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Physicochemical Study on Leuco Triarylmethane Dyes; Photolytic Coloration of 4,4-Diaryl-3,4-dihydro-1(2*H*)-phthalazinones

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A solution of dichloroethane containing crystal violet hydrazide (CVH) underwent a rapid photolytic coloration upon ultraviolet (UV) irradiation. When 5% ethanol–dichloroethane was used as a solvent, the dye formation was more efficient and the 620 nm band for triarylmethane dye continued to increase in intensity as the 270 nm band for CVH decreased.

The solvent dependency of the fluorescence spectra clearly showed that raising the ratio of ethanol to dichloroethane accelerated the photoionization of CVH. However, the actual dye formation was not efficient due to substantial reversion to the leuco derivative, 5.

Keywords——leuco triarylmethane dye; photocoloration; photoionization; UV-vis spectrum; fluorescence spectrum

In a previous paper of this series,[1] it was demonstrated that 4,4-bis-(*p*-dimethylaminophenyl)-7-dimethylamino-3,4-dihydro-1(2*H*)-phthalazinone (**1a**) [crystal violet hydrazide (CVH)] and its analogs underwent a normal chlorination followed by an unusual deanilination process at the C-4 position on heating with phosphoryl chloride, providing a special case of carbon-carbon bond cleavage.

In an earlier paper,[2] we briefly mentioned the exceptional sensitivity of (**1a**) and its analogs to ultraviolet light to form a deep blue color, in contrast to 3,3-bis-(*p*-dimethylaminophenyl)-6-dimethylaminophthalide [crystal violet lactone (CVL)], and 3,3-bis-*p*-dimethylaminophenylphthalide [malachite green lactone (MGL)], which readily undergo heterolytic cleavage of the lactone ring on exposure to weak acids, *i.e.*, electrophilic reagents, but are photostable in terms of the gross structure.

As part of our continuing physicochemical studies on triarylmethane dyes from both theoretical and practical points of view, we have examined in more detail the action of ultraviolet radiation on this essentially new class of leuco derivatives of triarylmethane dyes. 4,4-Disubstituted-3,4-dihydro-1(2*H*)-phthalazinones remain a very poorly investigated class of the well-known phthalazine molecules;[3] in the present paper, the behavior of CHV on UV irradiation and the mechanism of its coloration are described and discussed.

Experimental

Material——4,4-Bis-(*p*-dimethylaminophenyl)-7-dimethylamino-3,4-dihydro-1(2*H*)-phthalazinone (1) [crystal violet hydrazide (CVH)] was prepared by heating crystal violet lactone (CVL) with hydrazine hydrate in aq. ethanol as described previously.[2] CVH was further purified by recrystallization twice from ethanol to give colorless needles, mp 266°C. Ethanol and dichloroethane ($ClCH_2CH_2Cl$) used for UV measurement were of guaranteed grade quality, purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Ultraviolet Irradiation——A solution (6.51×10^{-5} M) of CVH in dichloroethane or 5% ethanolic dichloroethane was irradiated with a grating monochromator (Model CRM-FA, Japan Spectroscopic Co., Japan) with 2 kW xenon lamp. A bandwidth of 3 nm was used. The resulting solution was subjected to electronic spectral measurement at appropriate intervals.

Fluorescence Spectral Measurement——Fluorescence spectra and intensities were measured with a Shimadzu RF-501 spectrofluorophotometer in 10×10 mm quartz cells; spectral bandwidths of 7.5 and 10 nm were used in the excitation and emission monochromators, respectively. The fluorescence spectra, and excitation and emission maxima are uncorrected.

Results

In a preliminary experiment,[2)] CVH (**1**) was found to be extremely sensitive to ultraviolet radiation. When chloroform–ethanol solution containing a small amount of CVH (**1**) was irradiated with a 400 W high-pressure mercury lamp for a short period (*ca.* 30 s), it displayed an intense deep greenish-blue color. Similar behavior was also observed with a solution of 4,4-bis-(*p*-dimethylaminophenyl)-3,4-dihydro-(2*H*)-phthalazinone (**2**) [malachite green hydrazide (MGH)], but the color was less intense. A solution (6.51×10^{-5} M) of CVH in dichloroethane was irradiated with a grating monochromator in the range of 200—700 nm with 3 nm bandwidth. It was found qualitatively that 360 nm was the most effective wavelength for the coloration of (**1**). Thus, detailed study of this coloration process was performed on CVH at 360 nm.

Figure 1 shows the electronic absorption spectral change of CVH as a function of irradiation time in the range of 220—700 nm when dichloroethane alone was used as a solvent. The 270 nm band due to the starting CVH decreases as the 620 nm band increases on irradiation. However, on further irradiation, the 620 nm band seems to level off despite the continuing decrease in the 270 nm band of starting CVH. As no other characteristic absorption spectrum could be found during this spectral change, it can be assumed that the original CVH and also some of the

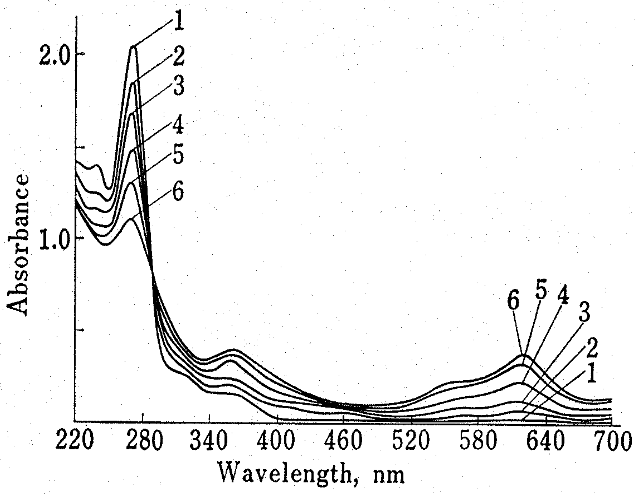

Fig. 1. Successive UV-vis Spectra during the Irradiation of 6.51×10^{-5} M CVH in Dichloroethane

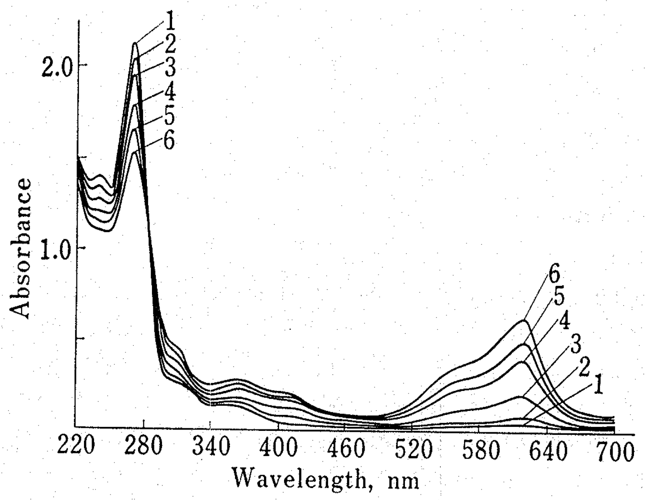

Fig. 2. Successive UV-vis Spectra during the Irradiation of 6.51×10^{-5} M CHV in 5% Ethanol–Dichloroethane

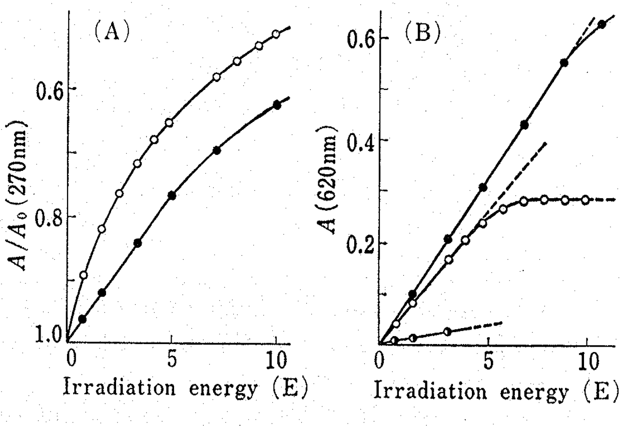

Fig. 3. Relative Rate of CVH Disappearance (A) and Dye Formation (B)

—○—: in dichloroethane.
—●—: in 5% ethanol-dichloroethane.
—◑—: in ethanol.
$E=4.43\times10^{-6}$ Einstein/cm² sec.
A, absorbance; A_0, absorbance of unexposed solution.

carbocation of CVH or triarylmethane dye had been photolyzed into small aliphatic fragments whose electronic absorption could not be detected with the solvent used.

The electronic spectral changes of CVH are reproduced in Figure 2, with 5% ethanol–dichloroethane as a solvent. Curve 1 is that of the original unexposed solution and this absorption spectrum is essentially similar to those obtained when dichloroethane alone was used as the solvent, except in degree. In this solvent, in contrast to the above case, the 620 nm band did not level off. Thus, continuing irradiation increases the intensity of the 620 nm band in parallel with the decrease in the 270 nm band of starting CVH.

Furthermore, the rate of dye formation and disappearance of CVH are plotted as a function of irradiation energy in Figure 3. Figure 3 clearly indicates that the rate of disappearance of CVH is rapid in pure dichloroethane, whereas the rate of dye formation is slow. Dye formation also does not occur to as great an extent as in the case of 5% ethanol–dichloroethane. However, on further irradiation of the solution, some photochemical process such as self-quenching may occur, since the extinction coefficient of the 620 nm band seems to level off in both cases.

Based on the above observations, we deduced the following scheme for the photolytic coloration of CVH (Chart 1).

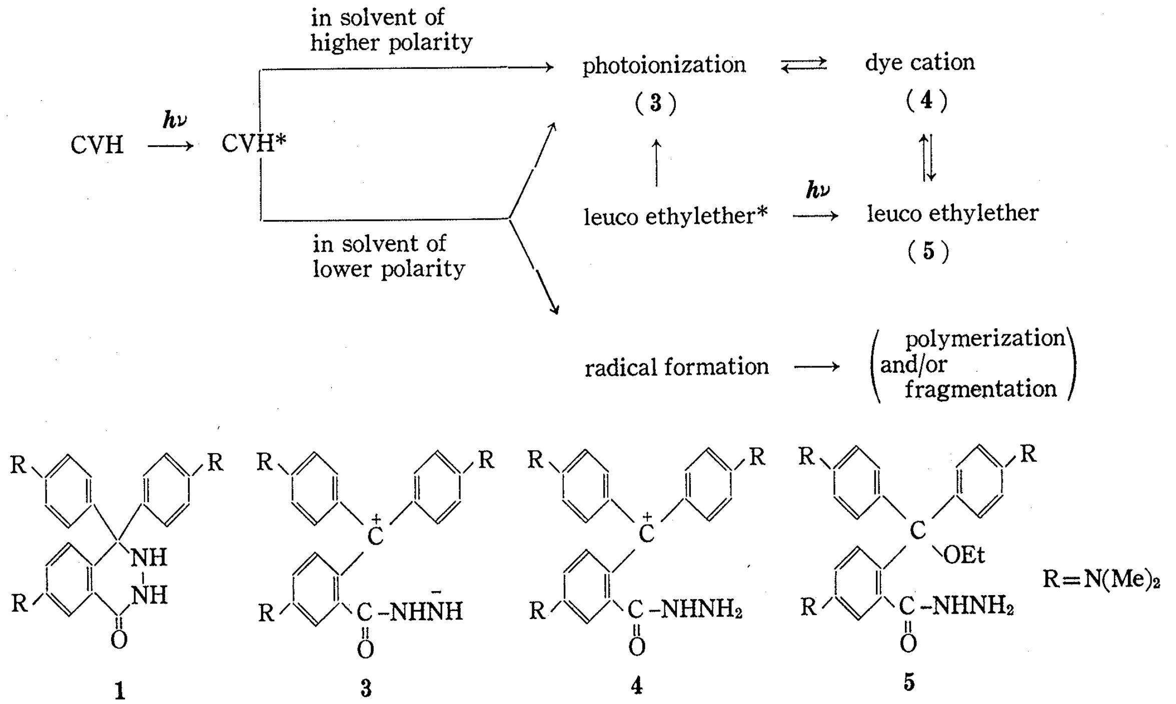

Chart 1

Discussion

Comparison of the spectral changes in these two solvents disclosed several interesting features. When dichloroethane alone was used as a solvent, the 360 nm band is as large as the 620 nm band, whereas the 620 nm band is much larger than the 360 nm band in 5% ethanol–dichloroethane, *i.e.*, there appears to be a solvent dependence of the 360 nm band intensity. The UV spectrum of crystal violet shows the 360 nm band (as intense as the 620 nm band), and that of Michler's ketone shows an intense 359 nm band. Thus, this band could be ascribed to a conformational isomer in which conjugation throughout the molecule is difficult. Furthermore, the spectral change does not show any clear isosbestic point, particularly in pure dichloroethane, which indicates that this photolytic process is a consecutive or complex reaction rather than a unit reaction, so that a minor radical formation process or fragmentation must take place concurrently.

Triarylmethane leuco derivatives are well known to exhibit photocoloration and/or photochromic behavior, and the mechanism of these coloration processes has been intensively studied.[4] The occurrence of photodissociation (heterolytic cleavage) is now widely accepted, and this may also be the major process for CVH, since the electronic spectra showed a 620 nm band upon irradiation, which is nearly identical to that of triarylmethane dye cation derived from crystal violet and crystal violet lactone. Some evidence in support of this view was provided by the following observations.

The energy in the π-π^* excited state must somehow be transferred to a σ-σ^* C–N state for triarylmethane dye formation, and if the σ-σ^* state can become zwitterionic in a polar solvent, as suggested by Dauben *et al.*,[5] the crossing between π-π^* and σ-σ^* states will be increased in a polar solvent along the reaction coordinate.

In fact, the intensity of the fluorescence spectrum of CVH drastically decreased upon increase in the solvent polarity, *i.e.*, increase of the ratio of ethanol to dichloroethane, and finally no fluorescence was observed in pure ethanol under otherwise identical conditions, shown in Figure 4. This decrement of the fluorescence intensity in a polar solvent could be ascribed to an acceleration of the rate photodissociation (photochemical process) rather than to some other process such as intersystem crossing, since greater rates of 620 nm band increment and 270 nm band decrement were observed as the solvent polarity was increased (*vide supra*).

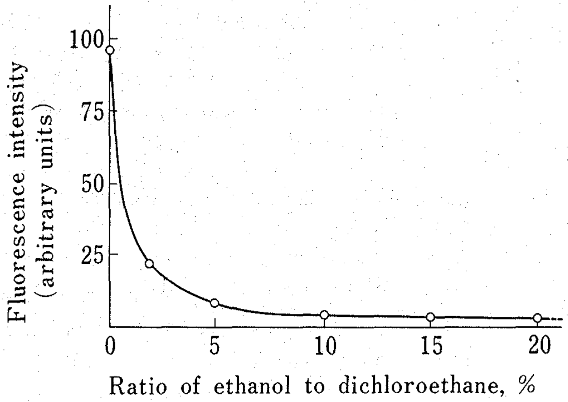

Fig. 4. Dependency of Solvent Polarity of CVH Fluorescence (λ_{ex}; 360 nm, λ_{em}; 436 nm)

Thus, these results clearly indicate that the energy originally localized in S_1 (π-π^*) is transferred effectively to a σ-σ^* C–N state in a polar solvent, leading to photodissociation. However, the actual dye formation was not effective in ethanol, as shown in Figure 3. This is probably due to substantial reversion to the leuco derivative caused by nucleophilic attack of ethanol. This was confirmed by the observation that the addition of ethanol to a solution whose electronic spectrum showed an intense 620 nm band caused a substantial decrease in the intensity of the band relative to that of the 270 nm band. Thus, it can be concluded that, in this solvent system, the most effective dye formation occurred in 5—7% ethanol–dichloroethane solution.

Theoretical calculations on the difference in propensity toward photolytic coloration between the 3,4-dihydrophthalazinone ring and the phthalide ring are in progress.

References and Notes

1) M. Kuzuya, T. Usui, F. Miyake, S. Ito, S. Nozawa, and T. Okuda, *Chem. Pharm. Bull.*, **29**, 2856 (1981).
2) M. Kuzuya, T. Usui, F. Miyake, S. Ito, S. Nozawa, and T. Okuda, *Chem. Pharm. Bull.*, **28**, 3561 (1980).
3) N.R. Parel, "The Chemistry of Heterocyclic Compounds," Vol. 27, R.N. Castle, Ed., John Wiley and Sons, New York, 1973, Chap II, p. 323.
4) *a*) E. Holmes, *J. Phys. Chem.*, **61**, 414 (1957); *b*) A.H. Sporer, *Trans. Faraday Soc.*, **57**, 983 (1961); *c*) D.N. Shigorin, M.A. Pak, and U.I. Kozlov, *Zh. Fiz. Kim.*, **41**, 1220 (1967); *d*) R. Mcnair, *Photochem. and Photobiol.*, **6**, 779 (1967); *e*) M.A. Pak, D.N. Shigorin, and G. Ozerova, *Dokl. Acad. Nauk.* (*SSSR*). *Phys. Ser.*, **186**, 311 (1969); *f*) M. Herz, *J. Am. Chem. Soc.*, **97**, 6777 (1975).
5) W.G. Dauben, L. Salem, and N.J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975).