

THIONINE TRIPLET RELAXATION IN PYRIDINE: A COMPLETELY TIME-RESOLVED FÖRSTER CYCLE[†]

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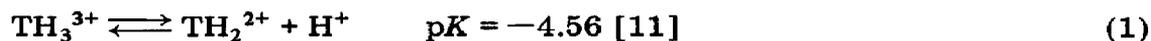
Summary

The deactivation pathway of the thionine triplet (³TH⁺) in pyridine was investigated using microsecond laser flash spectroscopy. It was found that the electronic relaxation of the triplet ³TH⁺ occurs via protolytic dissociation to the triplet ³T which, after radiationless decay to the ground state T, is reprotonated to TH⁺. The unique feature of this deactivation pathway is that it represents a Förster cycle where all steps can be conveniently followed by flash spectroscopy in the microsecond time regime. The energy of the triplet state ³T was estimated to be 150 ± 6 kJ mol⁻¹.

1. Introduction

Thionine, which is the fundamental representative of the class of phenothiazine dyes, has served as a convenient model compound in many studies of photoredox reactions with excited triplet states [1 - 10]. It has been recognized that, as in the ground state, a number of protolytic forms must exist in the excited triplet state.

The following equilibria have been established in the ground state (the pK values refer to aqueous solutions):

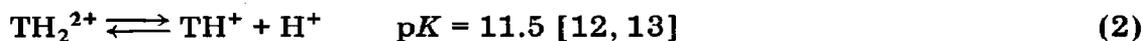


[†]Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

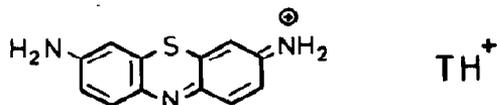
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^{††}The value of $K_a = 47.3$ reported by Rabinowtch *et al.* [14], which corresponds to a pK_a value of -1.33, must be considered as a misprint as can be seen from the published spectra. The correct value should read pK_a = -0.33 which is in good agreement with the value found by Vogelmann [12].



where TH^+ represents the well-known intensely blue coloured species



In the excited triplet state the forms $^3\text{TH}^+$ and $^3\text{TH}_2^{2+}$ have been well characterized with energies of $163 \pm 6 \text{ kJ mol}^{-1}$ and $126 \pm 10 \text{ kJ mol}^{-1}$ [5] respectively[†]. Their protolytic equilibrium is characterized by a $\text{p}K$ of 6.3 in water [1, 3] and 7.0 in methanol [15]. As has been noted, distinct redox potentials can be attributed to them which account well for their different reactivities [16].

Whereas nothing is known at present about the triplet form $^3\text{TH}_3^{3+}$, some information on the triplet ^3T has been published by Bonneau and coworkers [17]. Although they did not give the absorption spectrum of this triplet form, they reported the corresponding $\text{p}K_a$ of $^3\text{TH}^+$ as 9 in water and 10.5 in methanol.

During our studies of thionine triplet reactivity we found that in pyridine the relaxation behaviour of the triplet form $^3\text{TH}^+$ shows an unexpected complexity. In this paper we show that the triplet form T plays an essential role in this relaxation which occurs in three distinct kinetic steps, all of which can be followed by microsecond flash spectroscopy and represent a unique example of a conveniently time-resolvable Förster cycle.

2. Experimental details

2.1. Materials

Thionine (Merck) was purified as described in ref. 18. The solvents used, which were all reagent grade obtained from Merck, were pyridine (water content less than 0.01%), methanol and acetonitrile. The acetonitrile was dried using the procedure described in ref. 19. Before the flash experiments the solutions were purged with nitrogen (oxygen content less than 6 ppm) to remove oxygen.

2.2. Apparatus

The flash experiments were performed in a kinetic flash spectrometer using a flash-lamp-pumped dye laser (Electrophotonics model 3) as the exciting light source. Rhodamine 6G was used as the laser dye and the laser

[†]The energy of $^3\text{TH}_2^{2+}$ given in ref. 5 is based on an erroneous literature value for the $\text{p}K_a$ of TH_2^{2+} . When the correct $\text{p}K_a$ of -0.33 is used, a value of $125.5 \pm 10.4 \text{ kJ mol}^{-1}$ is obtained.

was tuned to 590 nm (pulse duration (full width at half-maximum) 2 μ s; beam diameter, approximately 0.5 cm; pulse energy, 500 mJ). The solutions were flashed in a cylindrical cuvette with an optical path length of 10 cm. The exciting laser beam and the probe light beam passed through the cuvette in an almost collinear path along the cuvette axis. The apparatus is described in detail in ref. 20.

3. Results

3.1. Ground state spectra

A solution of thionine in dry pyridine shows an absorption spectrum which is very similar to that observed in other polar solvents such as water or methanol except that in pyridine the long-wavelength absorption maximum is found at 614 nm, *i.e.* it is slightly red shifted with respect to water ($\lambda_{\text{max}} = 596$ nm) and methanol ($\lambda_{\text{max}} = 598$ nm). On addition of either acids or bases the spectrum (Fig. 1) changes owing to the shift of the equilibrium

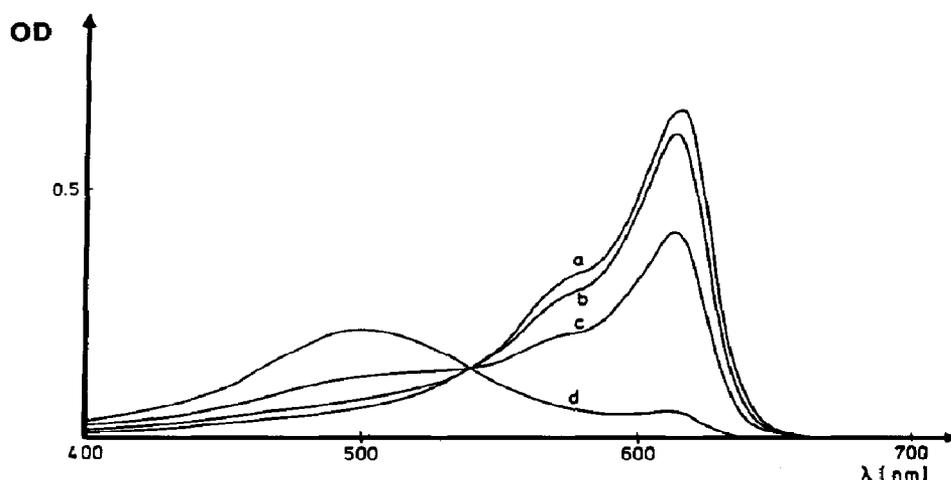
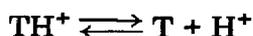


Fig. 1. Absorption spectra of thionine (2×10^{-5} M; 0.5 cm cuvette) in various media: curve a, pyridine containing 2.5×10^{-4} M HCl; curve b, neat pyridine; curve c, pyridine containing 0.1 M 2-picoline; curve d, neat 2-picoline.

Since curve a represents the limiting case for acidified pyridine solutions, it is evident from curve b that a small fraction of the basic form T is present in neat pyridine, indicating the basic character of the solvent. If the still more basic solvent 2-picoline is used, the equilibrium can be almost completely shifted to form T. The ratio of the equilibrium concentrations in the two solvents agrees fairly well with the ratio of the K_b values of the corresponding solvents as measured in dilute aqueous solution (1.7×10^{-9} for pyridine and 9.1×10^{-9} for 2-picoline).

3.2. Transient absorption

Flash spectroscopy experiments were performed using very low concentrations of thionine ($c = 1.6 \times 10^{-6}$ M) in order to ensure that no bimolecular processes between the dye triplets or between the dye triplets and the ground state molecules (D-D processes [21]) occurred. The transient signals observed at four characteristic wavelengths are depicted in Fig. 2. The transient absorption band at 780 nm is characteristic of the triplet ${}^3\text{TH}^+$ which is formed during the laser flash excitation and decays with a decay time of about 5 μs .

The fast decay of the triplet TH^+ observed at 780 nm must be compared with the kinetics observed in other spectral regions. At 615 nm, where the absorption signal indicates changes in the TH^+ ground state population, only a slight TH^+ repopulation is observable during the first 50 μs after the flash. At 500 nm the absorption increases, reaching a maximum at about 40 μs ; these kinetics are rather slower than the decay at 780 nm. At 440 nm only a weak decrease of the absorption is detectable in the first 50 μs , similar to the ground state repopulation observed at 615 nm. From a comparison of the kinetic traces at 780 nm and 615 nm it is clear that the fast deactivation of ${}^3\text{TH}^+$ cannot be due to the process ${}^3\text{TH}^+ \rightarrow \text{TH}^+$. Therefore it is tempting to assume that a deprotonation process ${}^3\text{TH}^+ \rightarrow {}^3\text{T}$ is responsible for the ${}^3\text{TH}^+$ decay.

In order to obtain information on the spectral characteristics of the triplet form ${}^3\text{T}$, we investigated the triplet spectrum in basic aqueous and

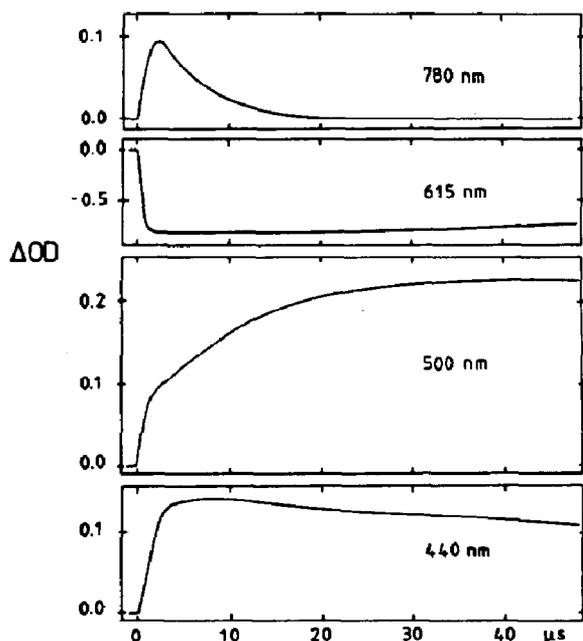


Fig. 2. Transient absorption signals obtained at four characteristic wavelengths on flashing 1.6×10^{-6} M solutions of thionine in an oxygen-free pyridine solution (optical path length, 10 cm).

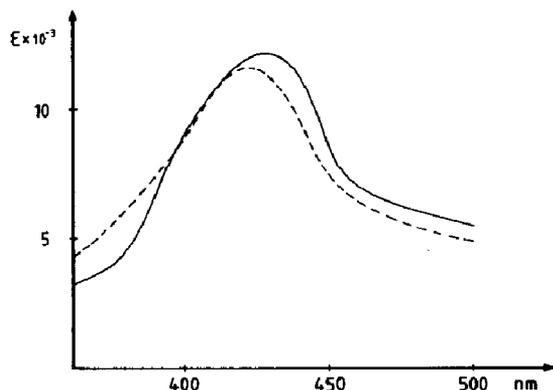


Fig. 3. Short-wavelength absorption spectra of ${}^3\text{TH}^+$ and ${}^3\text{T}$ in methanol: —, ${}^3\text{TH}^+$ in neat methanol (spectrum adapted from ref. 9); ---, ${}^3\text{T}$ in methanol containing 10^{-4} M NaOMe. The latter solution does not show the strong 780 nm absorption characteristic of the ${}^3\text{TH}^+$ form.

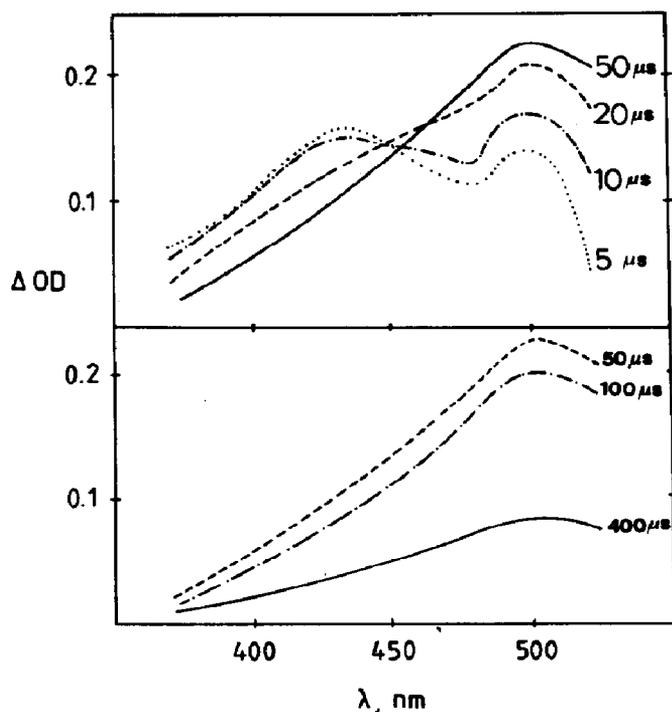


Fig. 4. Short-wavelength transient spectra (conditions as given in Fig. 2) recorded at various delay times after the laser flash.

methanolic solutions. Whereas on increasing the base concentration (NaOH or NaOMe) the lifetime of ${}^3\text{TH}^+$ decreased, as could be observed in the 780 nm band, the spectral characteristics in the short-wavelength region did not show major spectral (Fig. 3) or kinetic changes, *i.e.* the interconversion ${}^3\text{TH}^+ \rightarrow {}^3\text{T}$ does not cause a marked change in the kinetics observable in the short-wavelength region. However, if the triplet ${}^3\text{T}$ decays, formation of the

ground state form T should be observable. In fact the transient spectra observed at various delay times after the laser flash corroborate this hypothesis on the deactivation pathway of ${}^3\text{TH}^+$.

The transient spectra measured after delay times of between 5 and 400 μs are shown in Fig. 4. The spectrum obtained after about 5 μs shows absorption maxima at 440 and 500 nm. Within the first 50 μs the spectrum changes: the 440 nm maximum disappears and the absorption at 500 nm increases. We attribute the 440 nm maximum to the triplet forms ${}^3\text{TH}^+$ and ${}^3\text{T}$, and the absorption maximum at 500 nm to the ground state form T. After 50 μs the triplet decay seems complete, and the kinetic behaviour (lower part of Fig. 4) is now spectrally uniform. This should be due to the conversion of the ground state form T into the ground state form TH^+ . In fact a corresponding increase in the optical density can be observed at 615 nm, indicating repopulation of TH^+ at the same rate as the 500 nm absorption band decays. The whole transformation is completely reversible.

4. Discussion

4.1. Kinetic scheme and rate constants

The processes observed during the excitation of thionine in pyridine solution can be represented by the kinetic scheme shown in Fig. 5. The dominant form in the ground state is TH^+ which, after laser excitation into its first excited singlet state, shows a very rapid and efficient intersystem crossing to the first excited triplet state ${}^3\text{TH}$. This intermediate is found to decay with an overall rate constant of $2 \times 10^5 \text{ s}^{-1}$ which must be due mainly to the deprotonation process (rate constant k_1) since almost no ground state repopulation (which normally occurs with a rate constant k_0 of $(2 - 5) \times 10^4 \text{ s}^{-1}$) is observable during the decay of ${}^3\text{TH}^+$. From measurements in other solvents it is known that ${}^3\text{TH}^+$ is about 2 pK units more acid than TH^+ . Thus it is not surprising that, whereas the equilibrium fraction of T is just notice-

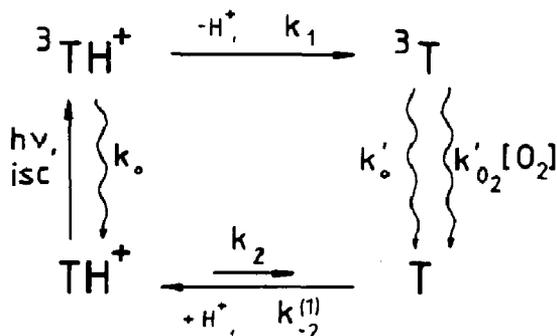


Fig. 5. Kinetic scheme for the observed relaxation behaviour of ${}^3\text{TH}^+$ in pyridine. The observed rate constants are as follows: $k_1 = 2 \times 10^5 \text{ s}^{-1}$; $k_0' = 6.1 \times 10^4 \text{ s}^{-1}$; $k_0'' = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k_{-2}^{(1)} = 3.3 \times 10^3 \text{ s}^{-1}$; $k_2 \approx 3.3 \times 10^2 \text{ s}^{-1}$.

able in the ground state, the corresponding equilibrium is on the 3T side in the triplet state.

The intermediate 3T decays to the corresponding ground state form T with a rate constant of about $6 \times 10^4 \text{ s}^{-1}$, which was evaluated from the rise time of the 500 nm absorption. The interpretation of this process as the decay of the triplet to the ground state is corroborated by the fact that the corresponding process becomes faster as the oxygen content is increased, *i.e.* we observe the process



The rate constant k'_{O_2} was estimated as about $2 \times 10^9 \text{ s}^{-1}$. After formation of the ground state T the original form TH^+ is recovered by an effective first-order protonation process with a rate constant $k_{-2}^{(1)}$ of $3.3 \times 10^3 \text{ s}^{-1}$. From the observation that the reaction is first order it follows that the protonating agent must be present in excess over the dye concentration which is about $1 \times 10^{-6} \text{ M}$. In fact, if it is assumed that the water content is only 0.01%, which would correspond to $5.6 \times 10^{-3} \text{ M}$, the water together with the bulk pyridine can form an acid-base system with sufficient buffer capacity to account for the observed reaction order. From the equilibrium concentrations in the ground state it follows that the rate constant of dissociation of TH^+ should be approximately $3.3 \times 10^2 \text{ s}^{-1}$.

4.2. Conditions for the kinetic observability of the Förster cycle

The reaction scheme shown in Fig. 5 represents a complete Förster cycle. The ground state equilibrium is disturbed by the protolytic reaction in the excited triplet state, and its re-establishment can be followed kinetically. This principle has been used before in the form of an excitation jump perturbation [22] of ground state protolytic equilibria in order to study the rates of protolytic processes in the ground state [23, 24]. However, we know of no example where all processes of the Förster cycle can be conveniently followed by microsecond spectroscopy in the same kind of experiment.

It is interesting to consider why neat pyridine constitutes a unique medium for such a case to be observed. Firstly, in order to see dissociation in the excited state and association in the ground state, the condition

$$pK^* < pH < pK \quad (5)$$

must hold, which of course can also be met in other solvents by using suitable buffers. However, in order to make all the processes kinetically observable with microsecond time resolution, the condition

$$10^6 \text{ s}^{-1} > k_1 > k'_0 > k_{-2}^{(1)} \quad (6)$$

must also be fulfilled. This condition appears to be rather crucial. In protic solvents, *e.g.* water or methanol, buffered at a pH where the ground state equilibrium is nearer TH^+ than T, $k_{-2}^{(1)}$ is always larger than 10^6 s^{-1} . There-

fore in such solvents the T form cannot be observed as an intermediate during the ${}^3\text{TH}^+$ relaxation.

We also attempted to attain the critical condition (6) in another aprotic solvent, *i.e.* acetonitrile, where the required basicity was achieved by dissolving gaseous ammonia to a concentration of 10^{-3} M. With this concentration about 10% T is present in the ground state, similar to the situation in neat pyridine. However, the process ${}^3\text{TH}^+ \rightarrow {}^3\text{T}$ is already too rapid in such a solution to be time resolved by microsecond flash spectroscopy and the protonation of T is too fast, so that, kinetically, the repopulation of the ground state TH^+ occurs at the same rate as the decay of the triplet state ${}^3\text{T}$. Neither ${}^3\text{TH}^+$ nor T are detectable as intermediates. Thus we feel that the acid-base properties of the solvent pyridine are unique in establishing the condition given in eqn. (6).

In conclusion we should like to note that the energy of the triplet state ${}^3\text{T}$, which has not yet been published, can be calculated using the Förster cycle. The Förster cycle relates the energy values of the triplet states ${}^3\text{TH}^+$ and ${}^3\text{T}$ to the respective $\text{p}K_a$ values in the ground state and the excited triplet state. $E({}^3\text{T})$ can then be calculated using the equation

$$E({}^3\text{TH}^+) - E({}^3\text{T}) \approx -2.303RT[\text{p}K_a({}^3\text{T}^{\ddagger}\text{H}^+) - \text{p}K_a(\text{TH}^+)] \quad (7)$$

with $E({}^3\text{TH}^+) = 163 \text{ kJ mol}^{-1}$ [5], $\text{p}K_a({}^3\text{TH}^+) = 9$ [17] and $\text{p}K_a(\text{TH}^+) = 11.5$ [12, 13] which gives a value of $150 \pm 6 \text{ kJ mol}^{-1}$ for $E({}^3\text{T})$.

Acknowledgment

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