Kinetic study of the photodecoloration mechanism of an inversely photochromic class of compounds forming spiropyran analogues[†]

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Abstract

The quantum yields and kinetics of the photodecoloration of five representatives of an inversely photochromic class of compounds, reacting to give spiro compounds related to the indolinospiropyrans by replacement of the chromene part of the molecule by an imidazodihydroquinoline fragment, were investigated by stationary illumination and nanosecond time-resolved laser flash spectroscopy. In particular, the role of the ground state of the open-chain *cis* conformer as an intermediate in spiro-bond formation (photodecoloration) and opening (thermocoloration) was quantitatively assessed.

1. Introduction

Photochromic compounds and their molecular transformations have attracted the interest of photochemists for many years [1–3] and are the subject of a recent comprehensive monograph [4]. The interest in these compounds is strongly focused on their intriguing potential as materials for optical data storage and processing, but the mechanisms of their transformations also continue to provide interesting problems for basic scientific research.

One class of photochromic compounds which has figured most prominently in this field is the so-called spiropyrans (*cf.* ref. 5) with their prototype compound 1,3,3-trimethylindolinospirobenzopyran (SP) (Scheme 1).

Here the spiropyran SP is a colourless compound which is photochemically transformed by UV absorption into an intensely coloured open-chain merocyanine chromophore M. The reaction is thermoreversible, but the rate of thermal decoloration (M → SP) may vary greatly, depending on the particular derivative [5, 6]. While the merocyanine form is most stable in the extended *trans* conformation, photochemical opening of the spiro bond or thermal ring closure will necessarily involve the passing of the system through a *cisoid* conformation denoted as X in Scheme 1. The identification of this conformer has attracted the interest of research workers [2, 7]. There is now ample evidence for its detectability [8–11] in highly viscous media at low temperature.

[†]Dedicated to Professor Schaffner on the occasion of his 60th birthday.

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Scheme 1.

Scheme 2.

Several years ago a variation of the spiropyran structure was developed by the research group of one of us (H. B.) at Basel [12, 13]. This variation was devised to yield inversely photochromic compounds, *i.e.* structures that are reversibly photobleached and undergo thermal coloration. The principle of these compounds is shown in Scheme 2.

The chromene chromophore of the spiropyran is replaced by a dihydroquinoline unit with its spiro-C-bound nitrogen atom further incorporated into another anellated imidazole ring. Thus, by protonation of the spiro form S, the imidazole-N-spiro-C bond becomes labile and a proton-induced thermal coloration occurs due to the formation of the open-chain conjugated chromophore TH⁺. Photochemically, a reversible decoloration of TH⁺ is observed whereby the form SH⁺ is regenerated. It has been suggested [12, 13] that thermocoloration of SH⁺ and photodecoloration of TH⁺ both involve the ground state of the open-chain *cis* isomer CH⁺. So far, however, no quantitative evidence has been provided.

In this paper, we present a detailed study by stationary and time-resolved kinetic measurements of the role of the open-chain *cis* conformer in thermocoloration and photodecoloration of some compounds of type S.

2. Experimental details

2.1. Materials

The inversely photochromic compounds were synthesized at the Institut für Farbenchemie, Basel, by A. Keller (1 and 2 [14]) and R. Konstanzer (3–5 [15]). Compound 1 was available as a monovalent salt 1Tet⁺BF₄[−], 3 and 4 as divalent salts TH₂²⁺(ClO₄[−])₂ and 2 and 5 as neutral spiro compounds.

The solvent used was methanol (Merck, p.A.). For acidification, suitable amounts of 5 n aqueous HCl (Riedel de Haen, Fixanal) were added.

2.2. Instrumentation

Absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV-visible spectrophotometer. For continuous irradiation experiments, a mercury high pressure light source (Osram HBO 200 W/2), combined with a 436 nm interference filter, was used. The solutions were irradiated in 1 cm fluorescence cuvettes, equipped with magnetic stirring and surrounded by a temperature-controlled support. For actinometry, the azobenzene *cis-trans* photoisomerization reaction was applied following the method of Gauglitz and Hubig [16].

The equipment used for laser flash photolysis is described in detail in refs. 17 and 18. The photolysing laser source was an excimer-laser-pumped dye laser of about 20 ns pulse width and 4–6 mJ pulse energy operated with the laser dyes Lambdachrome 4200 Stilben 3 (410–480 nm) or Lambdachrome 5000 Coumarin 307 (480–550 nm). Transient absorption was measured using a pulsed probe light from a high pressure xenon lamp (Osram XBO 150) and recorded on a Tektronix 7912 AD digitizer. For measuring temperature-dependent kinetics, the sample cuvette was housed in a temperature-controllable optical cryostat (Oxford LN₂) allowing for heating and cooling to adjust temperatures between liquid nitrogen temperature and 230 °C. In the present study, a temperature range of between –25 and 50 °C was used for determining the activation parameters of the ring-closure reaction.

3. Results and discussion

The following compounds with their spiro forms, denoted as 1SEt⁺, 2S, 3S, 4S and 5S, were investigated.

While 2S represents the basic structure, the effect of chemical variation in the indolino or dihydroquinoline part can be studied using compounds 3S–5S. As mentioned in Section 1, thermal ring opening (coloration) requires protonation at the exposed

Scheme 3.

imidazole nitrogen atom. In acidified solutions, the overall system of reactions to be considered is as represented in Scheme 3, which also shows the notation of the various rate and equilibrium constants. It can be seen that acidity of environment after thermal ring opening of SH^+ leading, via the potentially detectable open-chain conformer CH^+ , to the thermodynamically stable TH^+ , a second stage of protonation affording the species CH_2^{2+} and TH_2^{2+} eventually has to be taken into account. Since, in principle, this may cause some complications in the kinetic analysis if $\text{p}K_a^S$, $\text{p}K_a^C$ and $\text{p}K_a^T$ are not clearly separated, we found it convenient to start our investigation with the ethylated cation 1SEt^+ , where it is not necessary to work in acidified solutions and no protolytic complications are expected.

3.1. Stationary experiments with 1SEt^+ and 1Tet^+

As noted by Keller [14], solutions of the coloured salt $1\text{Tet}^+\text{BF}_4^-$ undergo efficient photobleaching whereby the spiro form 1SEt^+ is formed. We measured this reaction quantitatively using irradiation with the mercury line at 436 nm. A representation of the spectral change during this photoreaction is shown in Fig. 1. The long-wavelength absorption of Tet^+ disappears almost completely, while the typical absorption band of the spiro form SEt^+ with a maximum at about 280 nm is developed. The chemical change must correspond to a uniform reaction as follows from the perfectly linear E/E diagram (see Fig. 1(b)). The uniformity of the reaction does not necessarily mean that only two chemical species (Tet^+ and SEt^+) are present; a certain stationary concentration of CEt^+ may be present but in a fast equilibrium with SEt^+ . After the end of the reaction, a weak absorbance tail remains in the region around 400 nm which cannot be due to SEt^+ but may be attributed to some small equilibrium concentration of CEt^+ . For a quantitative determination of the quantum yield $\phi(\text{Tet}^+ \rightarrow \text{SEt}^+)$, the weak CEt^+ absorption at 436 nm can be neglected and the photokinetic curve may be analysed according to the relation [19] (see Fig. 2)

$$\log \frac{10^{E'} - 1}{10^{E'(0)} - 1} = \phi(\text{Tet}^+ \rightarrow \text{SEt}^+) \epsilon_{\text{Tet}^+} I_0 \, dt \quad (1)$$

where E' is the absorbance at 436 nm, and the meaning of the other quantities is obvious. The quantum yield obtained is $\phi(\text{Tet}^+ \rightarrow \text{SEt}^+) = 0.54 \pm 0.05$. If it is assumed that the photochemical step proper is a trans-cis photoisomerization, the effective value of $\phi(\text{Tet}^+ \rightarrow \text{SEt}^+)$ corresponds to

$$\phi(\text{Tet}^+ \rightarrow \text{SEt}^+) = \phi_{tc} \frac{k_{cs}}{k_{cs} + k_{ct}} \quad (2)$$

Fig. 1. (a) Absorption spectra recorded during irradiation at 436 nm of 1TEt^+ ($c = 2.75 \times 10^{-5}$ M) in methanol. (b) Demonstration of linear correlation of absorbance changes ΔE at two wavelengths.

Fig. 2. Plot for determination of photobleaching quantum yield of 1TEt^+ according to eqn. (1) (photon irradiance at 436 nm, $I_0 = 1.84 \times 10^{-9}$ einsteins $\text{s}^{-1} \text{cm}^{-2}$; extinction coefficient of 1TEt^+ at 436 nm, $31\,100 \text{ M}^{-1} \text{cm}^{-1}$).

The value found for $\phi(\text{TEt}^+ \rightarrow \text{SEt}^+)$ is of an order of magnitude typical for photochemical trans-cis isomerizations (e.g. stilbene, 0.50 [20]; 4-styrylpyridinium cation, 0.53 [21]) and may directly correspond to the quantum yield ϕ_{ic} . In this case, $k_{\text{cs}} \gg k_{\text{ci}}$, which is demonstrated below.

In the dark, the spiro form 1SEt^+ reverts to the open form 1TEt^+ with a rate constant of 0.03 h^{-1} (room temperature; solvent, methanol). In terms of the involvement of the open form 1CEt^+ , this rate constant may be expressed as

$$k(\text{SEt}^+ \longrightarrow \text{TEt}^+) = k_{\text{ct}}k_{\text{sc}}/k_{\text{cs}} = 3.5 \times 10^{-4} \text{ s}^{-1} \quad (3)$$

From the extinction coefficient of 1CEt^+ determined below and the weak long-wavelength absorbance in equilibrium with 1SEt^+ , the equilibrium constant may be estimated as

$$K_{\text{c/s}} = k_{\text{sc}}/k_{\text{cs}} \approx 0.07 \quad (4)$$

leading to $k_{\text{ct}} \approx 5 \times 10^{-3} \text{ s}^{-1}$.

In order to confirm the reaction scheme (see Scheme 3), it is instructive to investigate the behaviour of the dicationic forms TEtH^{2+} and CEtH^{2+} . The $\text{p}K_{\text{a}}$ value of the reaction

is 2.6. During irradiation of solutions of 1TEtH^{2+} (see Fig. 3), a uniform photoconversion takes place, yielding a spectrum which clearly indicates the conservation of the fully conjugated π system. Obviously, the photoreaction ends with the dicationic conformer 1CEtH^{2+} [14]. The spectral change, blue shift and decrease in the intensity of the long-wavelength absorption band, is similar to that observed with stilbene and hence consistent with this interpretation. The quantum yield of this photoreaction for an irradiation wavelength of 436 nm is $\phi'_{\text{ic}} = 0.57 \pm 0.05$. This is similar to the value of ϕ_{ic} for the monocation 1TEt^+ .

Whereas the spiropyran 1SEt^+ is not formed from 1CEtH^{2+} , it is possible to study the thermal formation of 1CEtH^{2+} when starting with 1SEt^+ in acidified solutions (see Fig. 4). For the overall process

a value of 1.1 is found for $\text{p}K_{\text{tot}}$, defined as

$$\text{p}K_{\text{tot}} = -\log \frac{[\text{SEt}^+][\text{H}^+]}{[\text{CEtH}^{2+}]} \quad (7)$$

Fig. 3. Absorption spectra recorded during irradiation at 436 nm of 1TEtH^{2+} ($c = 2.75 \times 10^{-5} \text{ M}$) in methanol.

Fig. 4. Spectral absorbance change due to a shift in the equilibrium $1\text{SEt}^+ - 1\text{CEtH}^{2+}$ with pH and determination of pK_a in methanol. The dye concentration was 2.75×10^{-5} M.

The form 1CEtH^{2+} thus produced, transforms to 1TETeH^{2+} only very slowly with a rate constant of $k'_{ct} = 3.4 \times 10^{-4} \text{ s}^{-1}$. As in the photochemical case ($\phi_{tc} \approx \phi'_{tc}$), this result is again very similar to that for the monocationic form (i.e. $k_{ct} \approx k'_{ct}$).

Using pK_{tot} we can write for pK_a^C

$$pK_a^C = pK_{\text{tot}} + \log(k_{cs}/k_{sc}) \quad (8)$$

which yields $pK_a^C = 2.15$, indicating that 1CEtH^{2+} is only slightly more acidic than 1TETeH^{2+} . This is a reasonable result.

3.2. Laser flash spectroscopic investigation of the photodecoloration step

The reaction sequence

can be kinetically resolved in detail when photoexciting TETe^+ with a short (approximately 20 ns) laser pulse. The transient absorption signals observed at some characteristic wavelengths are shown in Fig. 5. At $\lambda > 470$ nm, the signal consists of a single bleaching step ($\text{TETe}^+ \rightarrow \text{CEt}^+$) which is completed by the time the laser pulse is over. In the region $380 > \lambda > 470$ nm, the bleaching occurs in two steps, the first ending with the laser pulse and the second ($\text{CEt}^+ \rightarrow \text{SEt}^+$) clearly continuing after the laser pulse. For this second step which obeys monoexponential kinetics, a rate constant of $1.9 \times 10^7 \text{ s}^{-1}$ is evaluated. At $\lambda = 355$ nm, the fast step is not observed. Obviously this wavelength corresponds to an isosbestic point between TETe^+ and CEt^+ . In the region $320 > \lambda > 350$ nm, the initial fast process corresponds to a transient increase in absorbance ($\epsilon_{\text{CEt}^+} > \epsilon_{\text{TETe}^+}$). At 315 nm, the second, slower step is not apparent in the transient signal because here we have the isosbestic point between CEt^+ and SEt^+ . Finally, at $\lambda < 310$ nm, both absorption changes are positive. In this region $\epsilon_{\text{TETe}^+} < \epsilon_{\text{CEt}^+} < \epsilon_{\text{SEt}^+}$.

The transient signals observed are fully consistent with the sequence of eqn. (9). No transient absorption of an electronically excited intermediate is detected. This

Fig. 5. Transient absorption signals observed on laser flash excitation at 428 nm of 1TET^+ ($c = 4 \times 10^{-5} \text{ M}$) in methanol. The time profile of the laser pulse, observed by stray light detection (arbitrary units), is also shown.

interpretation is corroborated by the observation that oxygen has no effect on the observed transient kinetics. The long-time absorption changes induced by laser flash excitation are identical with those observed in steady illumination experiments (see Fig. 6). This observation provides an excellent basis for an absolute scaling of the absorption changes during the course of the laser-induced kinetics.

Due to the finite duration of the laser pulse (see Fig. 5) and the short conversion time of $\text{CET}^+ \rightarrow \text{SET}^+$, the transient absorption cannot be simply converted to the difference $\epsilon_{\text{TET}^+} - \epsilon_{\text{CET}^+}$ because the complete turnover may not be attained before the end of the laser pulse and/or because CET^+ may already be partially converted into SET^+ . A convolution procedure must be applied to determine the changes in the extinction coefficients $\Delta\epsilon_{\text{C/T}} = (\epsilon_{\text{CET}^+} - \epsilon_{\text{TET}^+})$ and $\Delta\epsilon_{\text{S/C}} = (\epsilon_{\text{SET}^+} - \epsilon_{\text{CET}^+})$ for any wavelength of observation. This procedure is based on the following expression for the actual time dependence of the transient absorption change ΔA

$$\Delta A(t) = \phi_{\text{ic}} \int_0^t I_{\text{abs}}(t') [\Delta\epsilon_{\text{C/T}} \exp\{-k_{\text{cs}}(t-t')\} + \Delta\epsilon_{\text{S/C}}(1 - \exp\{-k_{\text{cs}}(t-t')\})] dt'$$

Fig. 6. Comparison of the photochemical absorption changes obtained for 1Tet⁺ by continuous irradiation (full line) and laser photolysis (points). The laser results, corresponding to transient absorption changes recorded at 300 ns after the laser pulse, are normalized to fit the continuous illumination results at 400 nm.

$$= \phi_{tc} \int_0^t I_{abs}(t') \Delta\epsilon_{S/C} dt' + \phi_{tc} \int_0^t I_{abs}(t') (\Delta\epsilon_{C/T} - \Delta\epsilon_{S/T}) \exp\{-k_{cs}(t-t')\} dt' \quad (10)$$

Here $I_{abs}(t)$ is the photon concentration (number of einsteins per volume) absorbed by TET⁺ in the laser path through the cuvette. At times $t \gg k_{cs}^{-1}$ this expression simplifies to

$$\Delta A(\infty) = \phi_{tc} \Delta\epsilon_{S/C} \int_0^{\infty} I_{abs}(t') dt' \quad (11)$$

The concentration of photons absorbed may be related to the relative intensity $L(t)$ of the laser light, measured as a stray light signal (see Fig. 5)

$$I_{abs}(t) = \frac{N_I L(t)}{\int_0^{\infty} L(t') dt'} \frac{10^{E'(\infty)} - 1}{10^{E'(0)} - 1} = N_I I'_{abs}(t) \quad (12)$$

Here N_I is a normalization constant and $E'(0)$ and $E'(\infty)$ are the optical densities at the laser wavelength before and after the laser flash respectively. The latter expression takes into account the decreasing absorbance of the educt due to its bleaching during the laser pulse. Equation (12) is strictly valid only if the laser light is exclusively absorbed by the educt which, under the conditions of our experiments, holds true to a good approximation.

Comparing $\Delta A(\infty)$ with $\int_0^{\infty} I'_{abs}(t') dt'$ we obtain $N_I \phi_{tc} \Delta\epsilon_{S/C}$ from eqn. (11). The quantity $N_I \phi_{tc} \Delta\epsilon_{C/T}$ is obtained by fitting the numerically calculated integral (eqn. (10)) to the observed $\Delta A(t)$. Thus the ratio $\Delta\epsilon_{C/T}/\Delta\epsilon_{S/C}$ can be fixed. The absolute values

are obtained by the equation

$$\Delta\epsilon_{C/T} + \Delta\epsilon_{S/C} = \epsilon_{SEt^+} - \epsilon_{TEt^+} \quad (13)$$

The difference between the extinction coefficients $\epsilon_{SEt^+} - \epsilon_{TEt^+}$ is easily obtained from the continuous illumination experiments since TEt^+ and SEt^+ have non-overlapping spectral regions of absorption.

The complete spectrum thus evaluated for the intermediate species CEt^+ is shown in Fig. 7 together with those of TEt^+ and SEt^+ . As can be seen, the spectra of CEt^+ and TEt^+ are related to each other in a similar manner to those of $CEtH^{2+}$ and $TEtH^{2+}$. A hypsochromic shift of about 40 nm occurs for both CEt^+ and TEt^+ when the dications are formed.

As has been mentioned, the kinetics of the process $CEt^+ \rightarrow SEt^+$ are exhibited uniformly throughout the spectrum. They were measured as a function of temperature and the activation parameters were obtained. These are collected in Table 1 and are compared with those of the other compounds.

Fig. 7. Spectrum of intermediate $1CEt^+$, determined from the laser photolysis experiments, compared with those of $1TEt^+$ and $1SEt^+$.

TABLE 1.

Characteristic protolytic, photochemical and kinetic parameters of the inversely photochromic compounds investigated in methanol

Parameter	$1TEt^+$	$2TH^+$	$3TH^+$	$4TH^+$	$5TH^+$
$pK_a (TH_2^{2+})$	2.6	2.9	3.1	3.2	1.3
ϕ_{ct}	0.54	0.55	0.52	0.45	0.56
$k_{cs} (s^{-1}) (300 K)$	2.2×10^7	1.8×10^7	1.1×10^7	1.2×10^6	8.0×10^6
$E_a (kJ mol^{-1})$	28.5	30.2	32.3	37.7	30.2
$A (s^{-1})$	2.1×10^{12}	3.3×10^{12}	4.0×10^{12}	4.0×10^{12}	1.3×10^{12}

3.3. Investigation of spiro compounds 2S to 5S

With the results for compound 1SEt^+ as a reference, clearly interpretable kinetic results can also be obtained with the protonated compounds $2\text{--}5\text{SH}^+$. Thus for 2S the protolytic equilibrium

has a $\text{p}K_a^S$ value of 4.5 (see Fig. 8). The weak long-wavelength absorption indicates that here, as in the case of 1SEt^+ , some small fraction of 2CH^+ exists in equilibrium with 2SH^+ . On increasing the proton concentration, the equilibrium

is shifted (see Fig. 9) with an effective $\text{p}K_a(2\text{CH}_2^{2+} \rightarrow 2\text{SH}^+ + \text{H}^+)$ value of 1.2 (compare with 1.1 for 1SEtH^{2+}). At room temperature, thermal conversion of 2CH_2^{2+} to 2TH_2^{2+} occurs with a rate constant k'_{ct} of $3 \times 10^{-4} \text{ s}^{-1}$ (compare with $3.4 \times 10^{-4} \text{ s}^{-1}$ for 1CEtH^{2+}), whereas for 2SH^+ the rate constant of thermocoloration is $7 \times 10^{-6} \text{ s}^{-1}$ (compare with $8.3 \times 10^{-6} \text{ s}^{-1}$ for 1SEt^+).

Fig. 8. Spectral absorbance change due to a shift in the equilibrium $2\text{S} \rightleftharpoons 2\text{SH}^+$ with pH and determination of $\text{p}K_a$ in methanol. The sample concentration was $1.7 \times 10^{-5} \text{ M}$.

Fig. 9. Spectral absorbance change due to a shift in the equilibrium $2\text{SH}^+ \rightleftharpoons 2\text{CH}_2^{2+}$ and determination of $\text{p}K_a$ in methanol. The sample concentration was $1.5 \times 10^{-5} \text{ M}$.

Stationary illumination of 2TH^+ gives a quantum yield of photodecoloration of 0.55 (compare with 0.54 for 1TEt^+). Furthermore the results obtained by laser flash spectroscopy are also very similar to those of 1TEt^+ .

Characteristic data pertaining to the photochemical decoloration of the $n\text{TH}^+$ forms and the thermal ring closure (k_{cs}) are listed in Table 1. The spectra obtained for the intermediate forms 3CH^+ and 4CH^+ are presented in Figs. 10 and 11.

From the data in Table 1, it can be seen that the five compounds behave very similarly. The introduction of substituents in the indolino and imidazodihydroquinoline parts of the molecule causes only moderate changes in $\text{p}K_{\text{a}}$ values, quantum yields and rate constants. At room temperature, the rate constants of ring closure of the *cis* conformers are of the order of 10^7 s^{-1} which, to our knowledge, represents the

Fig. 10. Spectrum of intermediate 3CH^+ , determined from the laser photolysis experiments, compared with those of 3TH^+ and 3SH^+ .

Fig. 11. Spectrum of intermediate 4CH^+ , determined from the laser photolysis experiments, compared with those of 4TH^+ and 4SH^+ .

fastest thermal electrocyclic formation of a six-membered ring observed so far. For example, thermal cyclizations of the merocyanines forming indolinospiropyran occur with rate constants in the range 10^{-5} – 10^3 s $^{-1}$ [6]. The essential difference from the present cases is that in our compounds, the activation barrier of isomerization between the cis form and the thermodynamically more stable trans conformer of the open-chain conjugated system is higher than for the merocyanines. Hence, after the photoinduced conformational change $\text{TH}^+ \rightarrow \text{CH}^+$, the system is trapped in a conformation which is sterically favourable for the ring-closure step. Its rate constant (k_{cs}) is directly measured in our experiment. The conformational change associated with the activation step of ring closure in our experiments cannot be drastic since the "normal" frequency factors are several orders of magnitude higher than expected for six-ring formation from a conformationally unrestricted open chain. In the thermal decoloration of merocyanines leading to the spiropyran, the trans conformer dominates, and the effective rate constant measured for decoloration typically corresponds to the ring-closure rate constant of the cis conformer multiplied by the equilibrium fraction of cis conformers.

Although, after the photochemical trans–cis isomerization of our open-chain chromophore the olefinic double bond is in the appropriate configuration for successive ring closure, there may still be other internal rotations involved before spiro-bond formation can take place. A detailed study of the viscosity and temperature dependence of the (photoinduced) thermal ring-closure kinetics of 1Tet^+ [22], has revealed that the fast rate process (10^7 s $^{-1}$) observed after photochemical trans–cis isomerization of 1Tet^+ is mainly due to a rotational rearrangement (see Fig. 12). The ring closure proper, *i.e.* from the conformational minimum of CEt^+ which is closest to the SEt^+ configuration, occurs with a rate constant of 6×10^7 s $^{-1}$ at room temperature [22]. The rate constants reported in Table 1 are characteristic of the low viscosity limit

Fig. 12. At low viscosities, rotamers C_A and C_B are in fast equilibrium after photochemical isomerization of the trans isomer. Due to a preponderance of rotamer C_A , the effective rate constant k_{cs} for the process $\text{C} \rightarrow \text{S}$ is significantly smaller than the rate constant of the ring-closure step $\text{C}_\text{B} \rightarrow \text{S}$.

and correspond to the product of an equilibrium constant between cis rotamers C_A and C_B and the "proper" ring closure rate constant $k(C_B \rightarrow S)$.

4. Conclusions

We have spectroscopically identified the short-lived (ground state) cis conformers CH^+ as distinct intermediates in the photodecoloration of the inversely photochromic forms TH^+ of compounds 1–5. Thus the photochemical step in this photodecoloration corresponds to a trans–cis isomerization and is followed by a thermal ring-closure reaction. The latter process occurs with a rate constant of typically 10^7 s^{-1} at room temperature and with an activation energy of the order of 30 kJ mol^{-1} ; the thermal reversion of CH^+ to TH^+ is more than ten orders of magnitude slower than the ring-closure reaction. The ring opening $SH^+ \rightarrow CH^+$ is only 50–100 times slower than ring closure, meaning that the thermodynamic bias between SH^+ and CH^+ is at an optimum with respect to the maximization of the rate of thermal ring opening and the equilibrium ratio of SH^+ to CH^+ .

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