INVERSE PHOTOCHROMISM OF TRIPHENYLMETHANE DYE

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The photochemistry of triphenylmethane dye was investigated in organic solutions at room temperature. Malachite green oxalate showed photobleaching upon visible light irradiation and recovery in the dark in less polar 1,2-dimethoxyethane. Such inverse photochromism was due to the formation of leuco ester from photoassisted binding of cation and anion, and to thermal ionic dissociation. In polar solvents such as acetonitrile these reactions were not observed.

1. Introduction

Light has many superior properties such as wavelength, polarization, and coherency (ultra short pulse, focusing). In order to further increase the memory density in optical recording systems, so-called photon-mode optical memory employing photochemical reactions instead of thermal reactions, which are presently used in "optical" disks, should be developed. Photochromic systems employing polymers or Langmuir-Blodgett (LB) films have recently attracted much interest in view of their promising applicability to such purposes. The photochromism reported so far involves changes of chemical bonds such as ring opening and closure in spiropyans [1] or cis-trans isomerization in azobenzene [2]. These reactions might limit the thermal or cyclic stability and the response time for the optical recording especially in the solid states.

We have been studying photochemical and photophysical properties of ion-pair charge-transfer complexes [3-17]. By the use of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion as a counter ion of 4,4'-bipyridinium ions, we have achieved novel photochromism due only to the photoinduced electron transfer and thermal reverse reactions in organic solutions and in polymer or LB films [3-17].

We now report that ion-pair of triphenylmethane dye, malachite green, showed inverse photochromism *i.e.* bleaching by visible light irradiation and recovery in the dark in organic solutions. Such inverse photochromism was reported for crystal violet having similar structure as malachite green in tetrahydrofuran, but the reaction mechanism was not clarified [18].

2. Experimental

Material

Malachite green oxalate (abbreviated to MG^+OX^- , Kishida Chemical Co., reagent grade) was used without further purification. The counter ions (OX^-) of malachite green were exchanged with acetate (MG^+Ac^-). Molecular structure and abbreviation of the dye employed and its counter anions are shown in Fig.1. These ion-pairs were dissolved in 1,2-dimethoxyethane (abbreviated to DME), acetonitrile (abbreviated to ACN) and methanol by sonication for about one minute at various concentration and were kept at constant temperature in the dark.

Measurements

The solutions for photoreaction were degassed by repeated freeze-pump-thaw cycles. These samples were irradiated *in vacuo* at 20 °C by a Hamamatsu 150W Hg-Xe lamp through an L-39 cut-off filter ($\lambda_{\text{ex}} > 365 \text{ nm}$) and IR cut-off filter. The photoreaction was monitored by a JASCO Ubest-55 UV/VIS spectrophotometer at room temperature. ^{13}C -NMR spectra were measured with a JEOLGS1270 high resolution spectrometer.

Fig.1 Molecular structure and abbreviation of the dye employed and its counter anions.

Fig.2. Variation of absorption spectra of MG^+OX^- (10 μM) in mixed solvents of acetonitrile (ACN) and 1,2-dimethoxyethane (DME) at 20 °C with different volume ratio.

3. Results

The absorption spectra of MG^+OX^- ($10\ \mu\text{M}$) in mixed solvents of ACN and DME are shown in Fig.2. In polar solvent (ACN), MG^+OX^- showed strong absorption at 620 nm. The absorption with peaks at the visible region decreased with increasing the fraction of less polar solvent (DME). New absorption in the UV region with a peak at 265 nm increased showing an isosbestic point at 280 nm. If the counter ions (OX^-) were exchanged with Ac^- , such solvatochromism was observed even in ACN and methanol. The increase of solvent polarity increased again the visible absorption of MG^+ with concomitant decrease of the UV absorption.

Visible light irradiation ($\lambda_{\text{ex}} > 365\ \text{nm}$) of degassed DME solution of MG^+OX^- caused complete disappearance of blue color. The absorption spectra are shown in Fig.3 for DME solutions before (a, solid line) and after irradiation for 60 min (b, broken line) at $20\ ^\circ\text{C}$. The visible absorption of MG^+ disappeared and the UV absorption at 265 nm increased.

The time-dependence of the absorbance 625 nm of MG^+OX^- in DME solution during photoexcitation and subsequent storage in the dark is shown in Fig.4. The absorption of MG^+ at

Fig.3 Absorption spectrum of MG^+OX^- ($10\ \mu\text{M}$) in DME, (a) before and (b) after irradiation ($\lambda_{\text{ex}} > 365\ \text{nm}$) for 60 min *in vacuo* at $20\ ^\circ\text{C}$.

The insert shows the part of the spectral changes.

0.1 → 100%
1. → 10%
2. → 1%

Fig.4 Absorbance changes during photoexcitation and subsequent storage in the dark monitored at 625 nm for MG^+OX^- ($10\ \mu\text{M}$) at $20\ ^\circ\text{C}$ in DME.

625 nm recovered after about ten hours at 20 °C. Such photoinduced bleaching and dark recovery were repeated reversibly.

The absorbance changes at 625 nm are shown in Fig.5 during photoexcitation of MG^+OX^- at 20 °C in DME (●) and ACN (○). In more polar solvent (ACN), the absorption of MG^+ did not change by irradiation.

The absorbance changes at 625 nm are shown in Fig.6 during photoexcitation and subsequent storage in the dark of MG^+OX^- at 20 °C in mixed solvents of ACN and DME with different volume ratio. The extent of photobleaching, which occurred completely in DME, decreased with increasing the fraction of polar solvent (ACN). After 24 hours, the absorption of MG^+ at 625 nm almost recovered in a 1/9 mixture. However the extent of recovery decreased with increasing solvent polarity as shown in Fig.6, for a 3/7 mixture.

4. Discussion

In less polar solvent, the new absorption at 265 nm coincided with that of leuco malachite green (LMG) shown in Fig.7 with carbon tetrahedral bonding (sp^3). It was confirmed by ^{13}C -NMR measurements. It is indicated that a contact ion pair of a cation (MG^+) and a counter anion (OX^-) formed a leuco ester by

Fig.5 Absorbance changes monitored at 625 nm during photoexcitation of MG^+OX^- (10 μM) at 20 °C in (●) DME and (○) ACN.

Fig.6 Absorbance changes during photoexcitation and subsequent storage in the dark of MG^+OX^- (10 μM) monitored at 625 nm at 20 °C in mixed solvents of ACN and DME with volume ratio; (●) 0 / 10, (○) 1 / 9, (▲) 3 / 7.

bonding between a center carbon of MG^+ and a carboxyl group of OX^- with a certain equilibrium constant as shown in Fig.7. Mono-anionic counter ion (Ac^-) formed more stable bonding with MG^+ . The presence of such an equilibrium between the bonding and ion pairs of carbocation and carbanion was reported for trimethylcyclopropenium cation and *p*-methoxyphenylmalononitrile anion [19-21], and 1,3,5-tricyclopropyl-tropylium cation and tris(7*H*-dibenzo-[*c,g*]fluorenylidene)methyl) anion [22]. It was also reported that MG^+ cation and bulky 4,4',4''-trinitrotrityl anion did not form bonding due to steric hindrance, but formed a radical pair by one electron transfer [23].

Fig.7 Molecular structure and abbreviation of leuco malachite green (LMG) and leuco ester.

The photobleaching and thermal recovery in DME solution indicated the change of the equilibrium between ion pairs and leuco esters due to the increased oxidation energy level of MG^+ by photoexcitation. In polar solvent (ACN), MG^+ and OX^- are strongly solvated, which makes it difficult to form contact ion pairs.

The almost irreversible photobleaching in mixed solvents (ACN/DME = 3/7) strongly suggested the formation of much stable colorless LMG due to electron and proton transfer from solvents.

5. Conclusion

The ion-pair malachite green dye showed reversible photobleaching and recovery in the dark in less polar 1,2-dimethoxyethane. Such inverse photochromism was due to the formation of leuco ester from photoassisted bonding of cation and anion, and to thermal ionic dissociation.

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