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Photoinduced ultrafast ring-opening reaction in trithianes in solution

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ABSTRACT

The ring-opening reaction of trithianes possessing aromatic substituents has been studied using femtosecond broadband UV–Vis transient absorption spectroscopy. Photocleavage of the C—S bond occurs during the short-lived (1.5 ps) singlet excited state of trithiane. The products are formed with excess of vibrational energy and cooling of the hot molecules occurs with a 12.1 ps time constant in acetonitrile.

1. Introduction

Polyatomic molecules possessing relatively weak carbon–sulfur bonds may undergo a photoinduced cleavage process [1,2]. This process likely occurs in the singlet excited electronic states. To explore the early events after photoexcitation, we apply femtosecond UV–Vis broadband transient absorption technique in order to trace the species involved in the photocleavage process to characterize their spectral signature and kinetic behavior. For ultrafast studies we have chosen 1,3,5-trithianes, because their photocleavage mechanism has been recently investigated by stationary photochemistry and laser flash photolysis studies [3–7]. Photocleavage process leads to the formation of an intermediate ***I*** (resonance structure between biradical and zwitterion, see Scheme 1). Reactivity of ***I*** found in methanol confirm bipolar nature of ***I*** and also indicates a heterolytic nature of the cleavage process [4]. Its formation rate has been measured to be faster than 40 ns [4]. Ultrafast studies should clearly resolve the rise of ring-opening product ***I***.

Recently, ring-opening of thiophene at one of the C–S bonds has been studied theoretically to explain ultrafast decay of the photoexcited S_1 state [8]. The photoinduced ring-opening process is not only important from a fundamental point of view, but plays a crucial role in photochromic reactions [9,10] and vitamin D_3 formation [11]. Its mechanism and dynamics have been extensively studied by time-resolved spectroscopy and theoretical quantum chemical calculations [11–26]. Typically ring-opening occurs in solution on a picosecond time-scale, and the following time-constants have been reported: <0.3 ps (cyclohexadiene [12,13], dihydrophenanthrene [16]), 0.7 ps (spiro-oxazine [17]), 0.9 ps (indolinospiropyran [18]), 0.95 ps (7-dehydrocholesterol [11]), 2.1 ps (indolyl-fulgimide [19]), <2–3 ps (trimethyl-thienyl maleic anhydride [20]), 12 ps (cyclooctatriene [21]), 20–60 ps (diarylethene [22]), 150 ps (bithiophene linked 2H-chromene [23]) and 2.1–325 ps (dithienylethene derivatives [24,25]). This Letter clearly resolves dynamics of ring-opening product formation (1.5 ps) upon photoexcitation of trithiane and reveals its precursor – trithiane in the singlet excited state.

2. Experimental

The femtosecond transient absorption system has been described elsewhere [27]. α-TPT (α-2,4,6-triphenyl-1,3,5-trithiane) was synthesized and purified by the methods described elsewhere [28,29]. The excitation wavelength was set to 266 nm, corresponding to the low-energy edge of the α-TPT absorption band (Fig. 1). The molar absorption coefficient at 266 nm for α-TPT in acetonitrile is 1800 $dm^3 mol^{-1} cm^{-1}$. The sample concentration was adjusted to an absorbance of 0.55 in a 1 mm flow cell. The pump pulse energy was about 10 μJ at the sample (0.65 mJ/cm^2) and the estimated number of photons absorbed per molecule in the excitation volume is 3.4×10^{-3}. To avoid rotational-diffusion effects, the angle between polarizations of the pump beam and the probe beam was set to the magic angle (54.7°) [30]. Transient absorption spectra were corrected for chirp in the probe continuum [31]. Kinetic analysis was performed by global fitting selected probe wavelengths to a sum of three exponentials and a constant offset. Convolution with a Gaussian response function was included in the global fitting procedure. The instrument response was approximately 300 fs (FWHM). Acetonitrile was chosen as solvent to minimize contribution from photophysical side-effects (e.g., two-photon absorption). All experiments were performed at room temperature.

3. Results and discussion

Excitation of α-TPT with 266 nm radiation pumps the molecule to the S_1, S_5 or S_6 excited singlet states as indicated by time-dependent density functional theory (TD-DFT) calculations [32,33] in the gas phase which predict that α-TPT has three transitions with large oscillator strength in the vicinity of 266 nm: at 281 nm ($S_0 \rightarrow S_1$,

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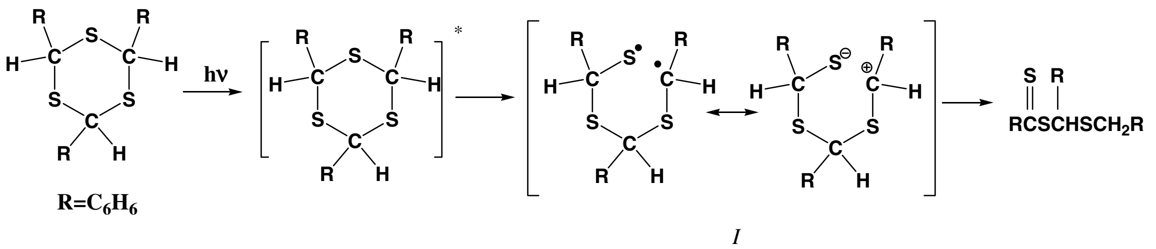


Scheme 1.

$f = 0.0263$), 267 nm ($S_0 \rightarrow S_5$, $f = 0.0232$) and 260.4 nm ($S_0 \rightarrow S_6$, $f = 0.0145$). Therefore, excitation at 266 nm may result in the population of a set of excited singlet states (see Fig. 1).

Ultrafast photolysis (266 nm) of α-TPT in acetonitrile produces the transient UV–Vis spectra of Fig. 2a. Initially, a broad transient absorption band is formed in the probe range 320–680 nm. At later times, within a 0.5–50 ps time window, the absorption bands near 350 and 650 nm decay, while a new band grows at 425 nm. At longer delay times, from 50 ps to 1 ns, no changes are observed in the transient absorption spectra. The band peaking at 425 nm can be assigned to the ring-opening product ***I***, which has been identified and observed by ns laser flash photolysis studies [3]. A 320 nm band is also observed at long delay times. Mostly this band corresponds to ***I*** (the same origin as the 425 nm band), but we can not exclude a contribution from the dithioester product, $C_6H_5C(=S)SCH(C_6H_5)SCH_2C_6H_5$.

Kinetic traces at selected probe wavelengths (350, 425, 500, 550 and 680 nm) are shown in Fig. 2b. Global fitting at representative wavelengths were performed and the resulting time-constants (0.5 ps, 1.5 ps and 12.1 ps) are given in Table 1.

The longest time constant (12.1 ps) can be attributed to vibrational cooling in the ring-opening product. Indeed, the time dependence of the band integral [34] lacks a 12.1 ps component (Fig. 3), reflecting the fact that this time constant does not correspond to population dynamics. Moreover, inspection of the amplitudes associated with the 12.1 ps component (Table 1) reveals the rise of the transient absorption signal in the band center (around 425 nm) and the decay in the blue (around 350 nm) and red (500–680 nm) wings. Thus, it reflects the narrowing of the transient absorption band due to vibrational cooling of the nascent ***I*** species [35–38]. Both the band narrowing and 12.3 ps time constant are consistent with other reports of vibrational cooling of polyatomic molecules in acetonitrile [39,40].

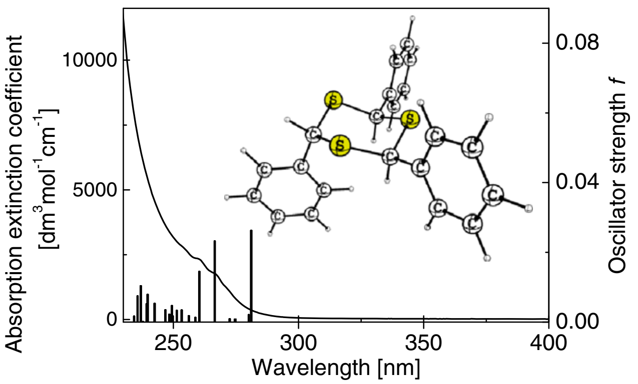


Fig. 1. Steady-state UV–Vis absorption spectrum of α-TPT in acetonitrile (solid line, left axis). The vertical bars indicate the positions and oscillator strength f of the electronic transitions calculated by TD-DFT at the B3LYP/6-111+G(d,p) level (right axis). The optimized structure of α-TPT at the B3LYP/6-31G(d) level of theory is shown in the inset.

The shorter time-constant (1.5 ps in Table 1) can be assigned to the decay of the S_1 population (pronounced in 500–680 nm probe range) and to the rise of the ring-opening product (around 425 nm). This S_1 state is formed with about 500 fs time constant (see the inset of Fig. 2b), consistent with initial excitation of higher excited singlet states ($S_n > 1$) in addition to S_1. In contrast to the 500–550 nm probe range, signal at 350 nm is formed instantaneously and decays with a 500 fs time constant, which may indicate the presence of S_n absorption. At 680 nm, almost instantaneous rise of the signal is also observed but 500 fs component is weak and has a negative amplitude. It can be rationalized if S_1 and S_n have very similar extinction absorption coefficients near 680 nm. Note that, analysis of the 500 fs time constant is only tentative, since it is close to instrument response function FWHM (300 fs).

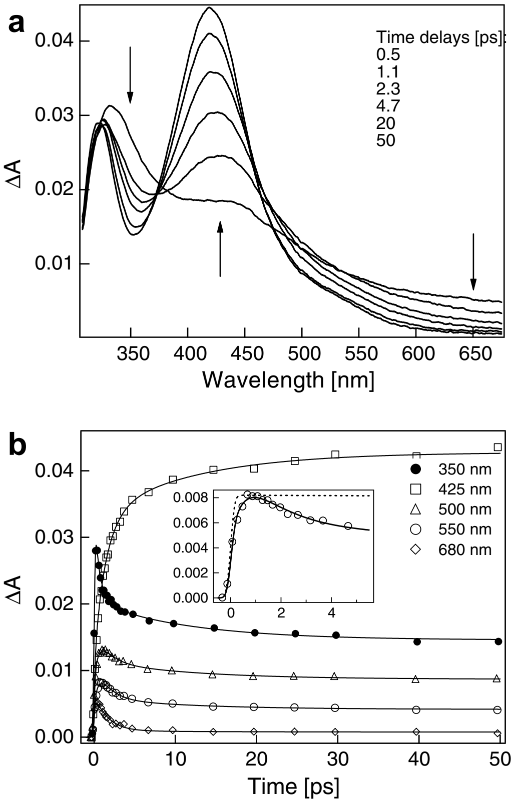


Fig. 2. (a) Transient absorption spectra recorded from 0.5 to 50 ps after photoexcitation of α-TPT in acetonitrile at 266 nm. (b) Time-dependence of the transient absorption signal at selected 350, 425, 500, 550 and 680 nm probe wavelengths with best fit curves (solid lines). The model function was $\Delta A = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) + A_4$, where A_i are amplitudes and τ_i are time constants (global parameters). The inset presents early times of signal at 550 nm probe wavelength (circles) which rises slower (500 fs), than instantaneously formed long-lived population convoluted the instrument response function (dashed line).

Table 1
Global fit parameters for the kinetics in Fig. 2b

λ (nm)	τ_1 (ps)	A_1	τ_2 (ps)	A_2	τ_3 (ps)	A_3	A_4
350	0.50 ± 0.20	0.012	1.5 ± 0.30	0.002	12.1 ± 3.0	0.006	0.015
425		−0.003		−0.020		−0.010	0.042
500		−0.009		0.006		0.002	0.009
550		−0.007		0.007		0.002	0.004
680		−0.001		0.006		0	0.001

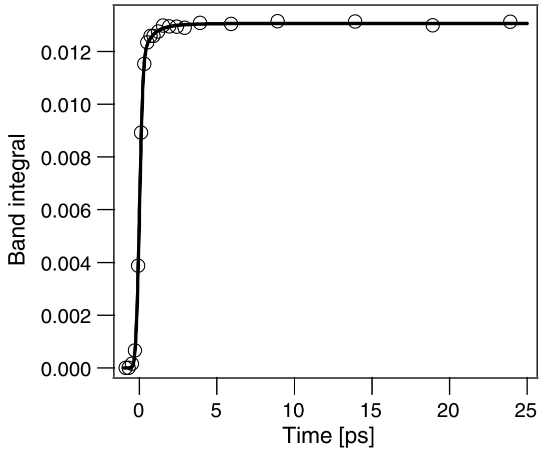
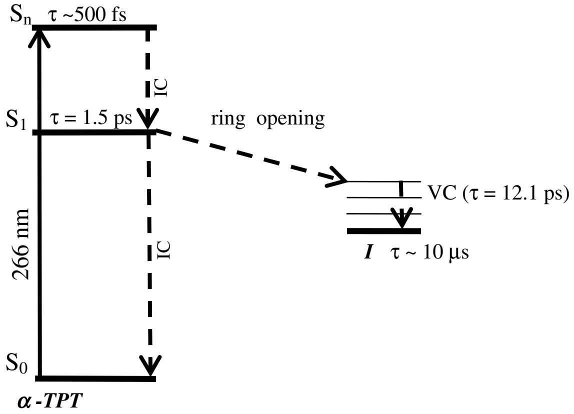


Fig. 3. Band integral (circles) calculated accordingly with formula proposed by Kovalenko et al. [34]. The solid line presents a two exponential function with set time constants (0.5 and 1.5 ps).



Scheme 2.

Involvement of the triplet state of α-TPT in the ring-opening process is unlikely as its presence would require extremely fast intersystem crossing (500 fs). Ultrafast changes in the molecular spin state occur rarely in organic compounds [41].

Time-resolved investigations of other ring-opening reactions [11–13,18,19] agree with our findings on α-TPT: bond cleavage occurs in the S$_1$ singlet excited state, the product is formed vibrationally hot and undergoes subsequent cooling by solvent molecules. For example, recent time-resolved IR studies of indolylfulgimide in acetonitrile revealed that its excited state lifetime is 4 ps, the E-isomer product in ring-opening process is born with excess vibrational energy and the cooling occurs on a 10–15 ps time scale [42].

Scheme 2 summarizes all photoinduced processes in α-TPT. The ring-opening product ***I*** is formed with a 1.5 ps time constant (λ_{max} = 425 nm). To the best of authors' knowledge, this Letter presents the first ultrafast study of ring-opening process caused by C–S bond cleavage.

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