Photochromism of azobenzene in the hydrophobic interlayer spaces of dialkyldimethylammonium-fluor-tetrasilicic mica films

M. OGAWA, M. HAMA* AND K. KURODA*†

PRESTO, Japan Science and Technology Corporation and Institute of Earth Science, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, *Department of Applied Chemistry, Waseda University, Ohkubo 3-4-1, Shinjuku-ku, Tokyo 169-8555, †Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Nishiwaseda 2-8-26, Shinjuku-ku, Tokyo 169-0051, Japan

(Received 6 November 1997; revised 1 March 1998)

ABSTRACT: Photochemical isomerization of azobenzene intercalated in the hydrophobic, interlayer spaces of swelling fluor-tetrasilicic micas exchanged with dialkyldimethylammonium ions, with the alkyl chain length from 10 to 18, was investigated. Thin films of the organoammonium-mica-azobenzene intercalation compounds were obtained by depositing a suspension of the organoammonium-micas (prepared using a toluene/methanol solution of azobenzene) on quartz substrates. The intercalated azobenzene showed reversible photochromic reactions induced by UV and visible light irradiation. The fraction of the photochemically formed cis-isomer in the photostationary states decreased with a decrease in temperature. The observed change in the photochemical reactions is thought to reflect changes in the states of the dialkyldimethylammonium ions in the interlayer space of the swelling fluor-tetrasilicic mica.

Intercalation of guest species into layered inorganic solids is one method of producing ordered inorganic-organic assemblies with unique microstructures controlled by host-guest and guest-guest interactions (Whittingham & Jacobson, 1982; Müller-Warmuth & Schöllhorn, 1994). Recently, photophysical and photochemical properties of intercalation compounds have been investigated extensively (Ogawa & Kuroda, 1995). The smectite group, one of a number of possible layered hosts, provides attractive features including large surface area, swelling behaviour, and ion-exchange properties which can organize organic guest species (Theng, 1974; Van Olphen, 1977). Since the smectites are transparent in the visible wavelength region and form stable colloidal suspensions and oriented films, their uses for photochemical studies have attracted increasing interest (Ogawa & Kuroda, 1995; Thomas, 1988), and the photochromism of viologen (Miyata et al., 1987) and fulgide (Adams & Gabbott, 1990) in the interlayer space of layered silicates has been reported. Photochromic behaviour is environmentally sensitive (Dürr & Bouas-Laurent, 1990), thus photochromism of organic substances in solid matrices has been investigated to to both elucidate and modify the photochromic behaviour. Indeed, the photochromic behaviour of the intercalated species was different from that observed in solution or other solid matrices, suggesting the applicability of layered clay minerals as a novel support to control photochromic properties.

We have been interested in the organization of azo dyes in the hydrophobic interlayer spaces of organoammonium-silicates (Ogawa, 1996; Ogawa et al., 1991, 1996). The photochromism of azobenzene and its derivatives due to cis-trans isomerization has been widely investigated (Dürr &
M. Ogawa et al.

Photocontrol of chemical and physical functions of various supramolecular systems has been studied vigorously using photochemical configurational change of azobenzene derivatives (Kumar & Neckers, 1989). The introduction of poorly water-soluble species into the hydrophilic interlayer space of layered silicates has been achieved by exchanging the interlayer cations with cationic surfactants. These organoammonium-clays have been studied as a precursor for pillared clays (Galarneau et al., 1995), selective adsorbates (Boyd et al., 1988a,b; Lee et al., 1990), membranes (Okahata & Simizu, 1989), catalyst supports (Hu & Rusling, 1991), and photoactive species (Seki & Ichimura, 1990; Tomioka & Itoh, 1991; Takagi et al., 1991; Ahmadi & Rusling, 1995; Ogawa et al., 1992b; 1993; 1995), among others (Lagaly, 1981; Ogawa & Kuroda, 1997).

In our previous study, solid-solid reactions have been used to achieve intercalation of \( p \)-aminoazobenzene and \( p \)-dimethylaminoazobenzene into organoammonium-montmorillonite and fluor-tetrasilicic micas. The intercalated azo dyes exhibited reversible photoisomerization in the hydrophobic interlayer spaces at room temperature. In this study, dialkyldimethylammonium-fluor-tetrasilicic micas have been used as the host materials in order to incorporate azobenzene (the molecular structure is shown in Fig. 1) as well as to react with them in the interlayer spaces. It has been suggested that the intercalated dialkyldimethylammonium ions exhibit gel-to-liquid crystal phase transitions (Seki & Ichimura, 1990; Okahata & Shimizu, 1989; Hu & Rusling, 1991; Ahmadi & Rusling, 1995; Vaia et al., 1994). Since phase transitions may affect the photochemistry of the adsorbed azo dyes, the photochemical reactions of azobenzene intercalated in the hydrophobic interlayer spaces of the organoammonium-silicates have been studied at different temperatures.

![Fig. 1. The molecular structure of azobenzene.](image-url)

**EXPERIMENTAL**

**Materials**

A swelling mica, fluor-tetrasilicic mica, TSM, (supplied by Topy Industries Co.), was used as the host material after removing non-expandable impurities by dispersion-sedimentation. The cation exchange capacity was 100 mEq/100 g clay (Ogawa et al., 1992a). Dialkyldimethylammonium (abbreviated to \( 2C_n2C_1N^+ \), where \( n \) denotes the carbon number in the alkyl chain; \( n=10, 12, 14, \) and \( 18 \) ) chlorides were obtained from Tokyo Kasei Industries Co. and used without further purification. Azobenzene (Tokyo Kasei Industries Co.) was used after recrystallization from ethanol.

**Sample preparation**

The \( 2C_n2C_1N^+ \)-TSMs were prepared by the conventional ion-exchange method in which Na-TSM was dispersed in aqueous solutions of appropriate organoammonium salts and subsequently washed with ethanol/deionized water mixtures repeatedly until a negative AgNO\(_3\) test was obtained. The organoammonium-TSMs were dispersed in a toluene/methanol solution of azobenzene at room temperature and the suspension was cast on a quartz substrate and dried in air, so that thin films formed on the substrate. In a typical experiment, 0.1 g of \( 2C_{18}2C_1N^+ \)-TSM was dispersed in 10 ml of azobenzene solution (4.9 \( \times 10^{-4} \) M). The thickness of the films, determined by a surface profilometer, was a few \( \mu \)m.

**Characterization**

X-ray powder diffraction patterns of the products were recorded on a Rigaku RINT 1100 diffractometer using Mn filtered Fe-K\(\alpha\) radiation. Absorption spectra of the films were recorded on a Shimadzu UV-3100PC spectrophotometer. The thin films of organoammonium-TSMs were used as reference, in order to reduce the effect of scattering on the absorption spectra and thus the spectra shown are difference spectra. The compositions of the products were determined by elemental (C,H,N) analysis (Yanaco MT-3).

**Photochemical reactions**

The photochemical reaction of the intercalated azobenzene was achieved using UV and visible
light irradiation from a 500 W super high pressure Hg lamp. (USHIO USH-500D) A band pass filter (Toshiba UV-D35), with the transmittance centred at 350 nm, was used for isolating the UV light. For the cis-to-trans reverse reactions, a sharp cut filter, HOYA L42 (cut off wavelength 420 nm) was used to obtain visible light. The reactions were monitored by the change in absorbance of the trans-isomer of azobenzene. A sample film was set in a cryostat with optical windows (Oxford DN-1704), and photochemical reactions were performed at constant temperatures from 100 to 360 K.

RESULTS AND DISCUSSION

Preparation of 2C₈₂C₁N⁺-TSMs

The basal spacings of the 2C₈₂C₁N⁺-TSMs and the amounts of the adsorbed 2C₈₂C₁N⁺ are listed in Table 1. The amounts of 2C₈₂C₁N⁺ adsorbed confirmed that the exchangeable cations were replaced almost quantitatively by 2C₈₂C₁N⁺ in all the samples investigated. There was a linear relationship between the d value and carbon number in the alkyl chains, which, given the observed basal spacings and the size of the alkyl-chain, suggests that the intercalated 2C₈₂C₁N⁺ formed paraffin-type aggregates in the interlayer space. Two types of arrangement of the intercalated 2C₈₂C₁N⁺ were expected; one was monomolecular coverage and the other was bimolecular coverage with the alkylchains inclined to the silicate sheet. It was not possible to determine which type of arrangement occurred here.

Intercalation of azobenzene into 2C₁₈₂C₁N⁺-TSM

The XRD patterns of the products obtained by the reactions between 2C₁₈₂C₁N⁺-TSM and azobenzene (at a molar ratio of azobenzene to 2C₁₈₂C₁N⁺ of 2) showed an expansion in the basal spacing from 3.4 to 3.9 nm, indicating that azobenzene had been intercalated into the interlayer space of 2C₁₈₂C₁N⁺-TSM. No further increase in the basal spacing was observed when an excess amount of azobenzene was added. The solid-state intercalation of p-aminoazobenzene, naphthalene, anthracene and pyrene into organoammonium-montmorillonites and TSMs also exhibited a limited interlayer expansion (Ogawa et al., 1991; 1992b, 1993, 1995, 1996).

It is very difficult to accommodate the large amounts of guest species achieved in the present studies into various surfactant aggregates in solution and at solid surfaces. It is considered that the layered silicates support the surfactants and maintain a layered organization even with such a large number of guest species. There is a possibility that azobenzene adsorbs at the external surface, but the relative contribution of the external surface to the interlayer space should be very small and therefore negligible.

In order to understand the reaction, the suspension of the 2C₁₈₂C₁N⁺-TSM in a methanol/toluene mixture containing azobenzene was centrifuged. The supernatant liquid contained azobenzene and the precipitate was not coloured. This suggests that azobenzene molecules were intercalated during solvent evaporation. The intercalation of p-aminoazobenzene and p-dimethylaminoazobenzene into various organoammonium-montmorillonites and TSMs by solid-solid reactions has already been reported (Ogawa et al., 1991, 1996). Since the products were obtained as powders, the intercalation compounds were embedded in poly(vinyl alcohol) films for the photochemical studies. In this study, the products were obtained as films so that the photochemical studies could be carried out without any pretreatment. Although the films were

<table>
<thead>
<tr>
<th>Sample</th>
<th>Basal spacing, nm</th>
<th>Amounts of adsorbed 2C₈₂C₁N⁺, mEq/100 g clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-TSM</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>2C₁₈₂C₁N⁺-TSM</td>
<td>3.40</td>
<td>97</td>
</tr>
<tr>
<td>2C₁₄₂C₁N⁺-TSM</td>
<td>2.80</td>
<td>99</td>
</tr>
<tr>
<td>2C₁₂₂C₁N⁺-TSM</td>
<td>2.59</td>
<td>97</td>
</tr>
<tr>
<td>2C₁₀₂C₁N⁺-TSM</td>
<td>2.39</td>
<td>97</td>
</tr>
</tbody>
</table>
slightly turbid, they were still useful for the photochemical studies.

**Photochemical isomerization of azobenzene in the interlayer space of 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM**

The loading of azobenzene in the photochemical study, was fixed at 1 mol azobenzene to 20 mol 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+} in order to avoid guest-guest interactions. The resulting intercalation compound showed no significant change in the basal spacing resulting from the small amount of the azobenzene present. The absorption spectrum of the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene intercalation compound is shown in Fig. 2a. The absorption band attributable to trans-azobenzene appeared near 325 nm, confirming the successful incorporation of azobenzene in the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM film.

The change in the absorption spectrum of the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene intercalation compound film upon irradiation with UV and visible light is shown in Fig. 2. The absorbance at 325 nm due to the trans-isomer decreased and the absorption band of cis-azobenzene appeared near 427 nm. The absorption spectrum of the photostationary state appeared after 5 min (Fig. 2b) under the experimental conditions employed in this study. Subsequent irradiation with visible light resulted in the recovery of the absorption band due to the trans-isomer. Figure 2c shows the absorption spectrum of the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene intercalation compound after visible light irradiation for 1 min. Further irradiation led to the complete recovery of the absorption spectrum recorded before the UV irradiation (Fig. 2a) and this reversible spectral change was observed repeatedly.

![Absorbance spectrum](image)

**Fig. 2.** The absorption spectra of the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene intercalation compound. The molar ratio of azobenzene to 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+} is 1/20: (a) before UV irradiation; and (b) after the UV irradiation at the photostationary state. Spectrum (c) was recorded after visible light irradiation for 1 min.
Therefore, the change in the absorption spectra upon UV irradiation followed by visible light irradiation was attributed to the photoisomerization of the intercalated azobenzene.

Since the thermally promoted reverse reactions took more than a day for complete recovery of the absorption spectrum at room temperature, an estimate of the reaction yields can be made. The change in absorbance of the trans-isomer suggests that the fraction of the photochemically formed cis-isomer was ca. 80% at the photostationary state at room temperature. This result indicates that the interlayer space of the $2\text{C}_{18}\text{C}_{1}\text{N}^+\text{-TSM}$ offered an environment where the intercalated azobenzene isomerized effectively.

The photochemical reaction was conducted at different temperatures (in the range 100–360 K) and Fig. 3 shows the absorption spectra at the photostationary states. High temperature may cause desorption of the azobenzene from the intercalation compound, so that the maximum temperature was restricted to 360 K in the present study.

The variation in the fraction of the photochemically formed cis-isomer (Fig. 4) suggests a change in the fluidity of the matrices surrounding the azobenzene molecules. The fractions of the photochemically formed cis-isomer were ca. 80% and did not change significantly above the discontinuity at 325 K, while the fraction of the cis-isomer decreased as the temperature decreased below 325 K. It has been observed that the quantum yields of trans-to-cis photoisomerization of azobenzenes in organic solvents decreases as the temperature decreases (Rau, 1990; Malkin & Fischer, 1962). Therefore, the gradual decrease in the fraction of the cis-isomer below 325 K is thought to reflect the change in the

![Fig. 3. The absorption spectra of the $2\text{C}_{18}\text{C}_{1}\text{N}^+\text{-TSM}$-azobenzene intercalation compound at the photostationary state. The molar ratio of azobenzene to $2\text{C}_{18}\text{C}_{1}\text{N}^+$ is 1/20: (a) before UV irradiation at 100 K and after UV irradiation at 100 K (b), 200 K (c), 250 K (d) and 300 K (e).](image-url)
M. Ogawa et al.

The temperature dependence of the fraction of the photochemically formed cis-isomer at the photo-stationary state for the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene intercalation compound. The molar ratio of azobenzene to 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+} is 1/20. Arrow indicates the phase transition temperature.

The microviscosity of the environment surrounding the azobenzene molecules.

The change in the state of surfactants in the interlayer spaces of smectites has been reported previously (Seki & Ichimura, 1990; Okahata & Shimizu, 1989; Hu & Rusling, 1991; Ahmadi & Rusling, 1995). Changes in the permeability of the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-silicate composites (Okahata & Shimizu, 1989), the thermal discolouration kinetics of the intercalated spiropyrane (Seki & Ichimura, 1990), the luminescence of the intercalated pyrenes (Ahmadi & Rusling, 1995) and the catalytic activity (Hu & Rusling, 1991) have been observed at a certain temperature and attributed to the change in state of the intercalated surfactant aggregate between gel and liquid crystalline states. Phase transition temperatures have been reported around 326–327 K for 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-montmorillonites (Seki & Ichimura, 1990; Okahata & Shimizu, 1989; Hu & Rusling, 1991; Ahmadi & Rusling, 1995). In the present system, the temperature dependence indicated a change at 325 K and this value is in agreement with those reported previously within the experimental accuracy (Table 2).

The variation in the \(d\) values for the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-silicates reported previously should be noted. The basal spacings of the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-montmorillonites are summarized in Table 2. The \(d\) values (4.24 nm) for the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-clays reported by Seki & Ichimura (1990), 4.83 nm (Okahata & Shimizu, 1989), and 4.3 nm (Ahmadi & Rusling, 1995) are larger than that for the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM, 3.40 nm, observed for the present system. Since the thickness of the alumino-silicate sheet of montmorillonite is similar to that of TSM, the difference in the basal spacings must correspond to the difference in the orientation of the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+} ions, which may cause the difference in the phase transition temperature. In the present system, the amount of the intercalated 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+} was just equivalent to the cation exchange capacity of the TSM as shown in Table 1. It is known that excess of guest species can be accommodated in the interlayer spaces of smectites as a salt and this phenomenon is referred as ‘intersalation’. The large \(d\) values reported in the literature (Seki & Ichimura, 1990; Okahata & Shimizu, 1989; Ahmadi & Rusling, 1995) may be due to the intersalation and/or the difference in the effective surface layer charge density. Although the difference did not cause a change in the phase transition temperatures, the effect of ‘intersalation’ on the properties of the complexes should be investigated further.

The \textit{cis}-to-\textit{trans} reverse reaction has been investigated at 100 K, but the intercalated azo dye did not isomerize (\textit{trans}-to-\textit{cis}) at that temperature. Therefore, the film was UV irradiated at room temperature (the \(c/s\)-fraction was ca. 80\%) and cooled to 100 K. The visible light irradiation at 100 K resulted in the effective recovery of the absorption band due to \textit{trans}-isomer. This observation indicates that the \textit{cis}-to-\textit{trans} reactions do not require fluid surrounding, while the \textit{trans}-to-\textit{cis} reactions were significantly restricted in rigid environments as observed for the photochemistry of azobenzene in organic solvents (Rau, 1990; Malkin & Fischer, 1962).

The \textit{effects of the alkyl chain length of the interlayer dialkyldimethylammonium ions on the photochemistry of the intercalated azobenzene}

In order to examine the effects of the alkyl chain length on the photochemistry of the intercalated azobenzene, the 2C\textsubscript{2n}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene intercalation compounds, where \(n = 10, 12\) and 14, were prepared by the same procedure used for the...
Table 2. Basal spacings and gel to liquid-crystalline phase transition temperatures for the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-silicates.

<table>
<thead>
<tr>
<th>Host</th>
<th>Phase transition temp/K</th>
<th>Basal spacings (nm)</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite\textsuperscript{a)}</td>
<td>327</td>
<td>4.24</td>
<td>Thermal discoloration of photomerocyanic to spiropyran</td>
<td>Seki &amp; Ichimura (1990)</td>
</tr>
<tr>
<td>Montmorillonite\textsuperscript{b)}</td>
<td>327</td>
<td>4.83</td>
<td>Permeation of fluorescent probe\textsuperscript{b)} and DSC</td>
<td>Okahata &amp; Shimizu (1989)</td>
</tr>
<tr>
<td>Bentonite</td>
<td>326</td>
<td>4.3</td>
<td>Pyrene luminescence</td>
<td>Ahmadi &amp; Rusling (1995)</td>
</tr>
<tr>
<td>Bentonite</td>
<td>327</td>
<td>not given</td>
<td>Electrochemical reduction of Trichloroacetic acid</td>
<td>Hu &amp; Rusling (1991)</td>
</tr>
<tr>
<td>TSM</td>
<td>328</td>
<td>3.4</td>
<td>Photochromism of azobenzene</td>
<td>This study</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} Kunipia G, Kunimine Industries Co.

\textsuperscript{b)} 1-(1,3,4,5-tetrahydroxycyclohexanecarboxyamido)naphthalene

preparation of the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene system and the photochemical reactions of the intercalated azobenzene were studied. The molar ratios of the loaded azobenzene to 2C\textsubscript{n}2C\textsubscript{1}N\textsuperscript{+} ions were adjusted to 1/20. The absorption band due to trans-azobenzene, around 326 nm (similar to that observed for the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene intercalation compound) was also present in the 2C\textsubscript{10-14}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene systems.

The photochemical reactions were conducted at selected temperatures and the fraction of cis-isomer formed at the photostationary state was determined from the change in the absorption spectra, which were similar to that observed for the 2C\textsubscript{18}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene intercalation compound (Figs. 3, 4) in that the fraction of cis-isomer decreased with decreasing temperature. There was a discontinuity around 290 K in the temperature dependence of the fractions of the photochemically formed cis-isomer for the 2C\textsubscript{12}2C\textsubscript{1}N\textsuperscript{+}-TSM-azobenzene intercalation compound. The fractions of cis-isomer were ca. 80% and did not change significantly in the temperature range of 290–360 K. Similar changes in the fraction of the photochemically formed cis-isomer have been observed for other systems and the discontinuities were observed at 300 and 280 K for 2C\textsubscript{14}2C\textsubscript{1}N\textsuperscript{+} and 2C\textsubscript{16}2C\textsubscript{1}N\textsuperscript{+}-TSMs, respectively. Although the phase transition temperatures estimated from the temperature dependence of photoisomerization for the 2C\textsubscript{14}2C\textsubscript{1}N\textsuperscript{+} and 2C\textsubscript{12}2C\textsubscript{1}N\textsuperscript{+}-TSMs were slightly different from those reported previously (296 and 288 K for the 2C\textsubscript{14}2C\textsubscript{1}N\textsuperscript{+} and 2C\textsubscript{12}2C\textsubscript{1}N\textsuperscript{+}-TSMs, respectively), (Okahata & Shimizu, 1989), there is a tendency toward lower phase transition temperatures with a decrease in the alkyl chain length. All these observations indicate that the photochemistry of azobenzene intercalated in the 2C\textsubscript{n}2C\textsubscript{1}N\textsuperscript{+}-TSMs was influenced by the state of the surrounding surfactant (2C\textsubscript{n}2C\textsubscript{1}N\textsuperscript{+}) ions.

CONCLUSIONS

Azobenzene has been intercalated into the hydrophobic interlayer spaces of the dialkylidimethylammonium-swelling micas. The intercalated azobenzene exhibits reversible trans-cis isomerization upon UV irradiation and subsequent visible light irradiation. The fraction of the photochemically formed cis-isomer at the photostationary states depends on the reaction temperature, suggesting a change in the state of the interlayer surfactants. The photochemistry of azobenzene can be controlled by its introduction into the organoammonium-silicates where the appropriate states of the intercalated alkylammonium ions can be controlled.

ACKNOWLEDGMENTS

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture. Waseda University also supported the study financially as a Special Research Project.
REFERENCES


