BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1951—1956(1972)

Photo-decoloration Process of the Reverse Photochromic Spirans

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(Received July 30, 1971)

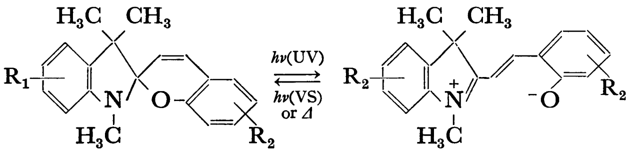
The unstable colorless form (A′) of the reverse photochromic spiran (SP-3) (1,3,3-trimethyl-5-methoxy-spiro[indoline-2,2′-benzopyran]-8′-carboxylic acid) was obtained in a stable state by vacuum evaporation (10^{-5} Torr) on a KBr substrate. It was confirmed by IR spectral analysis that reverse photochromism occurred between the colored (B′; merocyanine-like structure) and the colorless forms (A′; spiropyran). A colorless transient intermediate (X) was observed in the photo-decoloration process of the (SP-3). X was transformed into both A′ and B′. Thus the photo-decoloration efficiency ($\phi_{B'\to A'}$) depends on the ratio of the conversion from X to A′. State (B′) is stabilized in a polar or proton donative solvent. The life time of X is greatly influenced by the solvent as well as the stability of B′. The photo-decoloration efficiency ($\phi_{B'\to A'}$) of the spirans is effectively improved by substituting SP-2 with (methoxyl group) at 5-position. Whether X is observable or not depends on the substituent and its position. The reversibility of photochromic cycle of the spirans was restricted by the photobleaching of B′ by UV irradiation. It was observed that the photo-bleaching of B′ is accelerated in a degassed solution.

Derivatives of 1,3,3-trimethylspiro[indoline-2,2′-benzopyran] (SP-1) are well-known photochromic materials.[1]

The mechanism and kinetics of photo-coloration of spirans have been studied,[2] but detailed discussions on photo-decoloration process do not seem to have been made. This might be due to the unstability of the colored species of the photochromic spirans. It has been found that a compound substituted with –COOH at 8′-position (SP-2) exhibited reverse photochromism.[3] The colored form is more stable than the spiran form. The photo-induced bleaching of SP-2 and its derivatives were studied by means of flash photolysis.

The structure of the colored species of the reverse photochromic spirans is like that of a merocyanine dye, the colored form of the normal photochromic spirans. The color changes corresponding to the intramolecular transformation as follows.

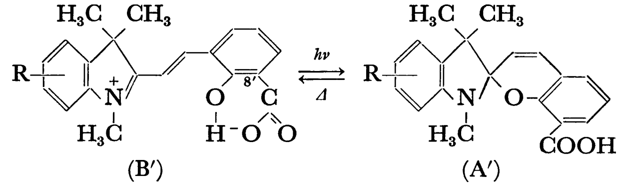
(a) normal photochromism



(A′) (B′)

Stable, colorless Unstable, colored

(b) reverse photochromism



(B′) (A′)

Stable, colored Unstable, colorless

Symbols A′ and B′ denote the colorless and the colored forms, respectively.

The existence of a colorless transient intermediate (X) was observed during the photo-decoloration of a reverse photochromic spiran (SP-3). In this paper, we propose a reaction scheme for the photo-decoloration process of the spirans.

We also describe the influence of both solvents and substituents on the photo-transformation and the effect of oxygen on the reversibility of the reverse photochromic process.

Experimental

Experiments were carried out with a set of flash spectrographic instrument (USHIO UFP-1). The half width of flash was 18 μsec with a power of 200 Joule/pulse. A quartz cell, 7 mmφ and 100 mm thick, was used at room temperature. The temperature of the solution during the measurement was kept constant in a range 5—60°C by using a doubly sealed quartz tube, in which water at constant temperature is circulated from a thermoregulated bath (Fig. 1).

The spirans are listed in Table 1. The photo-decoloration efficiency ($\phi_{B'\to A'}$) was obtained at a sufficiently low temperature (−40°C) to avoid thermal recoloration during measurements.

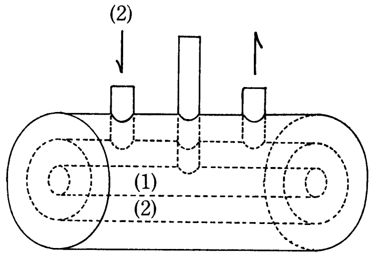


Fig. 1. Doubly sealed tube cell for measurement of flash photolysis at constant temperature.
1) sample solution, 2) circulated water

Results and Discussion

Molecular Structures of Colored and Colorless Forms of Reverse Photochromic Spirans. Reversible color change (photochromism) of spiropyrans has been confirmed to

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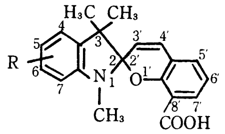
[1] Y. Hirshberg and E. Fischer, *J. Chem. Soc.*, **1954**, 297; R. Heiligman-Rim, Y. Hirshberg, and E. Fischer, *ibid.*, **1961**, 156.

[2] N. W. Tyer, Jr. and R. S. Becker, *J. Amer. Chem. Soc.*, **92**, 1289 (1970).

[3] I. Shimizu, H. Kokado, and E. Inoue, This Bulletin, **42**, 1730 (1969).

Table 1. Reverse photochromic spirans



No	Substituent, R
SP-2	H
SP-3	5-CH_3O
SP-4	4-CH_3O
SP-5	6-CH_3O
SP-6	5-Br
SP-7	5-CH_3CONH
SP-8	β-naphtho
SP-9	7-CH_3O
SP-10	5-Cl

be induced from intramolecular transformation between colorless spiropyran (A′) and colored merocyanine (B′) by irradiation of light. The colored form was formed on the rupture of C_{spiro}–O bond.

The photo-generated colored form (B′) was unstable, and the color diminished spontaneously when illumination was stopped. SP-1 substituted by –COOH at 8′-position (SP-2) and its derivatives are known to be "reverse photochromic" spirans. The colored form (B′) was more stable than the colorless one (A′) and was converted into A′ by irradiation with visible light. The color reappeared gradually when illumination was stopped.

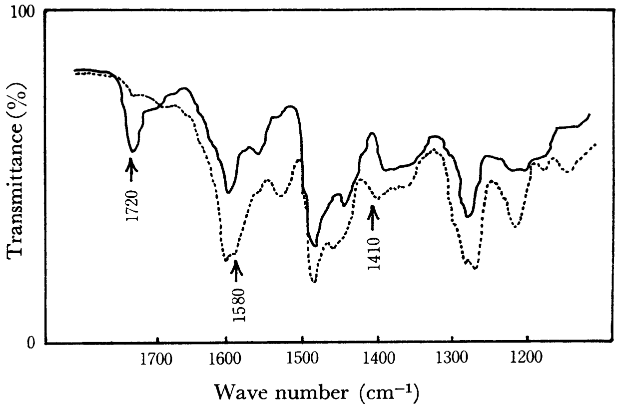
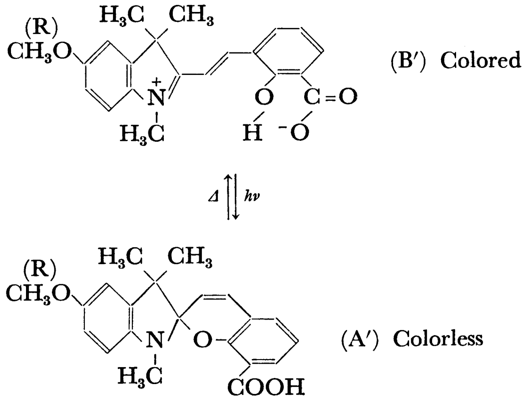


Fig. 2. I.R. spectra of the evaporated film of (SP-3) in the colorless and colored species on KBr.
(a) : ——colorless (b) : ······colored

When a layer of SP-3 (1,3,3-trimethyl-5-methoxy spiro[indoline-2,2′-benzopyran]-8′-carboxylic acid) was formed on a KBr crystal surface by vacuum evaporation, its (A′) state was preserved for a long time at room temperature. The IR spectra of A′ and B′ forms of SP-3 are shown in Fig. 2. The spectrum (a) almost coincided with that of the colorless form of SP-1 except for the bands at 1720 cm^{-1} and 3000—4000 cm^{-1} which are assigned to –COOH group. The colorless film on KBr crystal became gradually colored in the dark, and the IR spectrum was also transformed from (a) to (b) in the colored form. The band at 1720 cm^{-1} in (b) diminished and new bands due to CO_2^- appeared at 1580 cm^{-1} and 1410 cm^{-1}. The others were almost the same as the spectrum of colored form of SP-1. The structures of the colorless and colored forms (SP-3) were estimated as follows.



The stable colored form may be stabilized by a six membered ring between $-CO_2^-$ and –OH groups. The stable colored form was observed in all derivatives (presented in Eq. (2′)) having –COOH group at 8′-position. Thus the reverse photochromism of (SP-2) and its derivatives are given by Eq. (2′).

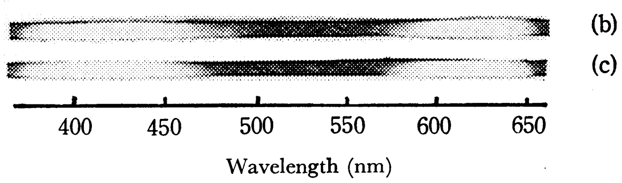


Fig. 3. Spectrographies of (SP-3) in acetone at each delay time (t) after illumination with flash light.
(a) before illumination.
(b) t=30 μsec.
(c) t=30 msec.

Photo-decoloration Process of SP-3. The color of the solution (ethanol, acetone, *etc.*) of SP-3 disappeared by irradiation with visible or ultraviolet light. Spectrograms of SP-3 in acetone at each delay time after illumination with flash light are shown in Fig. 3. Absorption band at visible range (near 550 nm) decreased just after illumination (delay time 30 μsec). The color reappeared partly within 30 msec after the illumination.

By photochemical analysis in the steady state, the coloration rate (A′→B′) k has been obtained at the same temperature in several solvents as shown in Table 2. Thus, there are fast and slow processes in the

Table 2. Specific rate constants ($k_{A' \to B'}$) of SP-3 in various solvents
(at room temperature)

Solvent	$k_{A' \to B'}$ (sec^{-1})
Methanol	1.82×10^{-3}
Ethanol	7.91×10^{-4}
2-Propanol	8.81×10^{-3}
Acetone	3.59×10^{-3}
Acetonitrile	5.45×10^{-3}

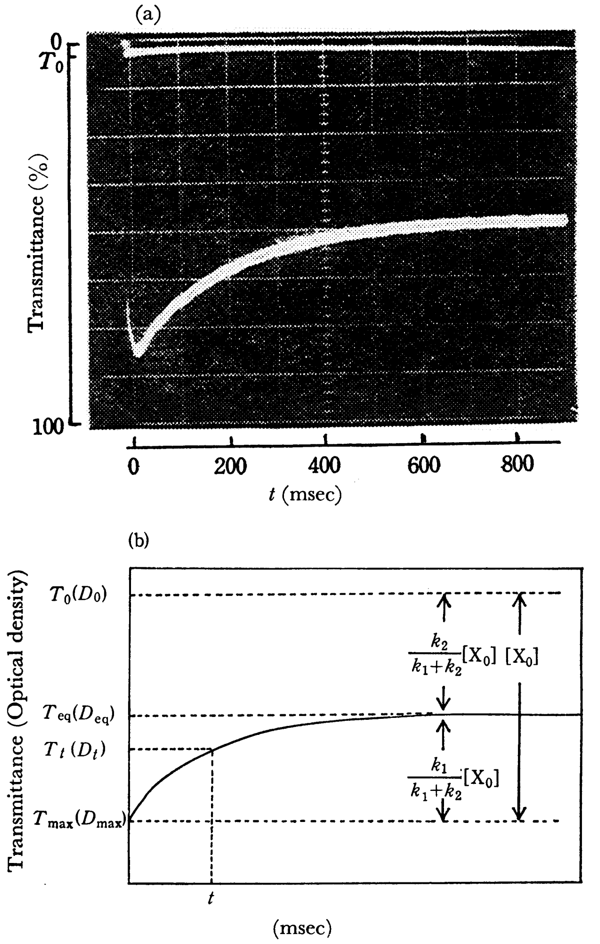


Fig. 4. Typical curve tracing the change in transmittance at λ_{max}(475 mμ) on the synchroscope and its diagram for the analysis.
(a): curve of SP-3 ethanol solution.
(b): diagram for analyzing of the curve.

recoloration of SP-3 solution. From the results, we assumed the existence of an intermediate state (X) during the course of photo-decoloration. Since no new band except for A′'s and B′'s could be observed, the absorption spectrum of X should resemble that of the colorless form.

When the change of B′ after illumination was traced at the absorption maximum (470 nm) by a synchroscope, a typical recoloration curve was obtained as shown in Fig. 4 (a).

The photo-decoloration process can be assumed as follows.

$$\mathrm{B}' + h\nu \longrightarrow \mathrm{B}^* \tag{3}$$

$$\mathrm{B}^* \xrightarrow{\text{fast}} \mathrm{X} \tag{4}$$

$$\mathrm{X} \xrightarrow{k_1} \mathrm{B}' \tag{5}$$

$$\mathrm{X} \xrightarrow{k_2} \mathrm{A}' \tag{6}$$

where $h\nu$, $k_1(k_2)$, and B* represent light quantum, specific rate of X→B′ (X→A′) process and the excited species of B′, respectively. The specific rates (k_1 and k_2) were obtained by the analysis of the recoloration curves as follows.

The rate equation for the reaction is

$$-\frac{\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} = (k_1+k_2)[\mathrm{X}] \tag{7}$$

By integrating, we have

$$\frac{[\mathrm{X}]}{[\mathrm{X}]_0} = e^{-(k_1+k_2)t} \tag{8}$$

where [X] and [X_0] denote the concentration of X at t(sec) and initial state just after flash. The values of [X_0] and [X] are converted into the optical density (D) at λ_{max} of B′ by means of the following equations.

$$[\mathrm{X}_0] = \frac{1}{\varepsilon_{\mathrm{B}'}l}(D_{eq} - D_{max})\frac{k_1+k_2}{k_1} \tag{9}$$

$$[\mathrm{X}] = \frac{1}{\varepsilon_{\mathrm{B}'}l}(D_{eq} - D_t)\frac{k_1+k_2}{k_1} \tag{10}$$

where $\varepsilon_{\mathrm{B}'}$ and l denote the absorption coefficient of B′ at λ_{max} and cell length, respectively. D_0, D_{eq}, D_{max}, and D_t give optical density as shown in Fig. 4(b).

From Eqs. (8), (9), and (10), we get

$$\ln\left(\frac{D_{eq} - D_t}{D_{eq} - D_{max}}\right) = -(k_1+k_2)t \tag{11}$$

A plot of $\ln(D_{eq}-D_t/D_{eq}-D_{max})$ against time t was linear for the photo-decoloration of SP-3 in ethanol as shown in Fig. 5. The slope gives the specific rate (k_1+k_2) 2.9 sec^{-1} at room temperature.

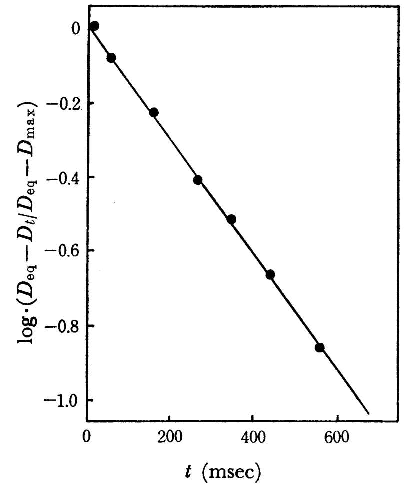


Fig. 5. A plot of log ($D_{eq}-D_t/D_{eq}-D_{max}$) against time ($t$) for SP-3 in ethanol at room temperature.

The ratio of the specific rates k_2/k_1 is given by

$$\frac{k_2}{k_1} = \frac{D_0-D_{eq}}{D_{eq}-D_{max}} \tag{12}$$

The values obtained for the photo-decoloration of SP-3 in ethanol are summarized in Table 3.

Arrhenius' plots for the specific rates k_1 and k_2 (Fig. 6) showed good linearity. Activation energy $\Delta E^{\neq}$ and

Table 3. Kinetic data obtained in the photo-decoloration of SP-3 in ethanol (at room temperature)

k_1+k_2 (sec^{-1})	k_1 (sec^{-1})	k_2 (sec^{-1})	k_2/k_1+k_2	$\Delta E^{\neq}$ (kcal/mol) X→A′	$\Delta E^{\neq}$ (kcal/mol) X→B′
2.9	0.38	2.5	0.87	20.3	18.6

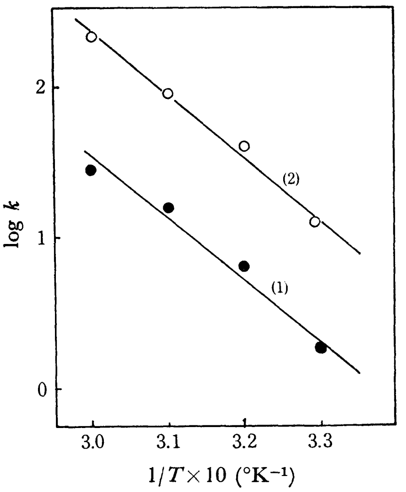


Fig. 6. The Arrhenius plots of SP-3 in ethanol.
(1): $\log k_1$ vs. $1/T$
(2): $\log k_2$ vs. $1/T$

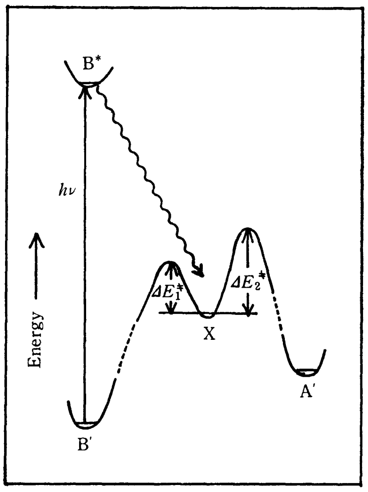


Fig. 7. Energy diagram showing the photo-decoloration process of reverse-photochromic spiran.

the pre-exponential factor A were calculated (Table 3) from these slopes and Arrhenius' law

$$k = Ae^{-\Delta E^{\ddagger}/RT} \tag{13}$$

An energy scheme for the photo-decoloration of SP-3 was assumed as given in Fig. 7. Colorless intermediate species (X) can be formed from the photo-excited state of B'. According to this assumption, X is transformed into the unstable colorless one A' in the ratio (k_2/k_1+k_2). Therefore, the photo-decoloration efficiency of B' seems to be determined by the product of the transition probability from B* to X and the conversion ratio (k_2/k_1+k_2) from X to A'.

Solvent Effect. The absorption band of B' in the visible region shifted towards longer wavelength in polar solvents, especially in proton donative solvents such as alcohol. Stokes' shift was observed in the fluorescence spectrum of an alcohol solution of B'. Typical curves of absorption and fluorescence spectra of B' are shown in Fig. 8. The ground state of B' which was supposed to be of Zwitter-ionic structure can be stabilized by interaction with polar solvents.

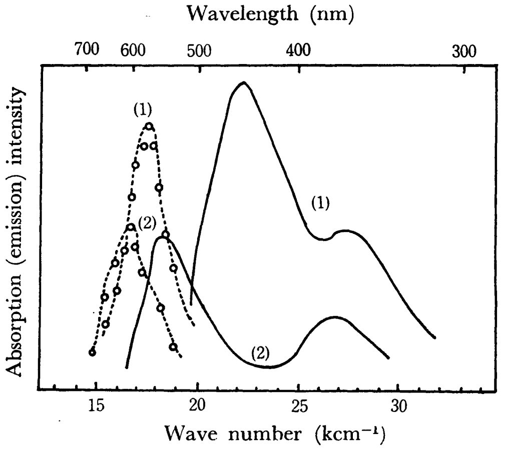


Fig. 8. Absorption and emission spectra of SP-2 in acetone and methanol.
(1): in acetone (2): in methanol

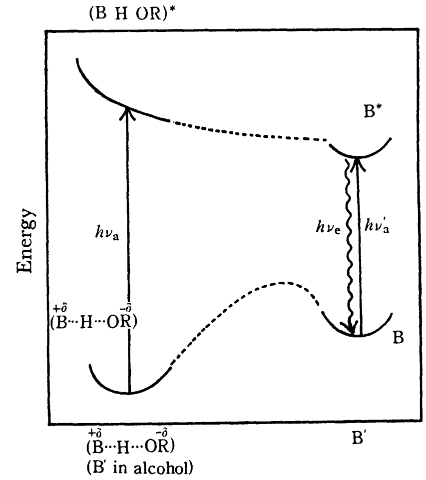


Fig. 9. Energy diagram illustrating large Stokes' shift of B in alcohol.
B': colored species
(B···H···OR): hydrogen bonded from with alconol (HO-R)
$h\nu_a$, $h\nu_a'$: absorbed photon
$h\nu_e$: emitted photon

The largest stability of B' was observed in an alcohol solution. This implies that the hydrogen bond would be formed between B' and alcohol. Stabilization of B' by solvent was supposed to cause the blue shift of the absorption band. Stokes' shift in alcohol was uncommonly large compared with that in acetone. This implies that some structural change of the system occurred in the equilibrium state of the excited species. Since the stabilized ground state of B' is supposed to be a hydrogen-bonded form $(B^{+\delta}\cdots H\cdots OR^{-\delta})$, it is considered that the rupture of the hydrogen bond (B' HOR) might occur in the excited equilibrium state. A schematic diagram is shown in Fig. 9 to illustrate the large Stokes' shift.

When the Brønsted acid such as hydrochloric acid was added, the colored species (B') was transformed into a yellow salt-type species (C; $B^+H\cdots X^-$).[4] C was photochemically converted into A' with a quantum yield of nearly 1. On the other hand, the quantum yield of photo-conversion from B' to A' was higher in proton donative solvents such as alcohol than in

TABLE 4. LIFE TIME OF THE TRANSIENT INTERMEDIATE (X) AND THE CONVERSION RATIO OF THE REACTION (X→A′) OF (SP-3) IN VARIOUS SOLVENTS (at room temperature)

Solvent	$k(1/\tau)$, sec^{-1}	$\eta_2(k_2/k_1+k_2)$
Methanol	0.57	0.85
Ethanol	2.9	0.87
2-Propanol	4.3	0.80
n-Butanol	8.2	0.84
Acetone	9.6×10^2	0.78
Acetonitrile	7.0×10	0.34

other solvents. The results also supported the view that the structure of ($B^{+\delta}\cdots H\cdots OR^{-\delta}$) was described as a hydrogen-bonded form in the alcohol solution of B′.

It is to be noticed that the life time (τsec) of X observed during the photo-decoloration of the reverse photochromic spirans was also influenced by solvents. Table 4 shows the specific rate constants ($k_1+k_2=k$ (sec^{-1})) and the conversion ratios ($\eta_2=k_2/(k_1+k_2)$) of the reaction to A′ from X of the SP-3 in various solvents. The value (k) was much smaller in alcoholic solvents compared with that in solvents such as acetone. X was stabilized with both the acidity as proton donor and the polarity of solvents. The value (η_2) was almost constant in alcohols and decreased in acetone and acetonitrile. The solvent effect on η_2 was less distinct than that on (k).

TABLE 5. KINETIC DATA ON THE REACTIONS (X→A′, X→B′) OF (SP-3) IN VARIOUS SOLVENTS.

Solvent	$\Delta E^{\ddagger}$ (kcal/mol)		A (sec^{-1})		$\Delta G^{\ddagger}$ (kcal/mol)	
	$\Delta E^{\ddagger}_{X\to A'}$	$\Delta E^{\ddagger}_{X\to B'}$	$A_{X\to B'}$	$A_{X\to B'}$	$\Delta G^{\ddagger}_{X\to A'}$	$\Delta G^{\ddagger}_{X\to B'}$
Ethanol	20.3	18.6	$10^{15.2}$	$10^{13.2}$	17.3	18.4
2-Propanol	19.8	22.5	$10^{15.5}$	$10^{16.6}$	16.3	17.3
Acetone	18.9	18.9	$10^{16.6}$	$10^{16.1}$	13.8	14.6

Kinetic data on the temperature dependence on the specific rate constants (k_1, k_2) in various solvents are summarized in Table 5. The large pre-exponential factor (A) and the high activation energy ($\Delta E^{\ddagger}$) were the inherent characteristics of the thermal transformations of the spirans (*e.g.* A′→B′, X→A′, and X→B′). The activated free energy ($\Delta G^{\ddagger}$) of the reactions increased in ethanol owing to the effect of the stabilization of X by the proton donative solvent.

The photo-decoloration efficiency ($\phi_{B'\to A'}$) of the reverse photochromic spirans should be determined by the product of η_1 and η_2 which are the ratios of the interconversions B*→X and X→A′ under the hypothetical reaction scheme for photo-decoloration. Because of the difficulty to determine the absolute value of η_1, we measured the relative value ($\eta_{1\mathrm{rel}}$) for (SP-3) in various solvents. The results are given in Table 6. The relative efficiencies (ϕ_{rel}) obtained with the steady light coincided qualitatively with the relative values ($S_{\mathrm{rel}}=\eta_{\mathrm{rel}}/(\eta_{\mathrm{rel}})_{\mathrm{ethanol}}$) as shown in Table 6. The deviation between ϕ_{rel} and S_{rel} might be caused by the neglect of the temperature effect on η_2.

TABLE 6. PHOTO-DECOLORATION EFFICIENCY OF SP-3 IN VARIOUS SOLVENTS

Solvent	$\eta_{x,\mathrm{rel}}$	η_2	S_{rel} [a]	$\phi_{(B'\to A')\mathrm{rel}}$
Methanol	0.69	0.85	0.68	0.53
Ethanol	1.00	0.87	1.00	1.00
Acetone	0.59	0.78	0.53	0.31
Acetonitrile	0.31	0.34	0.12	0.14

a) S_{rel} were obtained at room temperature.
$\phi_{(B'\to A')\mathrm{rel}}$ → −40°C.

Effect of Substituents. Photo-decoloration efficiency was influenced by the substituent in the indoline part of the reverse photochromic spiran (SP-2). Existence of X also depended on the substituent.

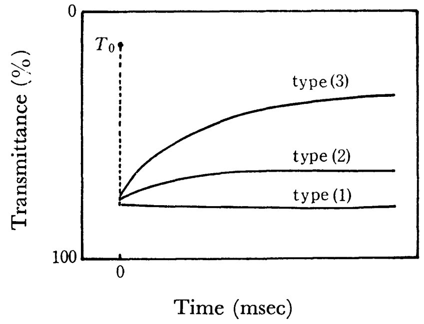


Fig. 10. Typical curves showing the changes of trasmittance at $\lambda_{\max}$, against time after flash illumination.
T: transmittance before illumination.

Typical curves of transmittance at the absorption maximum after the flash illumination are shown in Fig. 10. They can be classified into three groups. SP-2, 9, and 10 are of type 1, in which X could not be observed. It seemed that the photo-decoloration occurred in the process from B* to A′, or the energy barrier between X and A′ or B′ could be neglected. X was observed in SP-3, 4, 5, and 6 which are of type 3. SP-7 and 8 are of type 2, in which X was hardly detected at all by analysis. No explanation has been given on the influence of the substituents on the process.

Kinetic data on X of the spirans belonging to the type 3 are shown in Table 7. The longer the life time of X, the higher the interconversion ratio (η_2).

It was found that the photo-decoloration efficiency ($\phi_{B'\to A'}$) of the spiran substituted with an electron-

TABLE 7. LIFE TIME AND CONVERSION RATIO (η_2) OF THE REVERSE PHOTOCHROMIC SPIRANS

Spiran	Solvent	k(sec)$^{-1}$	$\eta_2(k_2/k_1+k_2)$
SP-3	Ethanol	2.9	0.87
	n-Butanol	8.2	0.84
	Acetonitrile	9.6×10^2	0.78
SP-4	Ethanol	7.6×10	0.49
	n-Butanol	1.0×10^2	0.65
	Acetonitrile	4.1×10^3	0.37
SP-5	Ethanol	4.8×10	0.77
	n-Butanol	1.9×10^2	0.72
SP-6	Ethanol	5.4×10^2	0.50
	n-Butanol	1.5×10^3	0.56

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4) I. Shimizu, H. Kokado, and E. Inoue, This Bulletin **42**, 1726 (1969).

releasing group (–OCH_3) was higher than that with an electron attractive substituent (–Br). These substituent effects were similar to those on stability of the colored form of the spirans of type 3 as given in Table 7.

Effect of the Dissolved O_2 on the Photo-bleaching of Spirans. Reversibility of spirans gradually decreased during repetition of the photo-interconversion between A′ and B′. The term "fatigue" of the photochromism was given to such a phenomenon. The fatigue process of reverse photochromic spirans depended largely on the dissolved oxygen and the photon energy of the light.

When a degassed ethanol solution of SP-3 was irradiated with a flash pulse with no filter, the existence of X was recognized during the decoloration process, but coloration was not completely restored. After the illumination of 4 pulses, no photo-decoloration occurred. The fatigue phenomenon was scarcely noticeable in a solution saturated with air.

No fatigue was observed even in the degassed sample when visible light (with a UV cut off filter) was passed on the solution. It was supposed that the fatigue from the irradiation of UV light, *viz.*, irreversible bleaching of the color was induced from the higher excited state. Deactivation from the higher excited state to the lower state may be accelerated by the dissolved oxygen in high efficiency.