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Photochemistry of azobenzene in sol–gel systems

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A B S T R A C T

The photophysical and photochemical behavior of azobenzene incorporated into sol–gel systems was studied. Sols doped with azobenzene were prepared by the hydrolysis of tetramethoxysilane. The absorption spectra of azobenzene in sols with and without HCl as a catalyst showed photochromism; UV irradiation changes trans-azobenzene to cis-azobenzene, which returns to trans-azobenzene by successive visible light irradiation. The results indicate that azobenzene is not protonated in the sol prepared by the present conditions. The absorption spectra showed that the azobenzene-doped xerogel prepared without HCl is mostly adsorbed on silica surfaces by the hydrogen bonding between the azo groups and silanol and/or water molecules. The adsorption did not affect photochromic behavior and photo-reversible changes were observed in the xerogels. UV photolysis of the azobenzene-doped xerogel prepared with HCl so produced protonated benzo[c]cinnoline that photochromic behavior was deteriorated. Surface modified xerogels were prepared from the mixture of tetraethoxysilane and methyltriethoxysilane in order to make clear the effect of the surface silanol groups. It was shown that the formation of the protonated benzo[c]cinnoline is suppressed by the introduction of Si–CH_3. These present results confirm that the acidic sites of Si–OH_2^+ of xerogels play an important role in the photochemical reaction of azobenezene in silica xerogels.

1. Introduction

The photoisomerization of azobenzene (AB) and its derivatives has been of much interest from the viewpoints of the fundamental mechanism of photoisomerization and its potential applications in optical switches and memories, molecular machines, and nanodevices [1,2]. The following two mechanisms have been proposed for the photoisomerization of trans-AB; with excitation to the S_1 (n,π*) state the isomerization proceeds via inversion about one nitrogen atom in the same molecular plane, while excitation to the S_2 (π,π*) leads to isomerization via rotation around the N=N double bond [1]. Fujino and Tahara, however, have suggested that the inversion mechanism may take part also in the isomerization following the S_2 (π,π*) excitation from the time-resolved Raman study [3]. Chang et al. have proposed that the rotation channel is operative for the photoisomerization of trans-AB in a nonviscous solvent, whereas the concerted inversion channel operates when the rotation channel is obstructed in a viscous solvent, in inclusion complexes or through chemical modification [1].

The photochemical studies of AB and its derivatives have been done in various environments such as Nafion membranes, cyclodextrins, zeolites, aluminophosphate, sol–gel glasses, lysozyme, and so on [4–15]. The inversion mechanism is considered to be operative in these environments, because the rotation channel is obstructed in such a restricted space. The AB systems follow two different reactions depending on the photolysis condition; upon excitation in a neutral medium, cis–trans photoisomerization occurs and photostationary mixtures of both isomers are obtained. When the photolysis is done in the acidic condition, AB changes to benzo[c]cinnoline (BC), and variable amounts of benzidine (BZ) are produced [16]. Photoirradiation of water-swollen Nafion-H^+ membrane soaking AB results in BC, and is also produced if the number of AB molecules in each water cluster of the Nafion membrane is greater than 2 [5]. Corma et al. reported that photolysis of AB in the presence of a series of acidic zeolites gives rise to BC and BZ [6]. Lei et al. also reported that photolysis of AB in aluminophosphate leads to the formation of BC and BZ and the Lewis acid sites of aluminophosphate are considered to play an important role in the photocyclization chemistry [7].

Sol–gel glasses doped with organic molecules are promising materials for photoresponsive materials [17–19]. For example, morphological and optical properties including nonlinear optical performance have been studied for azo-polymer-based sonogel hybrid composites and azo-dye confined SiO_2 sonogel films [20,21]. The sonogel host systems have provided thermal and mechanical stability protecting the activate chromophores and preserving their optical properties. Furthermore, photochromism becomes an excellent probe for the microstructure of matrices, because the reaction is sensitive to the microenvironmental factors such as polarity, viscosity, acid–base interactions, free volume and so on [10]. Therefore, photochromism of AB in sol–gel glasses is of considerable interest.

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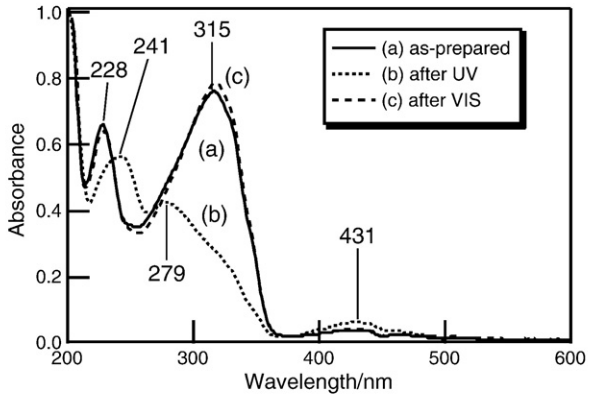

Fig. 1. Absorption spectra of azobenzene in a sol without HCl: (a) as prepared, (b) after UV irradiation for 1 h, (c) after subsequent visible irradiation for 1 h.

In this paper, we studied the photochemistry of AB in the sol–gel systems of tetramethoxysilane (TMOS), especially paying attention to the effect of acids.

2. Experimental section

Chemicals. Azobenzene (AB, Aldrich), benzo[c]cinnoline (BC, Tokyo Kasei), tetramethoxysilane (TMOS, Tokyo Kasei), tetraethoxysilane (TEOS, Tokyo Kasei), methyltriethoxysilane (MTEOS, Tokyo Kasei), ethanol (Tokyo Kasei), and hydrochloric acid (Wako) were used as received. Water was deionized and distilled.

Sample preparation. As a typical preparation condition, TMOS (5 mL), ethanol (5 mL, containing 10^{-3} mol/L AB or BC) and water (2.5 mL) were mixed together. A slight amount of HCl was added as a catalyst in some solutions: 200 μL of 0.1 M or 1 M. These solutions were divided into two equally and placed in a plastic beaker sealed with a pin-holed film after stirring for 1 h. Gelation occurred after a few days and the gels were dried at an ambient temperature for a month. Modified xerogels were also prepared from the 5 mL mixed solution of TEOS (2.5 mL) and MTEOS (2.5 mL), ethanol (5 mL with 10^{-3} mol/L AB), water 2.0 mL, and 500 μL of 0.1 M HCl. The error was estimated for the sample preparation to be less than 5%.

Measurements. Absorption spectra were recorded with a JASCO Ubest-50 spectrophotometer. Fluorescence spectra were taken with a JASCO FP-770 spectrophotometer. The accuracy of absorption measurement was ±0.3 nm and ±0.001 absorbance. The accuracy of fluorescence measurement was ±1.5 nm.

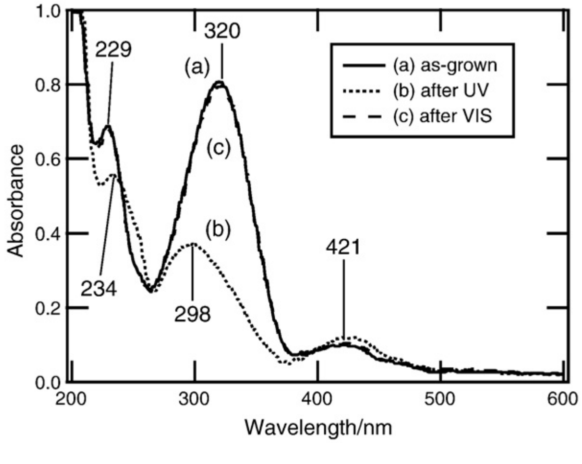

Fig. 2. Absorption spectra of azobenzene in the xerogel prepared without HCl: (a) as prepared, (b) after UV irradiation for 1 h, (c) after subsequent visible irradiation for 1 h.

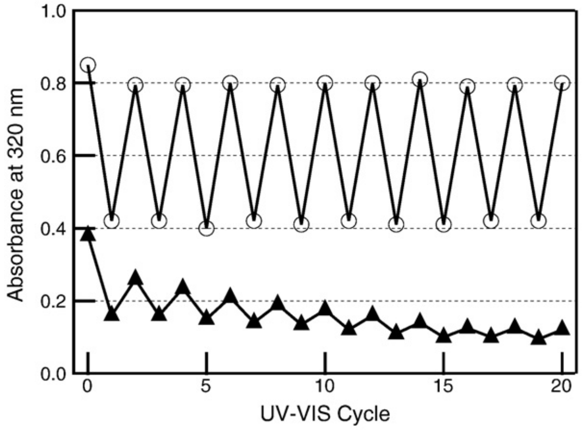

Fig. 3. Absorbance change at 320 nm of the azobenzene-doped xerogels prepared without HCl (○) and with 200 μL of 1 M HCl (▲) under repeated irradiation of UV and visible light for 3 min.

For photochromic measurements, samples were irradiated with a high pressure Hg lamp (Ushio, 500 W) through filters (Toshiba UV-D33s and IRA-25 S) for UV and (L-42 and IRA-25 S) for visible light. All measurements were done at room temperature.

3. Results

Fig. 1 shows the absorption spectra of AB in a sol without HCl measured as prepared (a), after UV irradiation for 1 h (b), and after subsequent visible irradiation for 1 h (c). Fig. 1a shows the peaks at 228 and 315 nm along with the very weak band 431 nm, corresponding to those of trans-AB. UV irradiation induced new bands at 241 and 279 nm, and increased the absorbance of 431 nm with decrease in the absorbance of the trans-AB bands, as shown in Fig. 1b. After being subsequently exposed to visible light, the spectrum returned to the initial one (Fig. 1c). These spectral changes indicate the reversible trans–cis–trans reactions of AB in the sol [7].

Similar photochemical changes were observed in the xerogel prepared from a sol without HCl. Fig. 2a shows the absorption spectrum of AB in the xerogel. The absorption spectrum has the peaks at 229, 320, and 421 nm, which are similar to those of the sol. A closer look reveals the spectral changes such as the red shift of the 315 nm band to 320 nm, and the blue shift and slight increase of the 421 nm band in comparison with that at 431 nm from the sol to xerogel. After

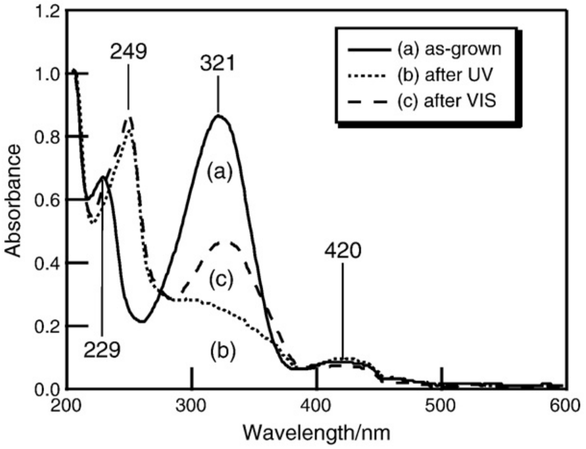

Fig. 4. Absorption spectra of azobenzene in the xerogel prepared with 200 μL of 0.1 M HCl: (a) as prepared, (b) after UV irradiation for 1 h, (c) after subsequent visible irradiation for 1 h.