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Photoreversible Photographic Systems. V. Reverse Photochromism of (Photospiran/Acid) System in Acetone

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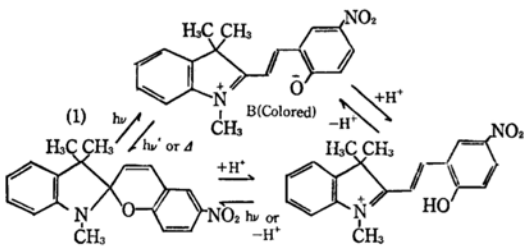
1,3,3-Trimethylindolino-6′-nitro-benzopyrylspiran (**1**) exhibits a photoreversible color change which is called "photochromism". However, it is transformed from a colorless form (A) into a colored form (C) which has a salt-like structure when acid such as malonic acid is added into acetone without irradiation with light. The color is bleached by irradiation with light. The color reappears thermally as the light source is removed. This photoreversible color change is termed "reverse photochromism". Another colored form (B) of compound (1) which has a merocyanine dye-like structure is converted into (C) as acid is added into the solution (B). The quantum yield of the photoconversion from C to A by irradiation with visible light depends on the solvent polarity. The quantum yield of the photoconversion from A to B also depends on the solvent polarity.

A photospiran 1,3,3-trimethylindolino-6′-nitro-benzopyrylspiran (**1**) is converted into a colored form (B) from the stable colorless one (A) by irradiation with ultraviolet light in organic solvents. The colored species (B) which is assumed to have a merocyanine dye-like structure is further transformed into another kind of colored species (C) as acid such as malonic acid (Brönsted acid) or $SnCl_4$ (Lewis acid) is added into the solution of B. The photospiran of the form (A) is directly transformed into the colored species (C) which is assumed to have a salt-like structure in the dark at room temperature, when acid is added in acetone. The colored species (C) is converted back into the colorless form (A) by irradiation with visible light. Therefore, the (photospiran(**1**)/acid) system in acetone exhibits a photoinduced reversible color change which is called reverse photochromism.

In this paper, the thermal or photochemical interconversion of the two isomers A and C is discussed. The molecular structures of A and C are given in Fig. 1.



A (Colorless) C (Colored)

Fig. 1. Reaction mechanism of reverse photochromism.
hν : ultraviolet light
hν′ : visible light
Δ : thermal

Experimental

Experimental procedures were the same as described in a previous paper,[1] expcept for filters. The visible

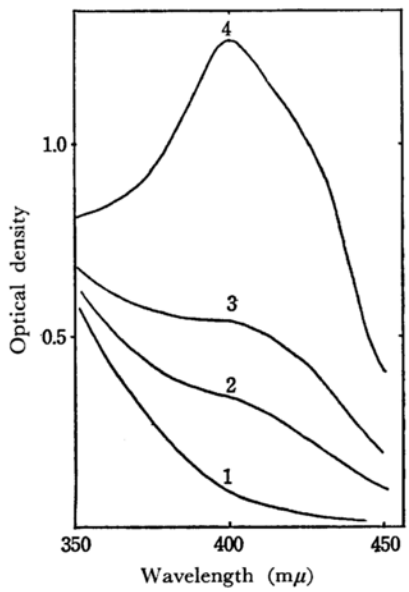


Fig. 2. Absorption spectra of (photospiran(**1**)/acid) system in acetone.
Photospiran (**1**) 6.9×10^{-5} mol/*l*.
Malonic acid 1) 9.9×10^{-4} mol/*l* 2) 5.0×10^{-3} mol/*l* 3) 9.9×10^{-3} mol/*l* 4) 8.9×10^{-2} mol/*l*

1) I. Shimizu, H. Kokado and E. Inoue, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 2344 (1967).

light was obtained with a high pressure mercury lamp fitted with the Toshiba glass filters (V-V40×2)×V-Y43. The light intensity entering the cell was determined by the potassium ferrioxalate actinometry.

Results and Discussion

A colored species (B) was transformed into another colored form (C) by the addition of acid in the organic solvent. The colorless species, however, did not undergo any change by the addition of acid at room temperature in the organic solvents except for acetone and methyl ethyl ketone. In acetone the colorless form (A) was converted into the colored form (C) in the dark by addition of malonic acid. A thermal equilibrium was established between A and C. The absorption spectral change of the system (photospiran/acid) in acetone is shown in Fig. 2. In the system, the equilibrium constant of the reaction Eq. (1) can be formulated as

$$\mathrm{A} + \text{acid} \rightleftarrows \mathrm{C}, \tag{1}$$

$$K = \frac{[\mathrm{C}]}{[\mathrm{A}][\text{acid}]} \tag{2}$$

$$[\mathrm{C}] = [\mathrm{A}_0] - [\mathrm{A}], \tag{2}$$

where [A], [acid] and [C] are the concentrations of A, (acid), and C, and $[A_0]$ is the initial concentration of A.

Since the experiments are carried out with an excessive acid, we have

$$[\text{acid}] \gg [\mathrm{C}].$$

Thus we obtain from **2** and **3**

$$\frac{1}{[\text{acid}]} = \frac{K[\mathrm{A}_0]}{[\mathrm{C}]} - K. \tag{4}$$

Equation (4) can be converted into Eq. (5) in terms of the optical density (D_λ) and the molar extinction coefficient (ε_λ) at the absorption maximum ($\lambda m\mu$) of the colored species.

$$\frac{1}{[\text{acid}]} = \frac{K\varepsilon_\lambda[\mathrm{A}_0]}{D_\lambda} - K. \tag{5}$$

Figure 3 shows the plots of 1/[acid] against $1/D_\lambda$ for the systems photospiran/malonic acid and photospiran/maleic acid. The values of K and ε_λ were obtained from Fig. 3 and are shown in Table 1. The equilibrium constant increases as the dissociation constant of acid in water increases.

The colored species (C) was transformed into the colorless one (A) by irradiation with visible light, but color reappeared when irradiation was stopped. This *reversible* color change could be repeated as many times as desired. The absorption spectral change of the reverse photochromic system which is induced by irradiation with light

Table 1. Equilibrium constant of the reaction Eq. (1) and molar extinction coefficient of (C) at the absorption maximum wavelength in visible region

Acid	K	ε_{405}	K_1
Malonic acid	58.5	2.2×10^4	1.40×10^{-3}
Maleic acid	201	2.2×10^4	1.42×10^{-2}

K_1 : dissociation constant of acid in water at room temperature

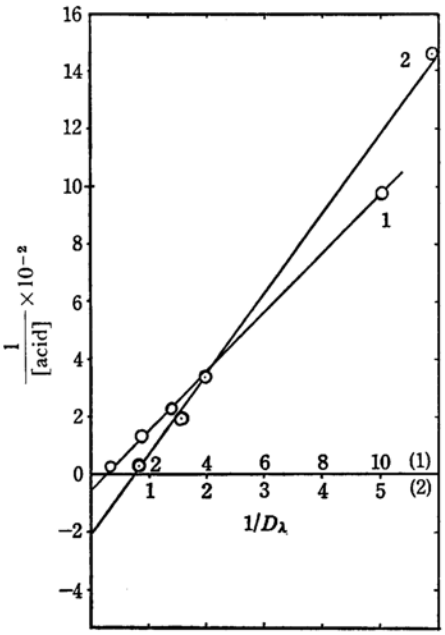


Fig. 3. Plots of $1/[\text{acid}]-1/D_\lambda$
1) Malonic acid
2) Maleic acid

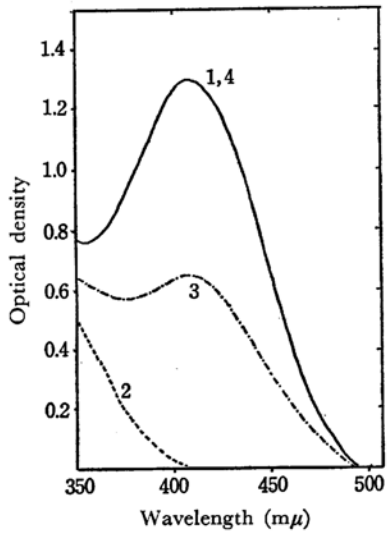


Fig. 4. Absorption spectral changes of the reverse photochromic system (photospiran (**1**) 1.1×10^{-4} mol/l + excess malonic acid).
1) Absorption spectrum of the system
2) After irradiation with visible light
3), 4) After standing the irradiated sample in the dark

is given in Fig. 4. The thermal reaction from A to C followed first order reaction kinetics. The activation energy for the thermal reaction from A to C was calculated as 31.9 kcal/mol. The Arrhenius plot is shown in Fig. 5.

The colored species (B) of the photospiran (**1**) could be isolated in a stable form and was converted into C by dissolving into various solvents containing malonic acid in excess. The absorption spectra and their change by irradiation with visible light in methanol are shown in Fig. 6. The thermal reaction from A to C in each solvent was so slow that it could be neglected. The quantum yield of photoconversion from C to A in acetone and the other various solvents by irradiation with visible light (4358Å) are given in Table 2. The quantum yield of photoconversion from C to A in acetone by irradiation with ultraviolet light (3650Å) changed with irradiation time. The quantum yield of decoloration *versus* irradiation time (irradiation with either 4358Å or 3650Å light) is shown in Fig. 7. In the case of interconversion of two isomers (C) and (A) under the action of ultraviolet light, a photoequilibrium was established by light (3650Å). It changes with the molar extinction coefficients of the two isomers and also with the quantum yields $\phi_{C\to A}$ and $\phi_{A\to C}$ of photoconversion in both directions C to A and A to C *via* B. In other words, the colorless species (A) absorbed ultraviolet light and the transformation to B took place. The colored species (B) was transformed

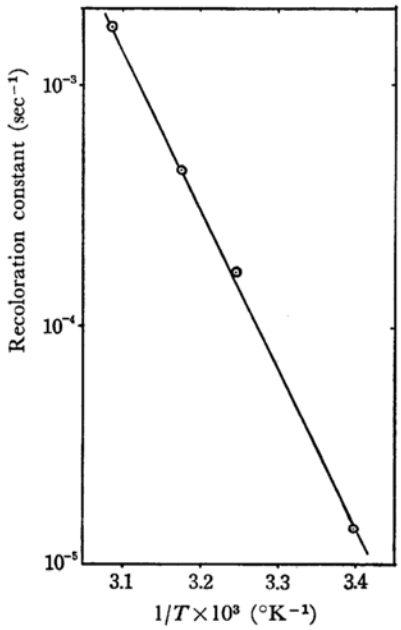


Fig. 5. Arrhenius plot for recoloration rate of the system (photospiran (**1**)/acid) in acetone.

ΔE: 31.9 kcal/mol

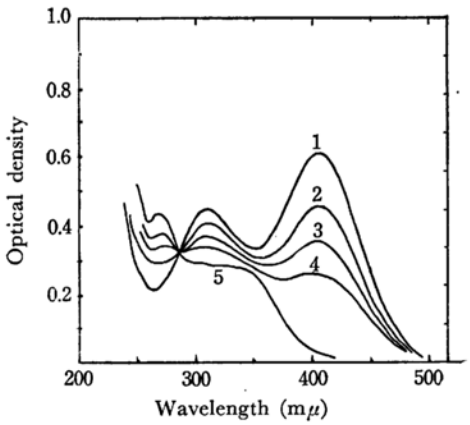


Fig. 6. The effect of irradiation with visible light on (photospiran (**1**)/malonic acid) system in methanol.

1) Absorption spectrum of the system ((**1**): 2.0×10^{-5} mol/l + malonic acid; 7.9×10^{-3} mol/l) in methanol.
2), 3), 4), 5) The progressive change of the spectrum of the system by irradiation with light.

TABLE 2. QUANTUM YIELD OF PHOTOCONVERSION FROM C TO A IN VARIOUS SOLVENTS BY 4358 Å LIGHT

Solvent	$\varepsilon_\lambda\times\phi_{C\to A}$	Quantum yield
H_2O	$(3.5\ 0.1)\times10^3$	0.16
CH_3OH	$(7.3\ 0.2)\times10^3$	0.33
C_2H_5OH	$(8.0\ 0.3)\times10^3$	0.36
i-C_3H_7OH	$(1.2\ 0.2)\times10^3$	0.55
n-C_3H_7OH	$(1.0\ 0.1)\times10^3$	0.46
Acetone	$(1.6\ 0.1)\times10^3$	0.73

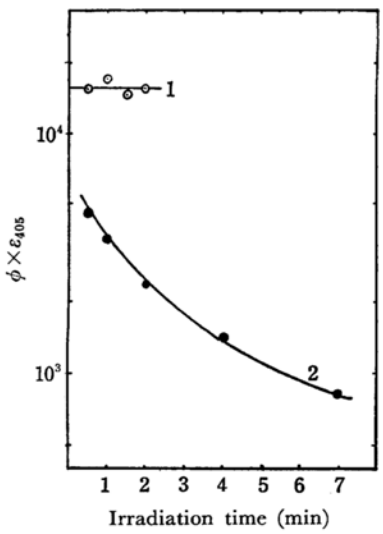


Fig. 7. Quantum yield of photoconversion from C to A in acetone *versus* irradiation time.

1) Irradiated with 4358 Å
2) Irradiated with 3650 Å

instantly into C by the reaction with excess acid in the solution. These reactions are

$$C + h\nu\ (3650\,Å) \xrightarrow{\phi_{C\to A}} A \quad (6)$$

$$A + h\nu\ (3650\,Å) \xrightarrow{\phi_{A\to C}} B \quad (7)$$

$$B + \text{excess acid} \xrightarrow{\text{fast}} C \quad (8)$$

The quantum yield $\phi_{C\to A}$ was claculated as described below.

The rate of the photoconversion is represented by Eq. (8).

$$\frac{d[A]}{dt} = -\frac{d[C]}{dt}$$
$$= I_\lambda\{\varepsilon_C\phi_{C\to A}([C_0]-[A]) - \varepsilon_A\phi_{A\to C}[A]\} \quad (9)$$

I_λ: intensity of the irradiation light at λ mμ

$\phi_{C\to A}$, $\phi_{A\to C}$: quantum yield of the photoconversion from C to A, or from A to C

$[C_0]$: initial concentration of C

t: irradiation time.

Since the reaction rates for both directions are equal at the photoequilibrium

$$\varepsilon_C\phi_{C\to A}\{[C_0] - [A_\infty]\} - \varepsilon_A\phi_{A\to C}[A_\infty] = 0 \quad (10)$$

$$[A_\infty] + [C_\infty] = [C_0] \quad (11)$$

we have

$$\frac{\phi_{C\to A}}{\phi_{A\to C}} = \frac{\varepsilon_A}{\varepsilon_C}\left(\frac{[C_0]}{[C_\infty]} - 1\right) \quad (12)$$

The solution of Eq. (9) is given as

$$I_\lambda t = \frac{1}{\varepsilon_C\phi_{C\to A}+\varepsilon_A\phi_{A\to C}} \ln\left\{\frac{[C]-[C_\infty]}{[C_0]-[C_\infty]}\right\} \quad (13)$$

$[A_\infty]$, $[C_\infty]$; concentrations of A and C at photoequilibrium. Plots of $\log\{[C]-[C_\infty]\}/\{[C_0]-[C_\infty]\}$ *versus* irradiation time at 3650Å in various solutions are given in Fig. 8. The observed linearity of the curves in Fig. 8 provides a support for the proposed reaction scheme represented by Eqs. (6), (7) and (8). The quantum yield of photoconversion from A to C *via* B is calculated from Eq. (12) using values of $\phi_{C\to A}$ in Table 2 and is shown in Table 3.

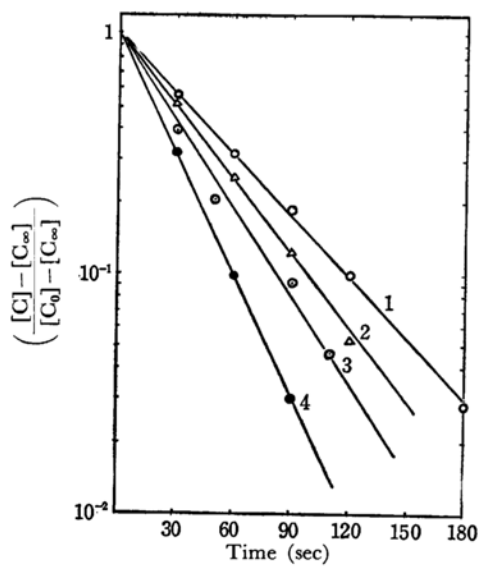


Fig. 8. The correlation $\log([C]-[C_\infty]/[C_0]-[C_\infty])$ with irradiation time for various solvents.
1) Methanol 2) Ethanol, 3) Isopropanol, 4) Acetone

Table 3. Quantum yield of rhotoconversion from A to C

Solvent	Quantum yield ($\phi_{A\to C}$)
CH_3OH	0.07
C_2H_5OH	0.15
i-C_3H_7OH	0.23
n-C_3H_7OH	0.23
Acetone	0.27

Irradiation light : 3650 Å

The quantum yield of photoconversion from (C) to (A) decreases as the solvent polarity increases. On the other hand, the quantum yield of photoconversion from B to A increases as the solvent polarity increases. In a previous paper,[1] we presented evidence for the existence of the different colored species (B) and (C) from absorption spectra. The colored species (B) is assumed to have a mercyanine dye-like structure and C a salt-like structure. The difference in the solvent effect on the decoloration efficiencies $\phi_{C\to A}$ and $\phi_{B\to A}$ gives another evidence for the existence of B and C. The quantum yield of photoconversion from A to C *via* B as shown in Table 3 decreases as the solvent polarity increases. The absorption spectrum of A, especially its longest wavelength absorption band is shifted to the longer wavelength as the solvent polarity increases. In polar solvents, the excited state of the colorless species (A) interacts with the solvent, and also the efficiency of radiationless deactivation may increase, thus the quantum yield of the photoconversion from A to C through B decreases.

Conclusion

The photospiran (**1**) in acetone is converted into a colored form as acid is added, and the colored form C is bleached by irradiation with visible light. Thus, the (photospiran/acid) system in acetone exhibits a reverse photochromism. The photoconversion efficiency from colored to colorless form is controlled by external factors such as the solvent polarity. The reverse photochromism of the system is shown in a polymer film such as styrene - maleic acid copolymer. The color image can be printed out directly on the reverse photochromic film by irradiation with visible light through the transparent original picture, and the image can be erased by heating.

The reverse photochromic system described above is promising for use as reusable photobleaching type photosensitive material which has photosensitivity in visible regions.