Reinvestigation on the photoinduced aggregation behavior of photochromic spiropyrans in cyclohexane

Yiting Li [a], Jinwei Zhou [b,*], Yanqiao Wang [b], Fushi Zhang [a], Xinqi Song [a]

[a] *Department of Chemistry, Tsinghua University, Beijing, 100084, China*
[b] *Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, China*

Abstract

Three photochromic spiropyrans (SP-1, SP-16, SP-4-SP) are investigated at carefully controlled condition. Special attentions are paid to the aggregation behavior and its effect on thermal decay of the colored form which is formed under UV irradiation. The three compounds show normal photochromism in $CHCl_3$. In cyclohexane solution, the spectrum of colored form of SP-16 has structures in the visible region. Detail analysis indicates that its photoinduced merocyanine form cannot form aggregate and the structures of the spectrum are believed to come from the *cis/trans* isomers of merocyanine form. For SP-1 in cyclohexane solution, it is found that only the dimer is formed under N_2 laser irradiation at 8°C, apart from the merocyanine monomer form. From E-diagrams and decoloration kinetics, it is known that only one linearly independent process exists in thermal decay of the colored form and there is an equilibrium between merocyanine monomer (B), colorless form (A) and the dimer (AB). In the decoloration process, the decoloration of B causes the shift of the equilibrium and which can further cause the dissociation of AB. This is the main route for the decoloration of AB. And all these results provide direct evidences that the composition of dimer is AB but not BB. From the effect of A concentration on the decoloration rate of the system, the formation constant (K) of AB is estimated to be 3.2×10^4. For a bis-indolino-spirobenzopyran supramolecular system SP-4-SP, the result indicates that it can promote the formation of dimer and retard the decoloration of the dimer thus formed efficiently.   © 1998 Elsevier Science S.A.

Keywords: Spiropyran; Photochromism; Dimer; Decoloration; Kinetics

1. Introduction

The spiropyrans are an important class of photochromic materials [1,2]. For which under UV irradiation, accompanying the heterolytic cleavage of the C–O bond of the colorless form (A) (Scheme 1), photomerocyanine (B) is formed and the absorption band shifts from UV to the visible region.

The colorless (A) form and the photoinduced merocyanine form (B) are different species with different polarities and reactivities. The photoinduced colored form can form chelates with metal ions when a coordinating group exist in the molecule [3,4], it can form aggregate in non-polar solvents [5–9] or in L–B films [10–12]. And all these can then affect the photochromic properties of the system such as decoloration rate and absorption spectrum significantly. In the work of Krongauz et al., they found that the colored merocyanine monomer (B) could interact with spiropyran molecules (A) to give dimer AB or charge transfer com-
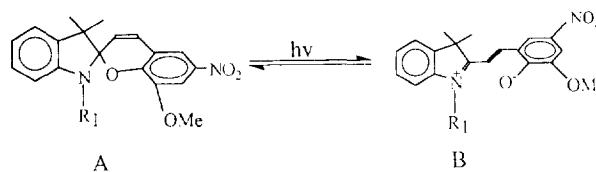
Scheme 1.

plexes A_nB ($n = 2,3$) [5–8]. Which then combined together to form highly dipolar microcrystals having a molecular stack structure. These microcrystals were coated with amorphous outer layer with the composition of AB, giving rise to a colloidal suspension of globules of about 0.1–0.4 μm diameter. Kalisky and Williams [13,14] studied the transient absorption of substituted 6-nitro BIPS. They observed a slow progressive red shift in the 640–670 nm region on photoirradiation and attributed the shift to the formation of J-aggregate-like stacks consisting of AB or A_nB ($n = 2,3$). Later, Lenoble and Becker [15] proposed that the aggregation process should be assigned to a bimolecular reaction between ^3X and B but not between ^3A and the closed spiropyran (A) in its ground state. Sato et al. reported that for SP in non-polar

* Corresponding author.

solvents under prolonged UV irradiation the colored mero-
cyanine crystal of large size (10–100 μm) was formed as a
precipitate [1,16,17]. The crystal thus obtained is much
larger than the quasicrystals reported by Krongauz et al. [7],
and the colored merocyanine in the crystals thus formed can
be stabilized for several days. In their work, the deaggregation
of photomerocyanine in fluid solution was studied for the first
time. And they found that in the very initial stage of aggregate
formation, anomalous nonexponential absorption decay at the
merocyanine monomer band and absorption band of the
aggregate form could be observed. This was attributed to the
deaggregation of the small aggregate (M_n) to the merocy-
anine monomer (B) in a stepwise way, which eventually
decayed to the uncolored spiropyran form (A). But the detail
mechanism for the decoloration process of the various aggre-
gates is not very clear. The reason for this is that the system
is too complex and there are too many species that coexist in
the system. And this generally causes difficulties in the deter-
mination of the kinetic parameters of each species in the
system.

In this paper, the effect of the molecule structure, concen-
tration, irradiation intensity on the formation of complex and
decoloration rate are studied under controlled condition. Then
the decoloration mechanism for the dimer is elucidated. For
comparison, the dimerization and its effect on decoloration
process are studied for a bis-indolino-spirobenzopyran supra-
molecular system.

2. Experimental

Spiropyrans (SP-1, SP-16, SP-4-SP) are synthesized
according to the literatures [2,18] and identified by conven-

tional methods. All solvents are analytically pure and
retreated before use. A Hewlett-Packard HP 8452 diode array
UV–Vis spectrophotometer is used to record the spectra. The
solutions are irradiated by a 500 W Xenon lamp equipped
with a grating monochromator or directly by N_2 laser (337.1
nm). A 1-cm cell equipped with micromagnetic stirrer is used
in the measurements.
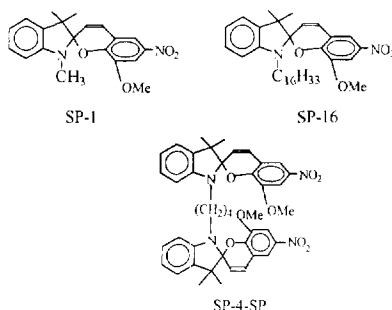
SP-1　　　　　　　SP-16

SP-4-SP

3. Results and discussion

3.1. Photochromic properties of SP-1, SP-16, SP-4-SP in CHCl₃

A strong absorption with high extinction coefficient
appears at 500–600 nm when the spiropyran in state A is
irradiated with UV light. The rate of decoloration to the col-
orless form (B → A) is measured by following the thermal
decay of the absorption band in the 500–600 nm region. Fig.
1a shows the visible absorption spectra of 2.2×10^{-4} mol/l
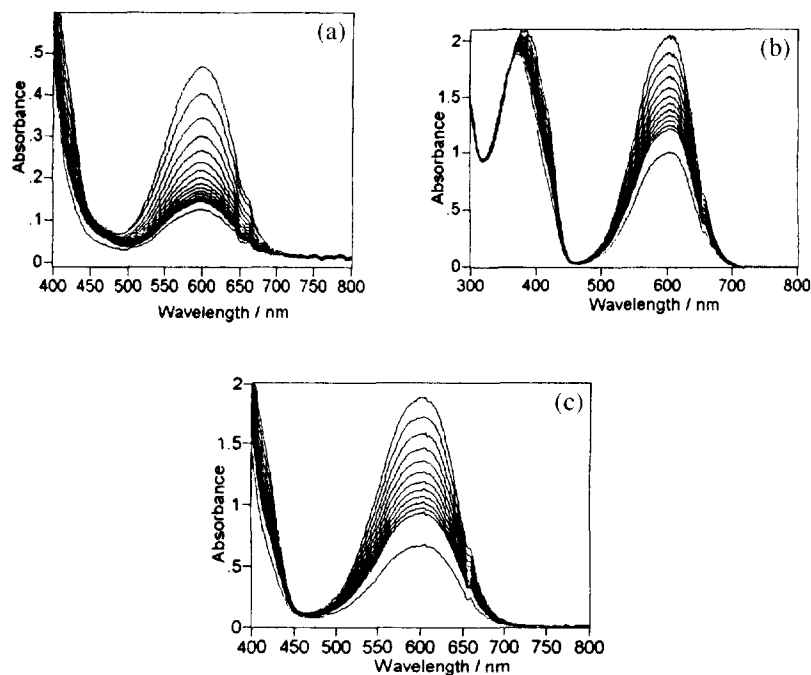SP-1 in CHCl₃ solution at different time after 3 min irradia-
tion by Xe lamp.

Fig. 1. Visible spectral variations of spiropyran in CHCl₃ after Xe-lamp irradiation for 3 min at 22°C. Time intervals: 5 s (a) 2.0×10^{-4} mol/l SP-1.
(b) 2.1×10^{-4} mol/l SP-16, (c) 1.7×10^{-4} mol/l SP-4-SP.
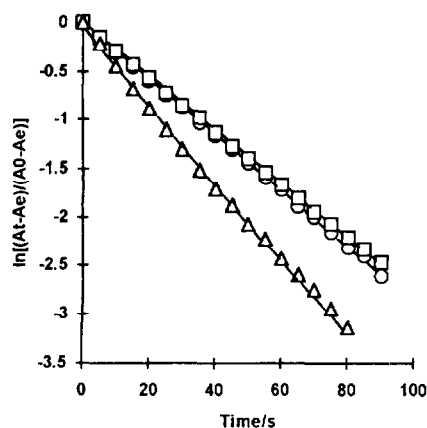
Fig. 2. First-order plots for the thermal decoloration of colored form of SP-1(△), SP-16(○), SP-4-SP(□).

The colored species thus formed can be designated as colored monomer B. For comparison, the decoloration processes of colored form of SP-16, SP-4-SP are also examined at the same condition (see Fig. 1b,c). By assuming that the decoloration kinetics are first order, Eq. (1) can be used to meet the decoloration process [19]:

$$\ln\frac{A_t-A_e}{A_0-A_e} = -kt \qquad (1)$$

where A_0, A_t and A_e denote the absorbance of the photomerocyanine form at time 0, t and infinite, respectively. From Fig. 2, three lines has been resulted. Then the decoloration rates for SP-1, SP-16 and SP-4-SP can be obtained to be 4.6×10^{-2} s^{-1}, 3.6×10^{-2} s^{-1} and 3.5×10^{-2} s^{-1}, respectively. It can be seen that the introduction of a long alkyl chain or another spiropyran molecule into the spiropyran moiety has no obvious effect on the shape and position of the colored form, but the decoloration rates of SP-16 and SP-4-SP are relatively lower than that of SP-1.

3.2. Elucidation of the decoloration process of SP-16 in cyclohexane

Fig. 3a and b show the visible spectral variations of 1.8×10^{-5} mol/l and 1.8×10^{-4} mol/l SP-16 in cyclohexane at different time after N_2 laser irradiation for 60 s, respectively. It can be seen that unlike in CHCl$_3$, the absorption spectrum of the colored form of SP-16 in cyclohexane shows some structures in the visible region. But an isosbestic point can be seen at 354 nm during the decoloration process. This implies that the process should be a simple reaction. In order to probe the decoloration process of SP-16 in cyclohexane in detail, an absorbance diagram (E-diagram) of the system is formulated [20]. In Fig. 3c, the absorbance at 600 nm is
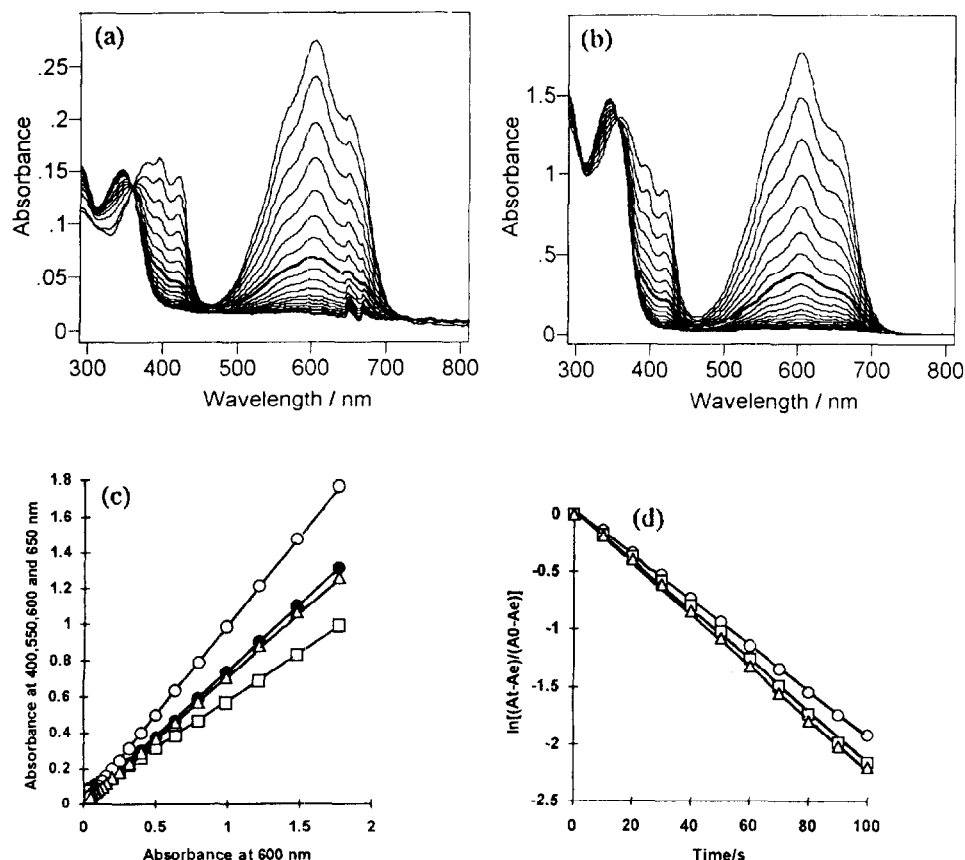

Fig. 3. (a) Visible spectral variations of 1.8×10^{-5} mol/l SP-16 in cyclohexane after N_2 laser irradiation for 1 min at 8°C. Time intervals: 10 s (b) Visible spectral variations of 1.8×10^{-4} mol/l SP-16 in cyclohexane after N_2 laser irradiation for 1 min at 8°C. Time intervals: 10 s (c) E-diagram of Fig. 3b, the absorbance at 600 nm is plotted against 400 nm (□), 550 nm (●), 600 nm (○) and 650 nm (△) (d) Decoloration rate plot of the open colored form of SP-16 at different concentrations. [SP-16] × 10^5 mol/l: 1.8 (○), 9.0 (△), 18 (□).

plotted against those at 400 nm, 550 nm, 600 nm and 650 nm during the decoloration for the system of Fig. 3b. Straight lines in the E-diagram indicate that the reaction is an uniform one. In other words, only one linear independent step is contained in the decoloration process. From Fig. 3d, it can be seen that the decoloration process follows the first-order kinetics very well and the variation in the concentration of SP-16 has little influence on the decoloration rate and the spectra shape of the colored form. It reveals that merocyanine form of SP-16 in nonpolar solvent does not form aggregate. A possible reason for the spectra feature of the colored form should be attributed to the cis/trans isomers of the merocyanine form. The introduction of a long alkyl chain could inhibit the aggregation of the colored form.

3.3. The photochromic properties of SP-1 in cyclohexane at 8°C

In the work of Krongauz et al., they found that for solutions of spiropyran in nonpolar solvents, there were more than four kinds of species coexist after UV irradiation, as A, B, AB and A_nB ($n = 2$–3) [5–8]. Apart from the colorless form A, the photoinduced colored merocyanine molecule B can interact with spiropyran molecules (A) to give dimer AB and other charge transfer complexes (CTC) (A_nB with $n \cong 2$–3). Which can then form aggregates with stack structure. The relative population of dimers and charge transfer complexes (CTC) depends both on light intensity and temperature because CTC formation involves an activation energy of about 22 kJ/mol associated with the interaction of dimers with further A molecules. At sufficiently low temperature and high light intensities, it is possible to obtain aggregates composed of dimer only [7]. For simplicity, the photochromic

properties of SP-1 under relative lower temperature and high UV irradiation are investigated in this work.

Fig. 4 shows the spectral changes of different concentration of SP-1 in cyclohexane at 8°C after UV irradiation. When the concentration of SP-1 is low (1.7×10^{-5} mol/l), the spectra of the colored form show some structures in similar with SP-16, but the relative intensity at 570 nm is higher. A reasonable explanation for this is that most of the colored form is in the monomer form and only a small part of it is in the AB form. When the concentration of SP-1 is increased, large difference in the absorption spectra in the colored form can be seen from that of SP-16 and a blue shift of absorption band is observed. This is caused by the formation of dimer AB. Another result drawn from Fig. 4 is that, in corresponding with the formation of AB, the decoloration rate of the colored form is retarded significantly.

Eckhardt et al. [21] found that in a polymer matrix, the variation in spiropyran concentration could result in a blue-shift in the visible spectrum and the retardation of the decoloration process. Another result in their work was that the decoloration process could not be described by first order kinetics and rate constants obtained by double exponential approximation to the decoloration process showed an obvious dependence on the spiropyran concentration. All these results implied that at least two linearly independent first order processes should coexisted in the decoloration process. The authors assumed that at high concentration, aggregation of photomerocyanine in the H-stacks occurred and a 'step-by-step' mechanism was used to explain the decoloration. During the decoloration process, the edge merocyanine molecules in the stack are converted to spiropyran form first, then the process is repeated, and short stacks disappear faster than long ones. In the recent work of Onai et al. [9], a similar
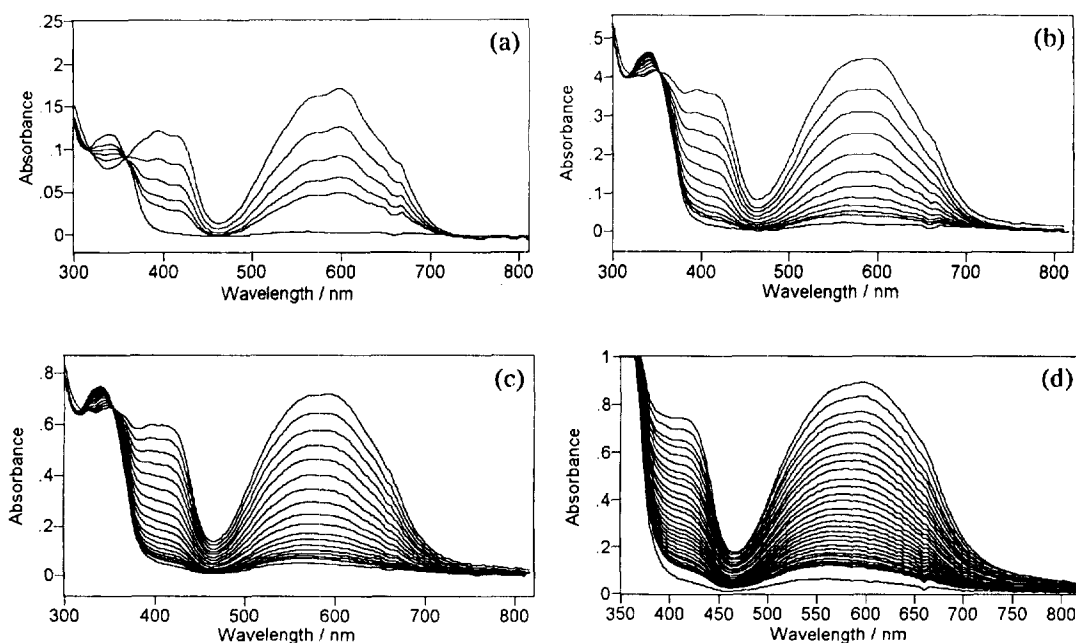

Fig. 4. (a) Visible spectral variations of different concentration of SP-1 in cyclohexane after N$_2$ laser irradiation for 1 min at 8°C. Time intervals: 20 s. [SP-1]: (a) 1.7×10^{-5} mol/l, (b) 6.5×10^{-5} mol/l, (c) 10.8×10^{-5} mol/l, (d) 21.6×10^{-5} mol/l.
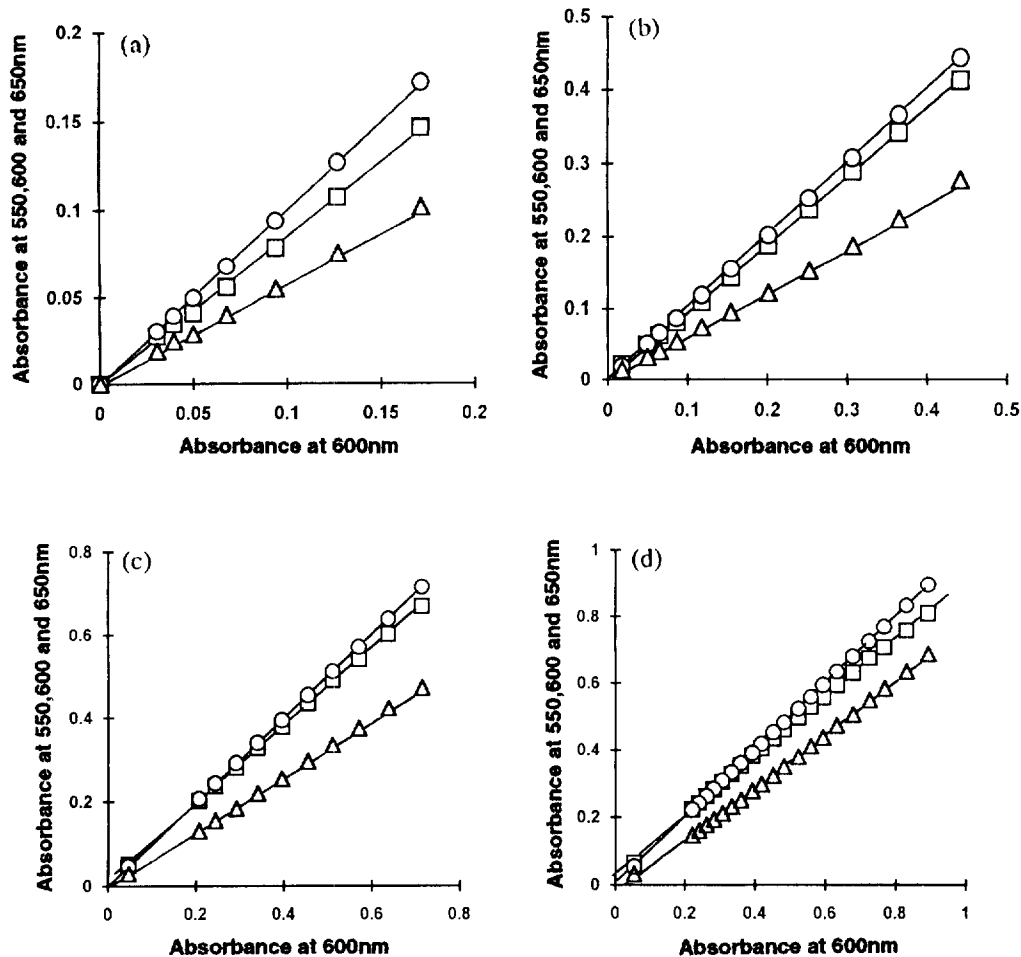
Fig. 5. E-diagram for the decoloration process of Fig. 4. The absorbance at 600 nm is plotted against absorbencies at 550 (□), 600 (○) and 650 (△) nm.

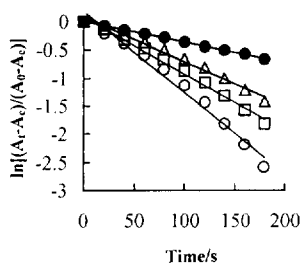Fig. 6. Decoloration rate plots of the colored form of SP-1 at different concentrations. |SP-1| × 10⁵ mol/l: 6.5 (○), 8.7 (□), 10.8 (△), 21.6 (●).

Table 1
Thermal decoloration rate constants at different concentrations of SP-1 in cyclohexane at 8°C

$|SP-1| \times 10^5$ (mol/l)	6.5	8.7	10.8	21.6
$1/|SP-1| \times 10^{-3}$	15.4	11.6	9.24	4.62
k_{ob} ($\times 10^3$ s^{-1})	14.3	10.1	7.8	3.7

stepwise decoloration mechanism was used to interpret the anomalous nonexponential decay kinetics for aggregate of spiropyran formed in aliphatic hydrocarbon solvents in the vary initial stage after UV irradiation. In present situation, for the concentration concerned, no obvious shift in the

absorption spectra during decoloration process can be observed. A possible reason for this is that temperature used in this work is relatively low, therefore, only dimer is formed in the system and A_nB with $n \geq 2$ is negligible. In order to find the detail mechanism for the decoloration process of the system, E-diagrams are plotted (Fig. 5). It can be seen that the absorbances at different wavelength show good linearities for the concentrations used. This indicates there is only one linear independent rate determining step in the decoloration process and such a result cannot be interpreted from the stepwise decoloration process of the aggregates. Fig. 6 gives the first-order kinetics plots of the decoloration processes at different concentrations, satisfactory linear plots are obtained. The decoloration rate constants at different concentrations of SP-1 obtained from Fig. 6 are listed in Table 1. It can be seen that the concentration of SP-1 has significant effect on the decoloration rate of the system. All these imply the existence of an equilibrium in the decoloration process of the system, and the equilibrium must be linear to B and the colorless form A must be contained in the equilibrium in some way.

For the chelate of colored form of spiropyran or spiro-oxazine with divalent metal ions, it was found that the thermal decoloration rate is decreased as the concentration of metal ion is increased [22,23]. There exists an equilibrium between

Scheme 2.
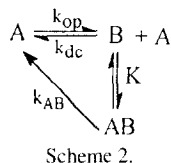
the colored form and its chelate with metal ion during the decoloration process of the chelate. The present case is quite similar and the only difference is that the acceptor is not the metal ions but the colorless spiropyran (A) itself. If this is true, the method used for treating the decoloration process of chelate of spiropyran or spirooxazine with metal ions can be used directly to the present system.

In Scheme 2, k_{dc} and k_{AB} are the decoloration rate constants of B and AB, respectively, K is the formation constant of dimer (AB). From Scheme 1, we have:

$$-\frac{d[AB]}{dt} - \frac{d[B]}{dt}$$

$$= \frac{d[A]}{dt} = k_{dc}[B] + k_{AB}[AB] - k_{op}[A]$$

$$= k_{dc}\frac{[AB]}{K[A]} + k_{AB}[AB] - k_{op}[A]$$

$$= \left(\frac{k_{dc}}{K[A]} + k_{op} + k_{AB}\right)[AB] - k_{op}[T]$$

(2)

where $[T]$ is the total concentration of A and AB and the meaning of the other terms are obvious from Scheme 1. Treating Eq. (2) by Flannery's method [24], Eq. (3) can be obtained

$$\ln\left(\frac{A_t - A_e}{A_0 - A_e}\right) = \left(\frac{k_{dc}}{K[A]} + k_{op} + k_{AB}\right)t$$

(3)

Comparing Eq. (3) with Eq. (1), we have:

$$k_{ob} = \frac{k_{dc}}{K[A]} + k_{op} + k_{AB}$$

(4)

There should be a linear relation between the observed decoloration rate and the reciprocal of the concentration of colorless form (A) (Fig. 7). Treating the data in Table 1 using Eq. (4), Fig. 5 is obtained. It gives a good linearity indeed, and $k_{op} + k_{AB} = 1.0 \times 10^{-3}$ s^{-1}, $k_{dc}/K = 9.8 \times 10^{-7}$ mol l^{-1} s^{-1}. The observed decoloration rate constant of the colored form consists of two parts: one is $k_{dc}/K[A]$ which corresponds to the decoloration route in which AB is in equilibrium with B and A. In the decoloration process, the decoloration of B causes the shift of the equilibrium and which can further cause the dissociation of AB. The other is k_{AB}, which comes from the direct decoloration of AB. The present results indicate that for the concentration concerned, the main route for the decoloration of AB comes from the first part. The contribution from the second part is very small and can be ignored. Moreover, k_{dc} can be estimated to be around 3.2×10^{-2} s^{-1}, then we have $K = 3.2 \times 10^4$.
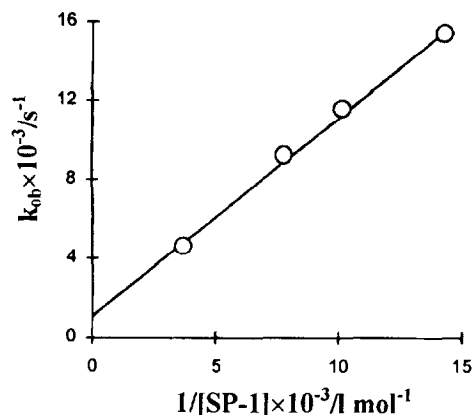

Fig. 7. Variation in the observed decoloration rate constants as a function of the reciprocal of SP-1 concentration.

In the work of Krongauz and Parsshutkin [5], the composition of the dimer was considered to be AB from the analysis of the quantum yield of the coloration process. But no further evidence can be found in the literatures thereafter. In the work of Lenoble and Becker [15], they suggested that the formation process of aggregate is a result of a bimolecular reaction between ^{3}X and B. If this is true, the exact composition of the dimer is BB. But in the present work, it has been proven that there is an equilibrium between B, A and the dimer formed. This clearly indicates the composition of the dimer is AB but not BB. The result of the works of Lenoble and Becker can be interpreted as follows: the aggregate observed by Lenoble and Becker is not a stable one, which decays within 24 μs, then it is not the dimer finally formed but an intermediate, and it can transform to AB some way, for example, by reacting further with colorless A molecule [5].

3.4. The photochromic properties of SP-4-SP in cyclohexane at 8°C

From the results above, we can see that the increase in concentration of SP-1 is helpful to form dimer AB and depress the decoloration rate. To research more efficient method for stabilizing the colored form, a bis-indolino-spirobenzopyran supramolecular system SP-4-SP is investigated. For this system, there are two units of photochromic spiropyran which are linked by a aliphatic chain, then we believe that dimer AB can be formed at very low concentration. Fig. 8a shows the visible absorption spectrum of low concentration of SP-4-SP (2.53 × 10^{-5} mol/l) in cyclohexane solution at different time after UV irradiation. It can be seen that the absorption spectrum has the same shape with that of SP-1 at high concentration. But structures caused by monomer form is vanished in the spectrum. This supports the promise of dimer structure in other way, because only dimer can be formed at such a low concentration and it is difficult to form other type of aggregates.

Similar with SP-1, its E-diagram gives good straight lines (Fig. 8b). From Fig. 8c, it can be seen that the decoloration
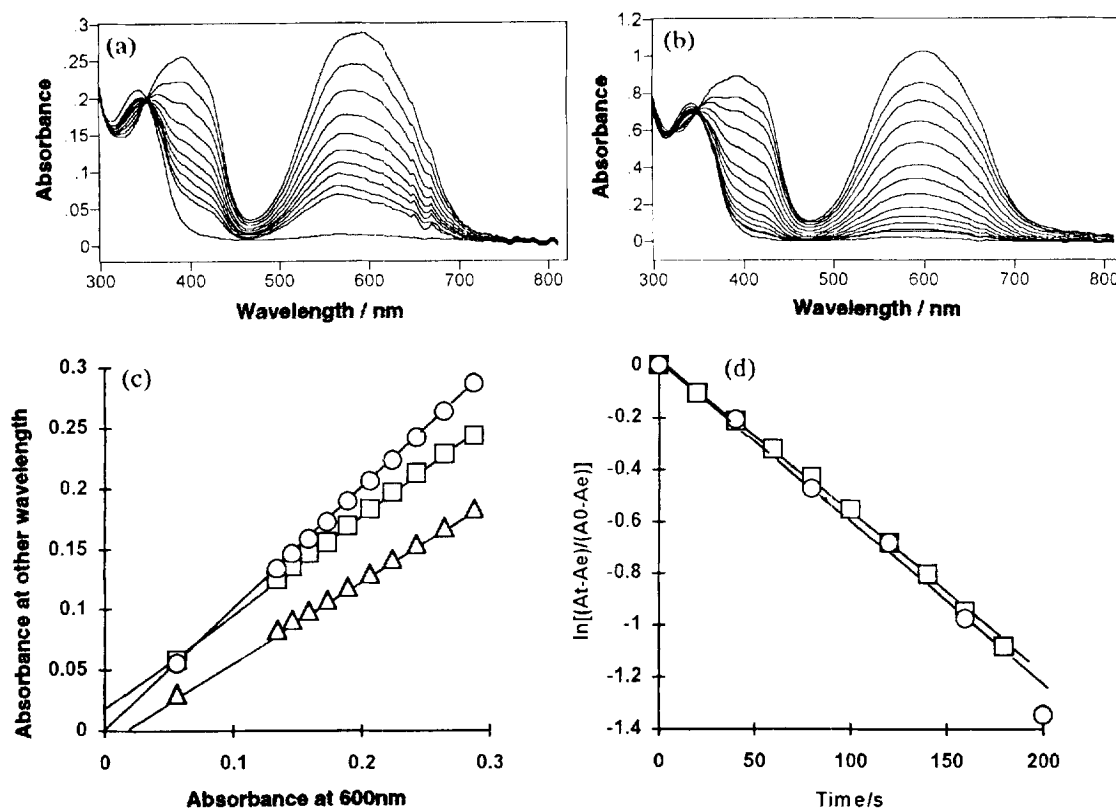
Fig. 8. (a) Visible spectral variations of 2.53×10^{-5} mol/l SP-4-SP in cyclohexane after N_2 laser irradiation for 1 min at 8°C. Time intervals: 40 s (b) Visible spectral variations of 1.0×10^{-4} mol/l SP-4-SP in cyclohexane after N_2 laser irradiation for 1 min at 8°C. Time intervals: 40 s (c) E-diagram of Fig. 8a. The absorbance at 600 nm is plotted against 550 nm (□), 600 nm (○), 650 nm (△). (d) Decoloration rate plots of the colored form of SP-4-SP at different concentrations. |SP-4|:2.53×10^{-5} mol/l (□), 1.0×10^{-4} mol/l (○).

of AB can be described by first-order kinetics very well. And its decoloration rate constant is 6.0×10^{-3} s^{-1} which is comparable with that of SP-1 at high concentrations. This demonstrates that apart from the formation process, the decoloration rate of dimer AB can also be adjusted efficiently by using a supramolecular system, SP-4-SP. Another result which can be seen from Fig. 8c is that the concentration of SP-4-SP has no obvious effect on the decoloration rate of colored form. This is consistent with the above viewpoint that the complexes formed in this system is dimer AB, which consists of just two molecular units and can be formed in a single SP-4-SP supramolecule easily. Then the variation in concentration will exert little influence on the spectra shape and decoloration rate of the system.

4. Conclusions

Three photochromic spiropyrans (SP-1, SP-16, SP-4-SP) are investigated at carefully controlled condition. Special attentions are paid to aggregation behavior and its effect on the thermal decay of the colored form formed under UV irradiation. Results obtained are as follows.

(1) The three compounds show normal photochromism in CHCl$_3$. introduction of a long alkyl chain or another spiropyran molecule into the spiropyran moiety has not obvious

effect on the shape and position of the colored form, but the decoloration rates of SP-16 and SP-4-SP are relatively lower than that of SP-1.

(2) For SP-16 in cyclohexane, the spectrum of colored form shows some structures in the visible region. Detail analysis indicates that decoloration process contains only one linearly independent rate determining step and obeys first order kinetics very well. Variation in concentration has no effect on the spectral shape and decoloration rate of the colored form. The structures of the spectra is believed to come from the cis/trans isomers of merocyanine form.

(3) For SP-1 in cyclohexane, the spectral shape and the decoloration rate of the colored form show critical dependence on irradiation intensity and the concentration of the colorless form. Under the condition used, apart from the monomer form, only dimer can be formed under N_2 laser irradiation at 8°C. From E-diagrams and decoloration kinetics, it is found that only one linearly independent process exists in the thermal decay of colored form and there is an equilibrium between the merocyanine monomer (B), colorless form (A) and the dimer (AB). In decoloration process, the decoloration of B will cause a shift of the equilibrium and which can further cause the dissociation of AB. This is the main route for decoloration of AB and is believed to support the promise that the composition of dimer is AB but not BB. From the effect of A concentration on the decoloration rate of the sys-

tem, the formation constant (K) of AB is estimated to be 3.2×10^4.

(4) For a bis-indolino-spirobenzopyran supramolecular system SP-4-SP, the result indicates that it can promote the dimer formation and retard the decoloration rate of the dimer very efficiently.

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