The Photochromism of Evaporated Photospiran

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Photochromism in spiropyrans has been extensively investigated. We have reported the photochromic properties of 1,3,3-trimethylspiro(indoline-2,2′-benzopyran) (I) on adsorbent,[1] in solution[2] and in polymer film,[3] however, any distinct photochemical reaction of microcrystalline spiropyrans has never been reported.

We should now like to report that the thin layer of spiropyrans prepared by means of vacuum evaporation revealed a distinguished reversible photochemical reaction (photochromism).

Photospirans used are listed in Fig. 1. The samples were prepared with a hand-made vacuum evaporator. Evaporation was carried out under a pressure of about 10^{-5} mmHg and at suitable temperatures. As the base materials, glass or quartz plates were used.

In most derivatives, evaporated photospirans formed transparent and colorless uniform layers under microscopic inspection. However, in some derivatives crystallization proceeded during the course of evaporation. Evaporated photospirans, as well as those in solution, have no absorption band in visible region, but have specific absorption bands in ultraviolet region. The colorless state is transformed into corresponding colored state by irradiation with ultraviolet light (Fig. 1). The absorption spectra of the colored state are shown in Fig. 2. They have maxima near 6000Å. This behavior is similar to the solution of spiropyran in a non-polar solvent such as benzene. This indicates that there are no important intermolecular interactions between spiropyran molecules. The dark decoloration of colored species of the evaporated spiropyran proceeded according to a first order mechanism. In Table 1, the rate constants and the activation energies of dark decoloration are shown. Apparently, the colored forms of spiropyrans in evaporated state are thermally more stable than in solution or in polymer film. The photodecoloration efficiency is about the same in solution or in polymer film.

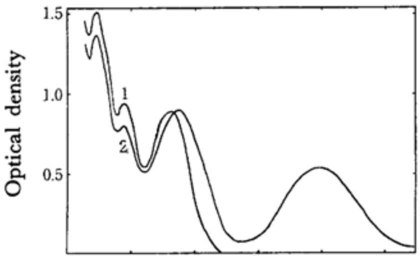

Fig. 1. Absorption spectra of evaporated spiropyran (III)

1. dark adapted 2. UV irradiated.

II $6'$-NO_2 derivative of (I)
III $6'$-NO_2-$8'$-OCH_3 IV 5-Cl-$6'$-NO_2
V 5-OCH_3-$6'$-NO_2 VI $6'$-OCH_3-$8'$-NO_2
VII $5'$-NO_2-$8'$-OCH_3 VIII $6',8'$-diBr

Some spiropyran such as II, crystallized during evaporation. In such circumstances photocoloration efficiency became very low and absorption spectrum was broadened. However, it was observed that such crystallization effect could be avoided by evaporation of the mixture of the compound with another derivative of spiropyran.

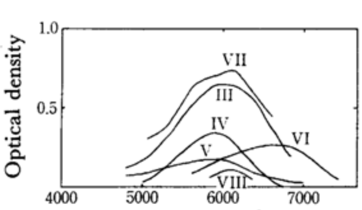

Fig. 2. Absorption spectra of the colored state of evaporated spiropyrans.

Table 1. Kinetic data evaporated spiropyrans

Spiropyran	Rate constant of dark decoloration at 30°C sec^{-1}	Activation energy kcal/mol
III	2.8×10^{-5}	31.8
IV	5.1×10^{-5}	36.6
VI	2.7×10^{-3}	35.2
VII	9.6×10^{-4}	24.8
VIII	6.6×10^{-3}	40.8

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1) E. Inoue, H. Kokado and H. Kobayashi, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **71**, 1288 (1968).

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

3) I. Shimizu, K. Yoshida, H. Kobayashi, M. Nakazawa, H. Kokado and E. Inoue, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **72**, 166 (1969).