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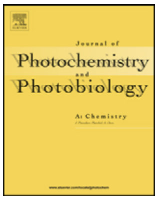

Photochemistry with thermal versus optical excess energy: Ultrafast cycloreversion of indolylfulgides and indolylfulgimides

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ABSTRACT

The dependence of the pericyclic ring-opening reaction of indolylfulgides and indolylfulgimides on excess energy is investigated by quantum efficiency measurements and by ultrafast spectroscopy. The ring-opening reaction shows a pronounced improvement of reaction efficiency up to a factor of 6, when excess energy is available either by increasing the temperature or by exciting the molecules above the 0–0-transition. Ultrafast spectroscopy allows to deduce time constants for the ring-opening reaction and leads to a theoretical model, where the redistribution of excess energy among different vibrational modes is considered. The analysis shows that excess energy supplied by optical excitation accelerates the ring-opening reaction less efficiently than thermal energy. Apparently vibrational relaxation from highly excited modes to modes promoting the ring-opening reaction is not completed within the ~10 ps duration of the ring-opening reaction.

1. Introduction

Fulgides and the associated fulgimides undergo light induced isomerisation, ring-closure and ring-opening reactions [1,2]. These reactions are related to the photochromism of these molecules, which is associated with the three photoisomers *C*, *E*, and *Z* (see Scheme 1) featuring different optical absorption spectra. It was shown in a number of previous investigations that physical properties, reaction quantum yields, and absorption characteristics of the isomers can be tailored by chemical substitution [3–9]. It was also reported that indolyl substituted fulgides/fulgimides may be thermally stable in the electronic ground state and that these molecules show a high resistance against photochemical fatigue [6,10]. This makes them interesting candidates for different applications as optical switches or memory elements [4–7,10–13]. The attachment of photochromic switches on surfaces explores a new class of materials with photoswitchable properties [14–20]. Photoswitches with thermally stable ground state isomers and different fluorescence properties are also excellent candidates for newly emerging microscopy techniques summarised by the acronym reversible saturable optical fluorescence transitions (RESOLFT) [21–24]. In the context of potential applications in photoswitching microscopy the fluorescence properties and switching capabilities (durability, quantum efficiency) of photochromic molecules are relevant [25]. The fluorescence dynamics of indolylfulgide photoisomers was investigated recently [26]. Indirect switching of attached molecular probes with high fluorescence yield was demonstrated [27].

In former studies we investigated in detail the ring-opening reaction of indolylfulgimides and -fulgides in different solvents with various ultrafast methods in the UV, VIS, and mid-IR [26,28–32]. A reaction scheme for the ring-opening reaction of the indolylfulgide and the indolylfulgimide is depicted in Fig. 1 [26,28]. After excitation from the electronic ground state (S_0) into the Franck-Condon (FC) region of the first electronically excited state (S_1), the system relaxes towards the minimum of the S_1 potential energy surface. From here the molecule converts back to the ground state S_0 after passing a barrier with an activation energy E_a. This internal conversion process may proceed via a conical intersection (CI) between ground and excited state and may reach the electronic ground state of either the ring-opened product *E* or the reactant *C*. Vibrational cooling of the hot molecules in the ground states (reactant and product) was found to occur on the 10 ps time scale [28,29]. It was shown that the ring-opening proceeds also directly from higher excited states with increased reaction yield [33]. This implies a violation of Kasha's rule [34] which was

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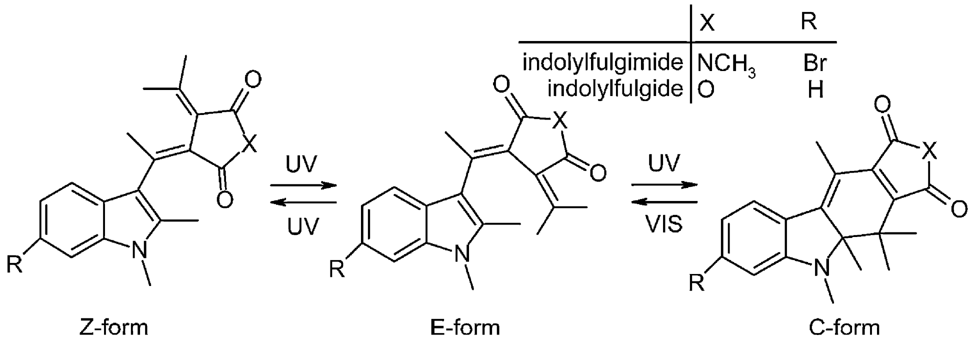

Scheme 1. The isomers (*Z*, *E*, and *C*) of the investigated indolylfulgide (R = H, X = O) and indolylfulgimide (R = Br, X = NCH_3). Arrows denote the possible photoreactions.

originally formulated for the fluorescence properties of molecules, but is extended meanwhile also to photoreactions [35]. Similarly the Kasha–Vavilov rule [36–38] states that the yield of fluorescence (photoreactions) is independent of the wavelength of exciting radiation [35].

The experimental observations show that typical times for cooling processes to the surrounding solvent are in the same temporal regime or even slower than the reaction time for ring-opening. Therefore, it can be assumed that the ring-opening in the electronically excited state may occur prior to thermal equilibration with the solvent. As a consequence optical excess energy in the electronically excited S_1 state, brought in by exciting the molecules far above the 0–0-transition, is not dumped to the surroundings before the photoreaction occurs. The related non-equilibrium may influence the reaction yield and dynamics of the ring-opening reaction, i.e. the ring-opening reaction may depend on the excitation wavelength and may violate the Kasha–Vavilov rule [36–38]. Reports in the literature on such a behaviour are rare [39–44].

In this study we present results from steady-state and femtosecond time-resolved absorption spectroscopy of the ring-opening reaction of an indolyl substituted fulgimide and fulgide in the visible spectral range. The quantum yield η of the ring-opening reaction is investigated as a function of temperature and optical excess energy in two different solvents. Time-resolved absorption experiments provide supplementary information on the reaction dynamics. A model is developed to account for the redistribution of optical excess energy and to describe the dependence of the ring-opening reaction on the excess energy.

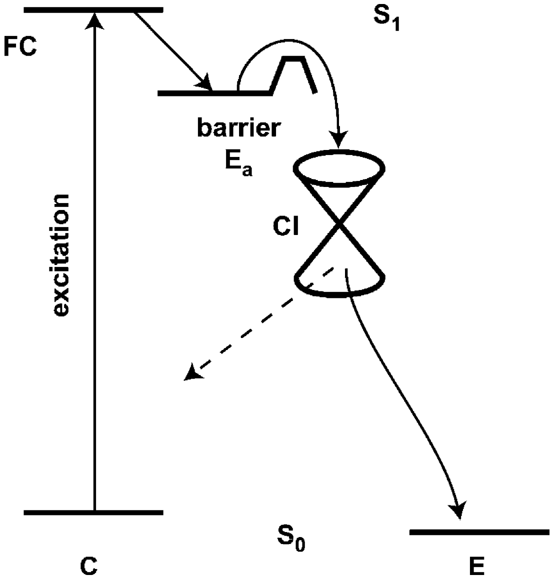

Fig. 1. Scheme of the ring-opening reaction of the indolylfulgimide and the indolylfulgide. After excitation from the electronic ground state S_0 of the *C*-form the molecule reaches the Franck-Condon (FC) region of the excited state S_1, which has low radiative coupling to the electronic ground state. Then it relaxes towards the minimum of the S_1 potential energy surface. From here the molecule converts back to the ground state S_0 over a barrier with an activation energy E_a by internal conversion (e.g. via a conical intersection CI).

2. Materials and methods

2.1. Sample preparation

The ring-opening reaction of two different optical switches is investigated (molecular structures see Scheme 1): an indolylfulgide (R = H; X = O) and the associated indolylfulgimide (R = Br; X = NCH_3). Via a substitution of the bromide at position R and the NCH_3 group at position X the indolylfulgimide can be covalently incorporated into complex switching systems. The synthesis of these molecular switches is published in Ref. [45]. For the experiments in the visible spectral range the molecules were dissolved either in toluene (Uvasol) purchased from Merck KGaA or acetonitrile from Sigma–Aldrich Chemie GmbH used without further purification. The solvents represent surroundings with strongly different dielectric constants (toluene: $\varepsilon = 2.379$ and acetonitrile: $\varepsilon = 35.94$). The *C*-isomers of both indolylfulgide/imide were photochemically prepared by steady-state illumination at 365 nm (10 mW) with a Hg(Xe) lamp (Hamamatsu, 8251) and an optical filter UG1 (Schott) until the photostationary state (PSS-365) was reached with a constant fraction of isomers in the *C*-, *E*-, and *Z*-form. All presented experiments were performed on samples in PSS-365. The PSS-550, containing a high concentration of the molecules in the *E*-form is obtained by visible illumination (Schott, KLC 2500 with optical filter OG550) of a PSS-365 sample, where all *C*-form molecules are converted to the *E*-form.

In the visible only the closed *C*-isomers of the indolyl substituted fulgimide and fulgide (see Scheme 1 and Fig. 2) show characteristic absorption bands at around 550 nm, while the *E*- and *Z*-isomers do not absorb here. As a consequence, photoexcitation of an isomeric mixture by light in the visible spectral range addresses the ring-opening reaction $C \rightarrow E$ exclusively. Therefore the *Z*-form content remains unchanged.

2.2. Stationary spectroscopy

Absorption spectra in the visible spectral range were measured using a spectrophotometer (PerkinElmer, Lambda19). For the measurements of the quantum efficiency of the ring-opening, the $C \rightarrow E$ reaction was initiated by illumination either at a fixed wavelength by a cw Nd:YAG laser at 532 nm (1 mW, LCM-T-11, Laser-compact Plus) or spectrally tunable by a system of XBO arc lamp and monochromator. For determination of the reaction yield η as a function of excitation wavelength the power of the excitation light