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ARTICLES

Femtosecond Time-Resolved Spectroscopy of Photoisomerization of Methyl Orange in Cyclodextrins

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The photoisomerization of methyl orange (MO) encapsulated in the cavities of α-, β-, and γ-cyclodextrins (CDs) was measured by the ultrafast transient lens (UTL) method and transient absorption spectroscopy. The signal for free MO was well-fitted to the sum of two exponential functions, except for the component of the optical Kerr effect (OKE), and their time constants were $\lesssim$1 (τ_1) and $\sim$10 ps (τ_2). The UTL signal of the 1:1 complex, in which one MO molecule was included in one CD molecule, was almost the same as that of free MO. On the other hand, MO in two α-CD molecules showed slower relaxation and considerably lower yield of cis isomer. Thus, there were clear confinement effects when MO was capped at both ends by two CD molecules. The observed changes of ultrafast dynamics and yield of the isomer were explained in terms of CD−MO interactions and a steric effect. In the case of γ-CD, which included two MO molecules as a dimer, these confinement effects were also observed even when each MO was capped on only one side (2:1 complex). These results showed that a strong intermolecular interaction was induced between two MO molecules by confinement in a nanospace and this also hindered the isomerization. In particular, the complex with two γ-CD molecules (2:2 complex) showed significantly slower relaxation than the others, and no cis isomer was formed. It seemed that the intermolecular interaction of two MO molecules was further enhanced by photoexcitation in the 2:2 complex and this resulted in the formation of an aggregate-like intermediate in the γ-CD nanocavity.

Introduction

It is well-known that some molecules behave unusually when encapsulated inside a nanometer-sized cavity.[1] Detection of the chemical and physical effects of inclusion, such as formation of an excimer, increase or decrease of reaction rate, and enhancement of fluorescence, is a subject of great current interest. Some of these effects occur on a picosecond to femtosecond ultrafast time scale, and a number of ultrafast time-resolved studies on confined molecules have been reported.[2−5] In the present paper, we focus on the photoisomerization of an azo compound included in the nanocavity of cyclodextrin (CD) to investigate the effects of inclusion on the ultrafast dynamics in the photoisomerization, which is one of the most fundamental ultrafast reactions.

CD is one of the most important host molecules providing a nanocavity. It is a truncated cone-shaped molecule with a

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hydrophilic outside and a hydrophobic hollow the diameter of which is several angstroms. Because of this structure, CD forms an inclusion complex with various organic molecules in aqueous solution. CD is even useful to investigate the effects of spatial restriction because the cavity diameter varies with the number of glucose units constituting CD, e.g., α-CD (5 Å) consisting of six units, β-CD (6.5 Å) consisting of seven units, and γ-CD (8 Å) consisting of eight units.[6,7]

Azobenzene derivatives are known to exhibit photoinduced trans−cis isomerization. Much interest has been directed toward this characteristic because of its possible application in photochemical switching devices or information storage systems.[8,9] The transient states and relaxation time constants of the photoisomerization of azobenzene (AB) and its derivatives have been estimated by transient absorption measurements. Though two possible routes, rotation and inversion, have been proposed for isomerization, it is still unclear which route is selected in $\pi-\pi^*$ excitation.[10−13] In addition, molecules that have the AB moiety are easily included into the cavity of CD mainly because of the hydrophobic interaction. In particular, methyl orange (MO) has a large binding constant, i.e., a large equilibrium constant for the 1:1 CD/guest complexation reaction. The inclusion complex of MO and CD has been a subject of NMR and absorption spectroscopy studies and various other measurements in the steady state.[14−20]

In this study, we measured the isomerization dynamics of MO confined in the CD cavity by the ultrafast transient lens method (UTL) and transient absorption spectroscopy (TA). UTL is a technique to detect the ultrafast change of the refractive index of a solution that accompanies the photoexcitation and relaxation processes with picosecond to femtosecond time resolution. It is well-known that the refractive index of a solution directly reflects nonradiative dynamics not only of solute molecules but also of solvent molecules. Most photoexcited substances go through a nonradiative relaxation process, which exhibits no fluorescence; therefore, UTL can be applied to much more systems than fluorescent measurements. Previously, this method has been used to measure the ultrafast relaxation process of β-carotene,[21] auramine O in organic solvent,[22] and ultrafine silver particles in aqueous solution.[23] Photoisomerization of aminoazobenzene in various organic solvents was also measured with UTL, and the ultrafast solute−solvent interaction component was successfully identified.[24] In addition, UTL is also sensitive to the molecular configuration change that induces the refractive index change. This feature is considered to be useful to get information on host−guest systems.

Experimental Section

The UTL principle and experimental apparatus have been described in detail elsewhere;[21,23] thus, they are only mentioned briefly here. When a solution is irradiated by light having a spatial distribution of intensity, typically a Gaussian type, a spatial distribution of refractive index is generated in the solution. This effect has been called the "thermal lens effect" because it mainly originates from heat, but it can occur before the light energy is transformed into heat, and many possible origins for it have been reported.[25,26] The UTL method detects this ultrafast change of the refractive index using the pump−probe technique. As the probe pulse passes through the sample solution, which has been irradiated by the pump pulse, the probe pulse is focused or defocused by a transiently generated lens. This change can be detected as an intensity change of the center area of the probe beam.

The output beam from a mode-locked Ti:sapphire laser (Coherent, MIRA 900F; centered at 800 nm, 76 MHz repetition) was divided into two by a beam splitter. One beam was used as a probe beam after passing through a computer-controlled optical delay line, and the other, to be used as a pump beam, was frequency doubled by a BBO crystal after being intensity-modulated by an acousto-optic modulator. The relative polarizations of the pump and probe beams were set parallel. The pump and probe beams were made collinear and focused on the sample cell by a convex lens ($f = 50$ mm). The refractive index change was detected as a change of the intensity of the center area of the probe beam using a small-area avalanche photodiode. The output of the photodiode passed through a preamplifier and a homemade passive band-pass filter before being sent to a lock-in amplifier. The response function of the whole system was about 400 fs.

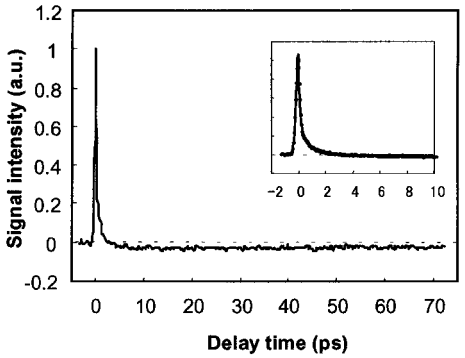

Figure 1. UTL signal of free MO fitted to a multiexponential decay of $\tau_1 = 10$ fs (for OKE of solvent and cell), $\tau_2 = 0.4$ ps, and $\tau_3 = 1.5$ ps.

For transient absorption measurements, a mode-locked Ti: sapphire laser (Clark, CPA-1000 seeded by Coherent, MIRA BASIC; centered at 800 nm, 1 kHz repetition) was used as a light source. The output was divided into two by a beam splitter and used as a pump beam and a probe beam. The pump beam was frequency doubled by a BBO crystal, and the probe beam was passed through an optical delay line and a 1 cm cell filled with D_2O to generate a white light continuum before being focused onto the sample cell with a convex lenses ($f = 300$ mm for the pump beam and $f = 200$ mm for the probe beam). A small part of the probe beam was divided to use as a reference. The intensities of the probe and reference beams were measured by a multichannel CCD spectrometer (Hamamatsu, PMA-11), and changes of the absorption spectra were calculated. The response function of the whole system was 200 fs.

MO (Nacalai Tesque), α-CD, γ-CD (Wako), and β-CD (Kanto Chemical) were used without further purification. They were dissolved in pure water. The concentration of MO was 0.3 mM for all sample solutions. To suppress adsorption of the sample onto the cell wall, which would influence the formation of cis isomer, the sample solutions were circulated using a quartz flow cell (optical path = 0.5 mm). All experiments were carried out at room temperature.

Results and Discussion

1. UTL Signal of Free Methyl Orange. A UTL signal obtained for MO in pure water (free MO) is presented in Figure 1. This signal includes the optical Kerr effect (OKE) as previously reported.[21−23] The OKE was estimated to last for 10 fs on the basis of the UTL signal of pure water. The decay of the signal was fitted by a multiexponential function convoluted with the instrumental response function (400 fs), giving two lifetimes of 0.6−0.9 ps (τ_1) and 8−13 ps (τ_2) following the OKE. The time constants, τ_1 and τ_2, obtained in our

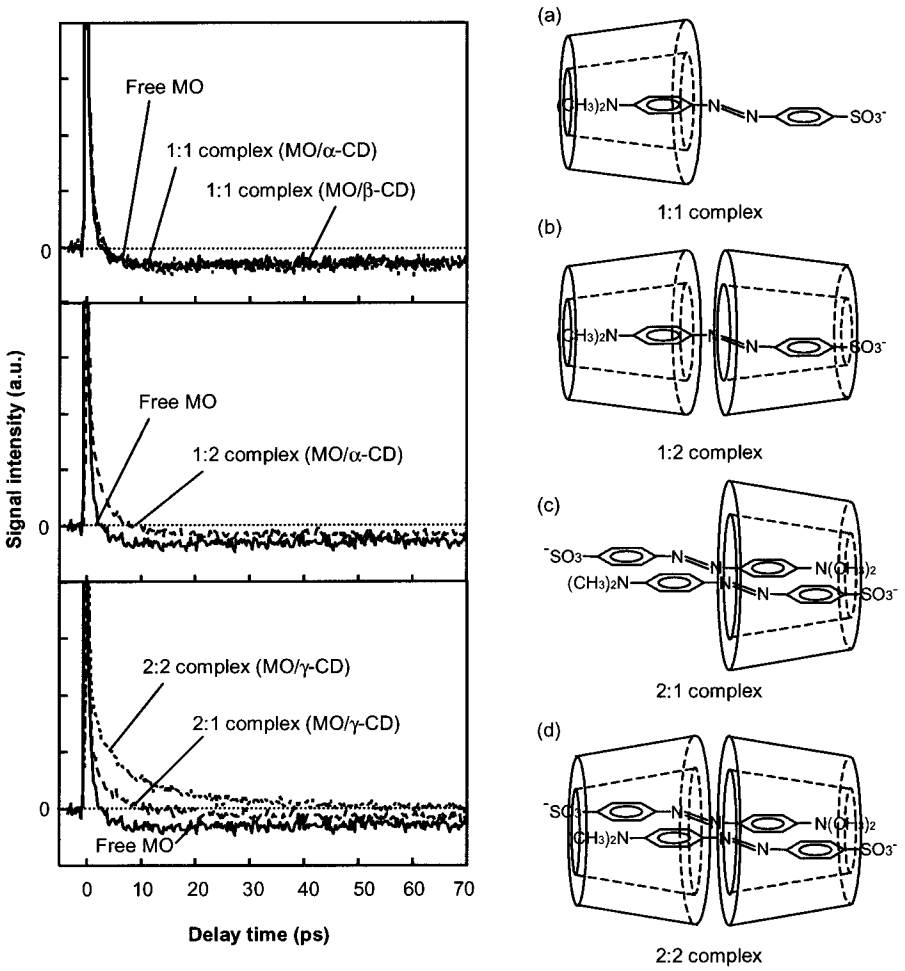

Figure 2. CD concentration dependence observed for MO (0.3 mM) in 0.3 mM (- - -) and 10 mM (···) CD solutions (left). The solid line corresponds to the signal for free MO. A schematic representations of the main inclusion complexes formed in each sample is shown on the right.

experiment were assigned to the decays of the first-formed trans-S_2 state to the vibrationally excited S_0 state and the vibrational relaxation of the S_0 state on the basis of their time scales. Although the time constants show somewhat different values when the functional groups of AB are different, our measurements and assignments were in good agreement with reported values for AB and its derivatives from the viewpoint of their time scale.[12] Then, the UTL showed a negative signal after ~2.5 ps of delay time and gradually recovered to zero. The refractive index of the cis isomer is smaller than that of trans isomer in ground state. Thus, the negative signal and its recovery reflect the formation of the cis isomer and cis−trans thermal isomerization, respectively.

2. UTL Signal of Methyl Orange in Cyclodextrins. It is known that MO and CD form several kinds of inclusion complexes. MO is included as a monomer or a dimer, depending on the cavity size of the CDs. Moreover, the guest molecule is included from one end by one host or from both ends by two hosts. Therefore, not only the difference in the CD diameter but also the difference of the inclusion ratio (i.e., inclusion from one end or both ends) should be considered distinctively.

The MO/CD ratio of inclusion complex depends on the concentrations of MO and CD and the kinds of CDs.[16,19] Previous reports have suggested that a 1:2 complex, in which one MO is capped by two CD molecules at both ends (Figure 2b), begins to form as the ratio of CD and MO concentrations ([CD]/[MO]) exceeds 1.[15] Considering this, CD concentrations of 0.3 mM and 10 mM were chosen to get predominantly 1:1 complex (Figure 2a) and 1:2 complex (Figure 2b), respectively. In the case of β-CD, it is implied that 1:1 complex was the main species even when the [CD]/[MO] ratio was rather large.[15] However, another absorption spectroscopic study shows the possibility that some degree of 1:2 complex can also be formed in higher concentration solution.[18] Thus, it is not necessarily clear whether 1:1 complex is major species or not. We prepared both samples of β-CD with the same concentrations as α-CD, 0.3 mM and 10 mM. On the other hand, γ-CD with the largest cavity included two MO molecules as a dimer. MO and γ-CD formed 2:1 complex (Figure 2c) in dilute CD solution and 2:2 complex (Figure 2d) in relatively concentrated CD solution.[16] For 0.3 mM MO, 2:1 complex was formed the most when CD concentration was about 0.3 mM, at which 60% of MO existed as 2:1 complex and 10% as 2:2 complex. In 10 mM CD solution, 70% of MO was in 2:2 complex and 15% in 2:1 complex.

UTL signals of MO (0.3 mM) in α-, β-, γ-CD (0.3 or 10 mM), where complexes of each ratio would form, were measured (Figure 2, left side). Time constants obtained by multiexponential fitting of UTL signals are listed in Table 1.

2a. MO/α-CD and MO/β-CD Complexes. We first consider the confinement effect when a MO was capped by a CD from one end. As a result, it was found that the 1:1 complexes with both α-CD and β-CD showed almost the same relaxation rate as free MO, though their cavity diameters differed. This means that confinement effects are not induced when CD caps MO from one end. A previous NMR study had suggested that α-CD includes MO on the *N*,*N*-dimethylaniline side and β-CD includes it on the benzenesulfonate side.[15] In both cases, the activation point (i.e., N═N moiety) is considered to be outside of the CD

TABLE 1: Kinetic Parameters for Isomerization of MO with and without CDs as Obtained from UTL and log *K* Values of CDs for MO

host	[CD], mM	MO/CD ratio[a]	τ_1, ps	τ_2, ps	m/ϵ_{400}[b]	log *K*[c]
none			0.6−0.9	8−12	0.1	
α-CD	0.3	1:1	0.6−1.1	6−12	0.1	3.95
	10	1:2	1.0−1.7	6−13	0.07	
β-CD	0.3	1:1	0.5−1.0	6−11	0.1	3.3
	10	1:1	0.5−1.0	6−11	0.1	
γ-CD	0.3	2:1	0.6−1.2	6−12	0.05	7.26
	10	2:2	1.1−2.0	13−17		

[a] The dominant complexation ratio in each sample. [b] Minimum value of the signal normalized by the absorbance at the excitation wavelength is reported; this indicates the isomerization yield. [c] *K* is a binding constant between CD and guest molecule.

cavity. These results indicated that the inclusion of the activation point of MO (N═N moiety) was crucial for inducing some confinement effects on the photoisomerization.

Next, we measured the 1:2 complex with α-CD, in which MO was encapsulated from both ends. As a result, two differences were observed in comparison with the signal of free MO. The faster relaxation component was slowed, while the absolute value of the minimum value (*m*) of the signal was 60% of that of free MO. The *m* value is linearly related to the amount of cis isomer formed by isomerization because the UTL signal intensity is linearly related to the concentration of photoexcited solute molecules in the solution. Another possible contribution we considered was the difference in absorbance at the excitation wavelength between some kinds of complexes. Thus, we normalized *m* values of the signals with the absorbance at 400 nm (ϵ_{400}) to estimate the extent of the cis isomer formation better. The m/ϵ_{400} values of 1:1 and 1:2 complexes were 0.1 and 0.07, respectively. This meant that the yield of cis isomer decreased 30% compared to that of 1:1 complex. These results showed that the yield of cis isomer became lower when MO was included from both sides.

We considered the mechanism of these confinement effects on ultrafast dynamics and the yields of cis isomer. Because effects on the dynamics must appear in the ultrafast region (<1.0 ps), it was not physical interactions, which need some molecular motions, but electrostatic interactions between excited molecules and the CD cavity that we considered to be the major cause for the difference. It is known that α-CD has a large dipole moment along the axis of the cavity. During isomerization, MO also has a dipole transiently at the activation point, i.e., the N═N moiety. As mentioned above, the dipole of α-CD affected the transient dipole of MO in the 1:1 complex only a little because the activation point was not included inside the cavity. On the other hand, in the 1:2 complex, dipole−dipole interaction became effective because the N═N moiety was completely included inside the CD cavity. Our results indicated that the dipole inside the α-CD cavity induced unfavorable effects on the formation of MO intermediate from the viewpoint of the electrostatic energy. This resulted in a slower time constant for the first step of photoisomerization (τ_1). On the other hand, τ_2 showed no remarkable difference compared to that for the 1:1 complex. It has been reported that both time constants from the vibrationally excited S_0 state to the trans isomer and to the cis isomer are almost the same.[10−12] Thus, even when some MO molecule went back via the vibrationally excited S_0 state to the trans isomer again, no remarkable change of τ_2 could be expected to occur. Next, we considered the difference in yields of cis isomer between 1:1 and 1:2 complexes. In the case of inclusion by two CD molecules from both ends, not only the unfavorable MO−CD interactions for the formation of reaction intermediate as mentioned above but also spatial constraint by two CD molecules from both ends should be considered important. It is known that there are wide rims of CD molecules facing each other in the α-CD system and the complexes are stabilized by hydrogen bonding between hydroxylic groups of facing CD molecules.[27] We expected this stable capsule-like structure to effectively hinder the rotation or inversion of the activation point, thus leading to the decreased yield of cis isomer in the small α-CD cavity.

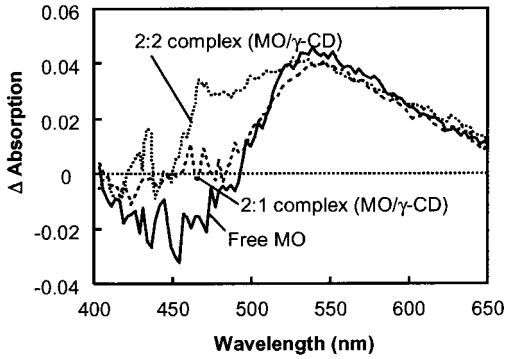

Figure 3. Comparison between the transient absorption spectra of free MO (0.3 mM) and MO in γ-CD. The solid line corresponds to the spectrum of free MO, long dashes to MO in 0.3 mM γ-CD solution, and short dashes to MO in 10 mM γ-CD solution.

It is worth noting that no difference was observed in time constants or yield of cis isomer between 0.3 and 10 mM β-CD solution (Table 1). As mentioned above, it is suggested but not yet clear that the 1:1 complex is actually the major species even when the concentration of β-CD is considerably high. Thus, our UTL measurements on the MO/β-CD system gave strong support that the 1:1 complex was the major species for β-CD even in higher concentration solution from the viewpoint of ultrafast dynamics of MO in CD.

2b. γ-CD/MO Complex. Although most AB derivatives easily form dimers at high concentration, MO does not form dimers.[28] In γ-CD, however, MO is known to be included as a dimer. Thus, we thought that the relaxation or isomerization dynamics of MO dimer following photoexcitation could be measured in γ-CD nanospace. Figure 2 and Table 1 show the results. When MO was included as a monomer, inclusion by one CD molecule did not hinder the isomerization as was seen in α-CD and β-CD complex systems. However, the isomerization of MO molecules in γ-CD was hindered even when they were included from one end (m/ϵ_{400} values of 0.5). This result suggested that the MO−MO interaction, which is effectively induced by inclusion in γ-CD cavity, was also responsible for the yield of photoisomerization. In the case of the isomerization of the 2:2 complex, the UTL signal was not negative and had much slower relaxation time constants than those observed in other MO−CD complexes. These results indicated that formation of cis isomer was completely inhibited, and moreover, the conformational change of excited MO molecules was also effectively hindered in the 2:2 complex. To our interest, in the case of the 2:2 complex, not only τ_1 but also τ_2 was remarkably elongated. This result indicates the formation of some specific long-lived intermediate in the γ-CD cavity. To obtain further information on this excited state, we measured transient absorption spectra of the 2:1 and 2:2 complexes and compared them to the free MO spectrum (Figure 3). In the spectrum for free MO soon after excitation, bleaching and absorption were observed near 460 nm and 540 nm, respectively. For MO in 0.3 mM γ-CD (2:1 complex), very weak bleaching was observed between 400 nm and 450 nm and

absorption at 460 nm was also seen. For MO in 10 mM γ-CD (2:2 complex), strong absorption in the blue region, where bleaching should be observed, and a similar absorption to that of free MO at 540 nm were observed. This specific absorption in the blue region indicated a different energy structure for the transient state from that of free MO was formed in the 2:2 complex. With such a specific intermediate, the aggregation-like strong interaction between 2 MO molecules can be considered. It is known that a parallel-type aggregation associated with a blue-shifted absorption peak takes place for some AB derivatives.[29] It is worth noting that similar effects are observed in a polymer system that shows intrachain aggregation (polymeric dyes S-119).[5] In our MO/γ-CD systems, two MO monomers were included in parallel and show a remarkable blue shift in their photoexcited intermediate. Thus, we believe that enhanced interactions like aggregation between two MO molecules are induced in excited states and that this results in the formation of a long-lived intermediate species. It is reasonably considered that the aggregation-like interaction effectively hinders the conformational movement. Thus, the intermediate inhibited transformation to cis isomer and it relaxed slowly again to the ground trans isomer state. This model explains well our result that the UTL signals returned to 0 without showing any negative value, i.e., any cis isomer formation. Our results indicate that monomers that do not form dimer in free solution show such a specific intermolecular interaction and form an aggregate-like intermediate in such a confined geometry.

Conclusion

Isomerization of MO/CD inclusion complexes was measured by UTL and transient absorption spectroscopy. These ultrafast dynamics measurements on 1:1 complexes gave further insight into the relation between the spatial arrangement and photoisomerization dynamics and the dominant formation of MO/β-CD 1:1 complex even at high concentrations. It was found that the hindrance effect is significant when MO was encapsulated from both ends by two CD molecules. Elongation of the fast relaxation component and low isomerization yield were explained by MO−CD dipole interaction and spatial constraints induced by inclusion from both ends, respectively. It was clarified that the nanospace formed by two α-CD molecules was unfavorable for the formation of the intermediate of photoexcited MO. Inclusion in γ-CD, in which 2 MO molecules were included as a dimer, was also investigated. The isomerization dynamics was affected even when MO was included from only one end by the CD molecule. In particular, isomerization did not proceed, and the relaxation rate of the signal was significantly slower for γ-CD/MO 2:2 complex. A long-lived intermediate, which had a different energy structure from that of free MO monomer, was found for the 2:2 complex. The formation of the specific intermediate was explained in terms of an aggregation-like strong intermolecular interaction between MO molecules, which was induced by close parallel packing of 2 MOs in the γ-CD nanospace. Our results for 2MO/2γ-CD systems showed the possibility of γ-CD providing a nanospace as a new reaction field that is able to induce specific intermolecular interactions and reaction intermediates that are not observed in free solution.

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