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Photoelectrical Response of Hydrochloric Salt of Photospiran

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Photospirans (1,3,3-trimethylspiro[indoline-2,2′-benzopyran] and its derivatives) are transformed from a colorless form (A) to a colored form (C) by adding acid (Brönsted or Lewis acid) in organic solvents. (C) is converted to a colorless form by irradiation with either visible or UV light, and is gradually restored after irradiation is stopped.

The term "reverse photochromism" is given to photoreversible color changes.

During the course of our studies on the reverse photochromism of spiran-acid systems, an electrical response was observed when the colored species (C) in organic solvents was irradiated.

To measure the electrical current of the solution, a cell with two Al plate electrodes (10×10 mm^2) 10 mm apart was set up. The measurement was carried out under constant voltage 2 V (d.c.) by a micro-micro Ammeter (TR-84B). A high pressure mercury lamp fitted with a glass UV cut filter was used as the irradiation source.

A typical electrical current curve of the butanol solution of hydrochloric salt of spiran (1) is shown in Fig. 1.

The electronic current of the solution increased

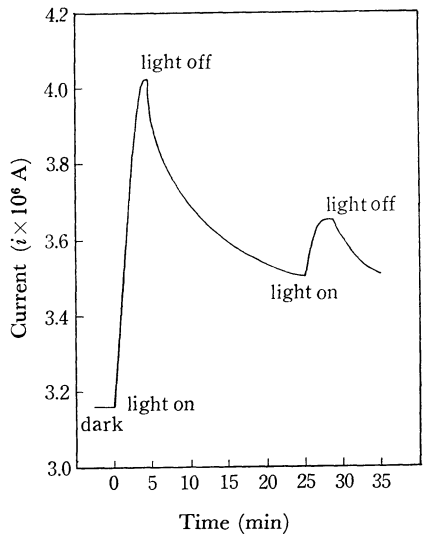


Fig. 1. Electrical current curve of the hydrochloric salt of spiran (1) in butanol.
concentration 1.7×10^{-4} mol/l
light intensity 2.1×10^{-3} W/cm^2

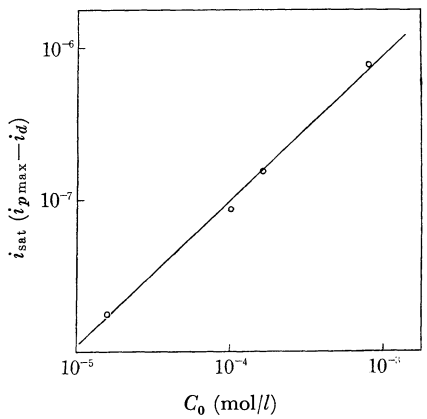
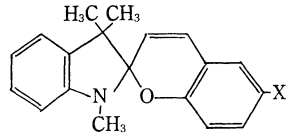


Fig. 2. Dependence of the maximum value of photocurrent on the initial concentration (C_0) of the salt.

$$[SPH]^+Cl^- \underset{\text{thermal}}{\overset{h\nu}{\rightleftarrows}} SP + H^+ + Cl^- \qquad (1)$$

(C) colored (A) colorless



SP

X: NO_2 (1), COOH (2)

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

by irradiation with light, and decreased when irradiation was stopped. The value of the saturated photo-current (i_{sat}) was proportional to the initial concentration of the salt of spiran (1) as shown in Fig. 2. The dark current of the solution also increased with concentration. Though the current decreased gradually after irradiation was stopped, it did not return to the initial value. The photocurrent of the solution is assumed to be due to the generation of electrical carriers by irradiation with light undergoing photoconversion from the colored species (C) to the colorless one (A) as shown in Eq. (1). The photo-dissociated carriers seem to be partially stabilized in solvent, and neither the color nor current of the solution returns to the initial value after irradiation is stopped.

The photoelectrical phenomena mentioned above were also observed in the solution of spiran (2).