *cis* monomer. In order for $V_{\ddagger} > V_B$ in these solvents, the rate-determining step in decoloration must be that of dissociation of a dimer, or of a dye–solvent complex. On the other hand, the rate-determining step in nonpolar solvents would be ring closure. The observation that $V_{\ddagger} < V_B$ then corresponds to formation of the spiropyran ring structure from an extended monomeric *trans* configuration of the colored transient.

It has been assumed[3,4,6] that structural reorganization in the spiropyran accompanying decay of color is substantial. Rehybridization of the spiro carbon requires rotation through 90° of the two portions of the molecules joined by this carbon, as the two ring systems pass from a coplanar to a noncoplanar configuration. The first absolute confirmation of this hypothesis is found in the results of nmr studies given in Table I. This is discussed here for its pertinence to the mechanistic analyses to follow. The two signals (δ 1.15, 1.25) assigned to CH_3 on the 3′ carbon in I are those expected for magnetically nonequivalent CH_3 groups in such a nonplanar structure. On the other hand, the single $(CH_3)_2C<$ resonance observed for the colored species confirms the equivalence of the 3′ methyls and the planarity of that species. From the foregoing structural confirmation, it appears possible that, if the transition state for decoloration is geometrically closer to the spiropyran product than to the planar colored transient, the decoloration kinetics may exhibit a viscosity dependence in isodielectric media. This hypothesis was tested by determining the rate of decoloration of the transient from I at 25° in solid paraffin and in a polystyrene film ($M \sim 2 \times 10^4$ g/mol). In the former, the half-life of the photoinduced colored transient was several days. In polystyrene the half-life was *ca.* 350 sec.[37] Nevertheless, the spectra of the colored species which were photoinduced in these highly viscous media were essentially the same as those described above for hydrocarbon solvents. In contrast, the half-life in the fluid hydrocarbons of the same colored species was <15 sec at 25°. Thus it is clear that increased viscosity impedes the rate of decoloration of I in hydrocarbon media and that the transition state for decoloration is most likely less planar than the highly colored transient.

The analysis to this point has led to certain qualitative conclusions based on spectroscopic and kinetic measurements. However, an important aspect of the chemical transformations in spiropyrans has not yet been considered, *viz.*, the electrostatic forces operative in the dynamic and equilibrium behavior of I and related spiropyrans. This will now be discussed in depth.

The process of reaction between ions is electrostatically described as that of bringing two point charges from infinite separation to the distance of closest approach in the transition state, $r^{\ddagger}$. The maximum work, W_m, and hence the electrostatic free energy change, $\Delta G_1{}^{\ddagger}$, for this process is

$$W_m = \Delta G_e{}^{\ddagger} = Z_+Z_-e^2/\epsilon r^{\ddagger} \quad (10)$$

It is readily shown,[38] therefore, that the rate constant for reaction between ions is

$$\log k = \log k_0 - (NZ_+Z_-e^2/2.3RT\epsilon r^{\ddagger}) \quad (11)$$

that is, the specific rate constant bears an inverse linear relationship to the dielectric constant ϵ, the slope of which depends on the product of the reactant ion charges. In the foregoing, k_0 is the rate constant in a solvent of infinite dielectric constant, and all other symbols retain conventional significance. These simplified laws apply only to dilute solution, solvation and ionic strength effects being neglected. Treatment of the data for I in single solvents according to eq 11, shown in Figure 8, is typically unsatisfactory in terms of the predicted linear relationship,[39] but a positive slope is evident for polar aprotic solvents. The positive slope of this trend is evidence, from eq 11, for reaction between oppositely charged centers in the colored transient. The diminished log $(k_f + k_r)$ in alcohols is understood as being caused by two effects—first, the liklihood that the reacting species in these solvents is largely dimeric, and, second, an increased stabilization of the polar colored transient by these hydrogen-bonding solvents. The magnitude of the effect is consistent with the energy of a weak hydrogen bond, *i.e.*, *ca.* 1–3 kcal mol^{-1}.[40]

If solvent viscosity η as well as the dielectric constant ϵ is taken into account, the correlation of Figure 9 is

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Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1962, p 131.

(37) The polystyrene–spiropyran film was coated from a toluene solution of the two. The amount of residual solvent in the film was not determined. However, it was found that the half-life of the transient from I increased with the age of the polystyrene film. The paraffin film was coated from a melt.

(38) Reference 36, p 144.

(39) Such behavior is well known for reaction between ions in different solvents, owing to specific solvent effects, including variations in solvent free volume, ion solvation, ionic size, degree of association of ions, and of solvent, etc. *Cf.*, *e.g.*, K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 392.

(40) This estimate is based on comparison of log $(k_f + k_r)$ for isodielectric solvents, one hydroxylic, the other polar aprotic, *e.g.*, ethanol *vs.* acetone.

obtained for log $(k_f + k_r)$ *vs.* $(\eta\epsilon)^{-1}$. The viscosities of solvents represented do not vary by over an order of magnitude, yet inclusion of the dependence of log $(k_f + k_r)$ on η^{-1} alters the correlation with ϵ^{-1}. In solvents of low ϵ a plateau emerges beyond which viscosity reductions exert little effect on log $(k_f + k_r)$.

More worthy of attention, however, is the behavior illustrated in Figure 10 for I, II, and III in dioxane–water mixtures. The parallel between the curve for LiI ion-pair association constants,[27] K_a, and that for decoloration rate constants of the spiropyrans is striking. This observation is not confined to the electrolyte illustrated here,[41] nor to only three indolinospiropyrans,[42] but is general to both types of compounds. That such unrelated species should exhibit so similar a behavior in these solvents is understood in light of the processes being compared. The ion-association equilibria involves the ratio of the the rate of the forward process of bringing two charges from infinite separation to an equilibrium distance r to the rate of the reverse separation. Thus this system is described by equations similar in form to eq 10 and 11, with log K_a varying inversely with ϵ.[43] Likewise, any specific solvent effects on log K_a would then be manifest, though not necessarily to the same degree, in log $(k_f + k_r)$.

Of further significance is the visible absorption spectra of the transient of I in dioxane–water solutions. Below 80 wt % dioxane, the spectrum resembles that in ethanol (Figure 2b), with maxima at 520–540 mμ. As dioxane content is increased beyond 80%, the visible absorption maximum shifts rapidly to *ca.* 580 mμ, and is very similar to that in pure benzene (Figure 2) at 90–100% dioxane. The point of discontinuity in spectral and kinetic behavior in these systems, *i.e.*, 80% dioxane, corresponds to the molar composition 1:1 dioxane-water. Atkinson and Mori[27] speculated the formation of a strong 1:1 H-bonding complex between water and dioxane to explain this discontinuity in their results on LiI association. Subsequently, by ultrasonic absorption studies, Hammes and Knoche[44] demonstrated the existence of a 2:2 H-bonding complex between dioxane and water. Thus an explanation for the LiI association behavior is found in a competition between dioxane and Li^+ for water in this concentration region. A similar explanation holds for the kinetic and spectral observations on spiropyrans; *i.e.*, a competition for water exists between dioxane and transient dye molecules. Although it is not illustrated here, very much the same phenomena is observed for I in 2-propanol–benzene mixtures. A discontinuity in the log $(k_f + k_r)$ *vs.* ϵ^{-1} curve at ~1:1 alcohol–benzene indicates parallel processes occur in this system.

A very similar occurrence has only recently been communicated[45] for the ratio of dimer to monomer absorption bands for the dye methylene blue in *t*-butyl alcohol–water solution. The same authors[45] have explained a solvent effect in terms of a dimer–monomer equilibrium for Brooker's dye VII in this solvent system (*t*-BuOH–H_2O).

The binary solvent system dioxane–water is unique, insofar as it allows a clear distinction between the monomeric and dimeric species of the colored species produced on irradiation of I, II, and III. The ionic nature of these species is confirmed by the inverse dependence of decoloration rate constants on solvent dielectric constant according to eq 11.[46] The respective values of $r^{\ddagger}$ are ~3 Å for dimer or dye–solvent complex dissociation,[47,48] and ~30 Å for ring closure from the *trans* monomeric dye. These $r^{\ddagger}$'s are calculated on the assumption of oppositely charged univalent reacting centers, *i.e.*, $Z_+Z_- = -1$, as indicated by the positive slopes of Figure 10.

C. Thermodynamics and Energetics. It remains to examine the derived thermodynamic data and energetics presented in Tables II–IV in light of the evidence already discussed favoring ionic monomer–dimer equilibria in solutions of indolinospiropyrans. To illustrate trends, attention will again be focused on the extreme cases of ethanol and benzene. The energy and entropy diagrams for the respective transformations in these two solvents are shown in Figure 13.

It is clear from Table II that the change in equilibrium constant, K_e, is in the direction anticipated, with less ionization occurring as the solvent becomes less polar. Likewise, the free energy change, ΔG, increases monotonically with decreasing polarity of solvent. The most striking features are the low endothermicities and negative entropies of reaction. All these effects are characteristic of ionization equilibria.[49] As before, a simple model may be applied to determine the effect of solvents of different dielectric constant on the ionization

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[41] See also T. L. Fabry and R. M. Fuoss, *J. Phys. Chem.*, **68**, 971, 974 (1964), and references cited therein.

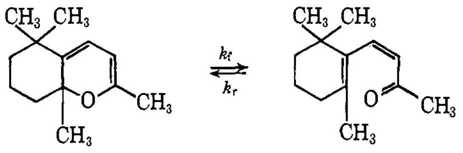
[42] Unpublished data, this laboratory.

[43] (a) R. M. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958); (b) W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

[44] G. G. Hammes and W. Knoche, *J. Chem. Phys.*, **45**, 4041 (1966).

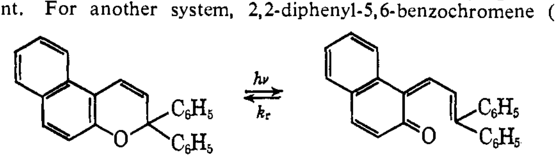
[45] M. J. Blandamer, D. E. Clarke, T. A. Claxton, M. F. Fox, N. J. Hidden, J. Oakes, M. C. R. Symons, G. S. P. Verma, and M. J. Wootten, *Chem. Commun.*, 273 (1967).

[46] Kinetic solvent effects on the thermal valence isomerization of a related α-pyran (IV) to *cis*-β-ionone (V), *i.e.*



IV V

are pertinent at this point. The structures of the participating species in the mobile equilibrium shown here were confirmed by others.[5a] A kinetic study in this laboratory, the details of which will be presented elsewhere, has shown the ratio k_f/k_r $(=K_e) \leq 10^{-1}$ at 25°; the first-order rate constant k_r (25°) falls in the range 1–3 × 10^{-3} sec^{-1}, regardless of solvent. For another system, 2,2-diphenyl-5,6-benzochromene (VI),



VI VII

values of k_1 at 25° are 7.5 × 10^{-2} (2-propanol) and 9.5 × 10^{-2} sec^{-1} (benzene). The energy of activation is ~11 kcal^{-1} mol^{-1} in both solvents. The contrasting 1000-fold variation with solvent of k_r (25°) for the spiropyran I serves to underscore the conclusion that the transients from the indolinospiropyrans are zwitterionic, and that quinoid structures are of minor, if any, significance. Further evidence in support of this conclusion is found in the fact that hydrochloride salts are readily obtained for indolinospiropyrans, and their transients, while all attempts in this laboratory to produce similar salts from IV and VI or their transients (V, VII) have been unsuccessful.

[47] This distance compares well with the interplanar spacing of ~3.4 Å in aggregates of 3,3′-bis(β-carboxyethyl)-5,5′-dichloro-9-methylthiacarbocyanine.[48]

[48] E. S. Emerson, M. A. Conlin, A. E. Rosenoff, K. S. Norland, H. Rodriguez, D. Chin, and G. R. Bird, *J. Phys. Chem.*, **71**, 2396 (1967).

[49] Reference 31, p 133 ff.

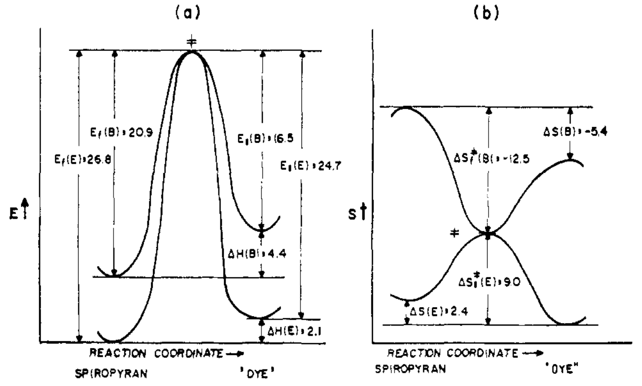


Figure 13. (a) Energy diagram for I in ethanol (E) and benzene (B), kcal mol^{-1}; (b) entropy diagram for I in ethanol (E) and benzene (B), cal mol^{-1} deg^{-1}.

of the spiropyran molecule. The electrostatic free energy change, ΔG_{el}, can be calculated from eq 10, and the corresponding electrostatic entropy change, ΔS_{el}, from

$$\Delta S_{el} = -(\partial \Delta G_{el}/\partial T)_P = (-Z_+Z_-e^2/\epsilon r)(\partial \ln \epsilon/\partial T)_P \quad (12)$$

Such a calculation for the four solvents in Table II reproduces the observed trends; *i.e.*, the electrostatic free energy change is inversely related to ϵ, and the entropy change is always negative but exhibits a minimum for $CHCl_3$.[49] However, it is likely that such agreement is fortuitous in the present instance, since absorption spectra of the colored species indicate a predominance of a dimeric species and/or a monomer-solvent complex in ethanol and acetone, while the monomeric dye prevails in benzene. Spectral and kinetic data show that $CHCl_3$ is close to benzene, *i.e.*, monomeric transients are dominant, but a higher amount of the transients absorbing at shorter wavelength are present. If solvents are thus distinguished on the basis of spectral considerations, the energetics for the monomeric species in $CHCl_3$ and benzene remain consistent with the predictions based on eq 12. The higher ϵ of $CHCl_3$ results in an increased K_e, and decreased ΔH, ΔG, and ΔS. In fact, the greater negativity of ΔS in $CHCl_3$ on comparison with benzene may be understood in part as reflecting the ability of $CHCl_3$ to hydrogen bond. If the monomeric dye were the dominant species in a solvent of higher ϵ than $CHCl_3$, one would predict from the electrostatic model, eq 12, a proportionally higher K_e and ΔS (this parameter would exhibit extremal behavior for $CHCl_3$), and lower ΔH and ΔG. The higher K_e values by a factor of $\sim 10^2$ in acetone and ethanol result from the preferred formation of dimeric and/or complexed species in these solvents. Hence, the thermodynamic parameters are composites of two terms, including ionization of the spiropyran, followed by dimerization or complexation of the colored species. The higher K_e's are a consequence of a slow dimer or complex dissociation relative to the faster ring-closure step. The negative entropy changes observed in all solvents are understood as the result of an ordering of solvent molecules in the vicinity of product ions. Since polar solvents are normally more structured than hydrocarbons, proportionally less negative entropy changes are characteristic of these systems.

The effects of varying solvent on the rate of color decay has been discussed. Inspection of Table III shows a dependence of the energetics of this same reaction on solvent. The values of $\Delta S_r^{\ddagger}$ are positive; E_r values ($= \Delta H_r^{\ddagger}$) are about 24 kcal mol^{-1} in the higher ϵ solvents ethanol, acetone, and the H-bonding solvent $CHCl_3$. The case in CCl_4 and benzene is distinctly different, $\Delta S_r^{\ddagger}$ being negative, and $E_r \simeq 16$ kcal mol^{-1}. These two extremes can be profitably discussed by reference to Figure 13. In benzene, the energy barrier for decoloration of 16.5 kcal mol^{-1} and the negative $\Delta S_r^{\ddagger}$ are seen as largely reflecting the formation of an ordered cyclic transition state from the *trans*-monomeric dye molecule.[50] The large energy barrier consists, in large part, of the resonance energy of the colored dye system. In contrast, the higher activation energy in ethanol corresponds to dissociation of a dimeric species or a "dye"-solvent complex. The positive $\Delta S_r^{\ddagger} = 9$ cal mol^{-1} deg^{-1} confirms this. It is estimated from the blue shift of the first $(n,\pi)^*$ [51] absorption band of the parent spiropyran I (332 mμ in ethanol *vs.* 336 mμ in benzene) that the ground state of the spiropyran is ~ 1 kcal mol^{-1} more stable in ethanol than benzene. Thus one can calculate from the data in Figure 13 that the transient "dye" in ethanol is about 3.3 kcal mol^{-1} more stable than that in benzene. This enhanced stability is a result of an exothermic dimerization and/or solvation of the polar species.

The energetics of the ionization of I can be considered on reference to Table IV and Figure 13. In contrast to the decoloration reaction, the rate constant for thermal coloration or ionization is practically insensitive to solvent. The negative entropy of activation in benzene for ionization is related to the ordering of solvent molecules around a polar transition state. The activation energy of 20.9 kcal mol^{-1} is now that for rupture of the C–O linkage in the pyran ring.

It would be anticipated[49] that the activation energies for the coloration reaction should be quite insensitive to solvent, since most factors determining the energy barrier for ionization are properties of the spiropyran.[14] That this is not the case, *e.g.*, $E_f = 26.8$ kcal mol^{-1} in ethanol, is a result of the approach used to generate the kinetic parameters describing the forward reaction. Thus thermodynamic quantities in ethanol refer to differences between spiropyran and colored dimer and/or complex. In the same solvent, kinetics of decoloration refer to dissociation of this species. The calculation of parameters for the forward reaction from these data neglects the intermediacy of the first-formed monomeric species, prior to dimerization and/or complexation. The E_r and $\Delta S_r^{\ddagger}$ calculated for polar solvents, therefore, simply represent the difference between spiropyran and the transition state for dimerization or complexation. In fact, the reaction path in these polar solvents is probably a double-barrier coordinate. The first and lower barrier corresponding to ionization would be followed by one higher for dimerizeration and/or complexation. The energy

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(50) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 254.

(51) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 186.

difference between the two transition states is substantially lower than that between I and the first transition state for ionization. On the other hand, a single-maximum potential energy diagram is sufficient for nonpolar solvents.

Conclusion

The complementary evidences gained from this spectral, kinetic, and equilibrium study lead to the conclusions that (a) the colored transients from indolinospiropyrans are zwitterionic; (b) these colored transients exist in solution as an equilibrium distribution distribution of steroisomers; (c) the dominant isomer in nonpolar solvents is a planar *trans*-monomeric species, while that in polar and hydroxylic media is a dimeric and/or associated species. It is shown that the effect of solvent on the visible absorption spectra of the transients from indolinospiropyrans parallels that for the ionic cyanine dyes.[20] This with the kinetic and equilibrium data presented indicate that contributions from quinoid species are probably minimal rather than dominant, as was previously thought[17] from spectral comparisons with the nonionic merocyanines.

An intriguing, but as yet unexplained feature of this work is the extremes of spectral and kinetic behavior exhibited by the indolinospiropyrans and the simple pyran and benzopyran.[46] In the latter cases the transient photoproduct appears to be a molecular species. In contrast, the action of the indolino nucleus in conferring definite zwitterionic character to the transient photoproduct from spiropyrans is dramatic. This apparent ability of the indolino substituent to stabilize ionic structures is of continuing research interest in this laboratory.

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The Fragmentation of Aliphatic Sulfur Compounds by Electron Impact

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Abstract: The energetics of formation of the molecule ion and sulfur-containing fragment ions have been examined for a number of simple aliphatic mercaptans and sulfides. The following fragment ion heats of formation have been obtained (all in kcal/mole): CH_3S^+, 214; CH_2SH^+, 220; $CH_3SCH_2^+$, 205; $C_2H_5S^+$, 202; CH_3CHSH^+, 197. The mass spectra of labeled sulfides and mercaptans have been compared with the analogous oxygen compounds. The sulfur compounds show increased intensities for the molecule ion and fragment ions originating by cleavage of the bond to the heteroatom, with a decreased abundance of ions originating by α cleavage. This is shown to be due primarily to the decreased stability of the ions formed by α cleavage in the sulfur compounds and not to the increased stability of RS^+ ions.

The mass spectra of simple aliphatic mercaptans and sulfides, when compared with the spectra of the corresponding alcohols and ethers, show significantly greater abundances of both the molecule ion and fragment ions formed by cleavage of bonds to the heteroatom, coupled with a reduced abundance of ions resulting from α cleavage with charge retention on the heteroatomic fragment.[1] The reasons for these differences are not clear; however, in terms of the quasi-equilibrium theory of mass spectra, they are most readily explained on the basis of the relative activation energies of the fragmentation reactions involved. The energetics of the fragmentation reactions have been reasonably well established for simple alcohols and ethers.[2,3]

Although several groups[4-8] have reported appearance potentials of fragment ions from organic sulfur compounds, no systematic investigation of the energetics of formation of the various isomeric ions has been made, with the result that the energetics of the fragmentation reactions in sulfur compounds are not clearly established. The present work reports such a detailed study for ions of empirical formula CH_3S^+ and $C_2H_5S^+$. During this study we have used extensive deuterium labeling to distinguish ionic structures which would otherwise have the same mass-to-charge ratio. The spectra of these labeled sulfur compounds, when compared to the spectra of the corresponding labeled alco-

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