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Femtosecond Spectroscopic Study on Photochromic Diarylethenes with Terthiophene

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Femtosecond Spectroscopic Study on Photochromic Diarylethenes with Terthiophene

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Photochromic ring-closure reactions of diarylethene derivatives with terthiophene (T3H, T3Me) have been examined by femtosecond transient absorption spectroscopy. The rate of the ring-closure reaction of T3H in n-hexane was estimated to be ~ 2.5 ps, which is very similar to that of T3Me in the same solvent. It was suggested that the ring-closure reaction proceeds through a concerted mechanism without any intermediates but not a two-step mechanism. The rate of ring-closure reaction was also dependent on the solvent polarity, suggesting that the charge transfer state in the excited singlet state plays an important role in the photochromic reaction.

Keywords: diarylethene; terthiophene; femtosecond transient absorption spectroscopy; Woodward-Hoffmann rule

INTRODUCTION

Diarylethene derivatives with thiophene oligomers have been proposed as a

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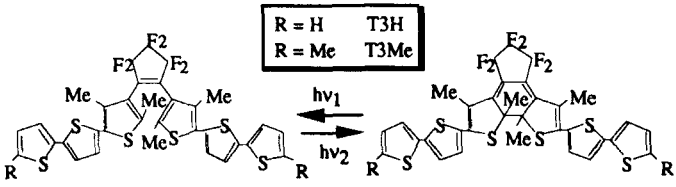
new class of multimode chemical transducers, in which the photochromic moiety acts as an optical switch unit [1,2]. The ring-closure reaction of diarylethenes belongs to the Woodward-Hoffmann type-pericyclic reaction and time-resolved studies have been done to analyze the dynamics of photochromic reaction [3,4], although a diradical species may be involved as an intermediate in two-step mechanism [3,5]. In the present study, the dynamics of photochromic reaction of diarylethene derivatives with terthiophene (T3H for terminal group of H and T3Me for Me, see scheme 1) in various solvents has been investigated by femtosecond transient absorption spectroscopy. The rate of the ring-closure reaction and the mechanism of photochromic reaction were discussed on the basis of these results.



SCHEME 1. Photochromic reaction of diarylethene derivatives with terthiophene.

EXPERIMENTAL

The samples were dissolved in spectroscopic grade solvents and allowed to flow through a 2-mm flow cell using a magnetic gyre pump. The reservoir solution was irradiated by a second harmonic (532 nm, ~ 200 mW) of a cw mode-locked Nd:YAG laser (Coherent Antares 76S) during the measurements to avoid the excitation of the photoproduct (closed form) and to recover the

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closed form to the open form. The second harmonic (~ 360 nm, 200 fs fwhm) of an amplified dye laser and a white-light continuum were used as an excitation pulse and probe and reference pulses, respectively. The details of the laser system were written in elsewhere [6]. The absorption signals were detected by a microcomputer-controlled ICCD detector at each optical delay. A temporal dispersion of the white-light continuum was corrected for the transient absorption spectra. The rise and decay curves were analyzed by a non-linear least-squares iterative convolution method.

RESULTS AND DISCUSSION

The absorption spectra of the open form of T3H and T3Me in n-hexane have a peak at ~ 350 nm, which is similar to that of terthiophene (3T). This result suggests that the interaction between two thiophene rings through central ethene moiety is very weak in both compounds. After the UV irradiation, T3H and T3Me show broad absorption spectra with a peak at ~ 640nm, corresponding to the characteristic absorption band of the closed form.

Figure 1 illustrates femtosecond transient absorption spectra of T3H in n-hexane. The spectrum just after the excitation has a peak at ~ 600 nm, and negative absorption at ~ 430 nm. A few ps later, the absorption spectrum in longer wavelength region becomes very broad and structureless. In addition, the negative absorption increases within a few ps and has a peak at ~ 420 nm. The transient absorption spectrum of T3H at later time region (3ns) is very different from that of the initial time region, in which the peak wavelengths are located at 470 nm, 560 nm, and 600 nm, respectively. The broad absorption spectrum with a peak at ~ 640 nm characteristic of the closed form of T3H is

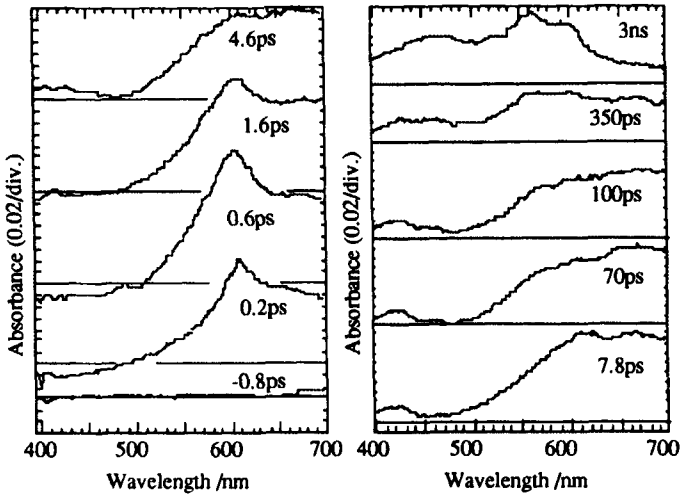

FIGURE 1. Femtosecond transient absorption spectra of T3H/Hexane.

very difficult to assign in the transient spectra up to 3 ns. This may indicate that the analysis of the rate of ring-closure reaction of T3H is difficult by the analysis of femtosecond transient absorption spectra based on the 640-nm absorption. To confirm the formation of the closed form, we have examined the transient absorption spectra in nanosecond to microsecond time scale using an oxygen-saturated solution to minimize the contribution of the triplet state absorption of T3H. The closed form with a peak at ~ 640 nm was clearly observed within a few hundreds of ns. However, the ring-closure reaction taking place with a rate constant of a few hundreds of ns is very difficult to consider, since the most of the ring-closure reaction of diarylethene derivatives are known to occur within a few tens of ps [2-4] and the quantum yield of the reaction of a diarylethene derivative having terthiophene is of the order of 0.1 [7]. We found that the difference absorption spectrum between the open and the closed forms of T3H has a peak at ~ 420 nm in addition to the

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absorption at ~ 640 nm, which can be used as an indicator of the ring-closure reaction. The absorption spectrum with a peak at ~ 420 nm observed at a few ps after the excitation is most probably due to the formation of closed form. The negative transient absorption just after the excitation at ~ 430 nm is considered to be stimulated emission from ^{1}T3H*.

The rise and decay dynamics of T3H in n-hexane observed at 425 nm was analyzed as illustrated in Figure 2. As shown in the Figure, a rise component corresponding to the formation of closed form was clearly observed. The rate of photochromic ring-closure reaction of T3H in n-hexane was found to be ~ 2.5 ps from the analysis of rise component. A similar rise and decay curve was observed at 425 nm for T3Me; the rate of the closed-form formation was estimated to be ~ 2.7 ps in n-hexane. In addition, the fast decay component with a decay constant of ~ 2.2 ps corresponding to the fast rise is observed at 610-nm absorption. The decay curve of T3Me at 610 nm was also analyzed and the fast decay constant was estimated to be ~ 2.7 ps in n-hexane, which is in good agreement with the rise component at 425 nm. Transient absorption spectrum of T3H just after the excitation with a peak at ~ 600 nm is safely assigned to the $S_n \leftarrow S_1$ absorption of the open form of T3H, because of the spectral similarity of ^{1}3T* in nonpolar solvents [8,9]. From these results, it is

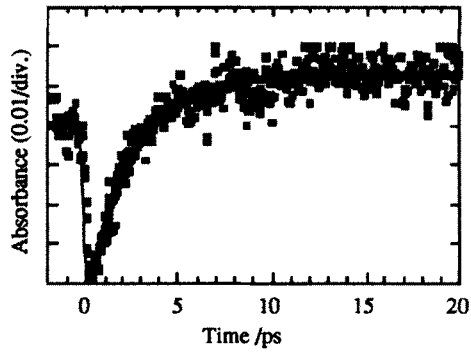

FIGURE 2. Rise and decay dynamics of T3H in n-hexane observed at 425 nm.

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suggested that the photochromic ring-closure reaction of diarylethene derivative with terthiophene proceed by a concerted one-step mechanism without any intermediate but not a two-step mechanism. The solvent polarity dependence was also examined both for T3H and T3Me. In polar solvent such as acetonitrile, the rate of ring-closure reaction was estimated to be 0.7 ps, which is three times faster than that in nonpolar n-hexane. This result suggests that the charge transfer state in the excited singlet state plays an important role in the photochromic reaction. Further analyses of transient absorption spectra and their temperature dependence will be published shortly.

Acknowledgments

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