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Decay dynamics of the triplet state of 2,6-dimethyl-4H-1-benzothiopyran-4-thione in solution

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Abstract

The phosphorescence decay kinetics and transient triplet–triplet absorption of 2,6-dimethyl-4H-1-benzothiopyran-4-thione (DMBTPT) were recorded in deoxygenated *n*-hexane, *n*-hexadecane and 3-methylpentane solutions. The measurements of DMBTPT in the triplet state were performed using a flash photolysis system with an excimer laser as excitation source. The triplet state decay constant at infinite dilution (k_0) and the self-quenching rate constant (k_{sq}) for DMBTPT at room temperature were determined from the Stern–Volmer equation. The results obtained confirm an essential contribution of the self-quenching process to the deactivation of the DMBTPT triplet state. The k_{sq} values suggest that this process is diffusion controlled, similar to other thioketones. Moreover, an analysis of the temperature dependence of τ^{-1} at different concentrations of DMBTPT in 3-methylpentane provides further evidence for a viscosity-controlled deactivation process.

Keywords: Decay dynamics; Triplet state; 2,6-Dimethyl-4H-1-benzothiopyran-4-thione

1. Introduction

Interest in the photophysical and photochemical properties of thioketones in their excited states has increased considerably in the last two decades. The photochemical properties of thioketones have been the subject of many investigations as they exhibit several unusual features, many aspects of which are not clearly understood. For example, thioketones show intense $S_2 \rightarrow S_0$ fluorescence [1–5] and phosphorescence [1,2,6–8] in liquid solutions at room temperature, as well as thermally activated delayed fluorescence from S_1 [9]. They also exhibit unusually efficient self-quenching in the S_2 and T_1 states [1,2,4–8,10–17], $S_0 \rightarrow T_1$ absorption [1,2,6,8] and photochemistry from higher excited singlet and triplet states [1,2,4–7,13–17]. In the photochemistry of thioketones, the triplet states are assumed to play a particular role. The decay dynamics of thioketone triplets have been studied previously by measuring the phosphorescence lifetimes and quantum yields [6–8,15], and by monitoring the triplet–triplet absorption in laser flash photolysis [10,11,16]. In liquid solutions, the bimolecular self-quenching of the triplet states of thioketones occurs at nearly diffusion-controlled rates [2,6–8,10,11,13–17].

The self-quenching process, namely the quenching of an excited state molecule (D*) by a molecule of the same compound but in the ground state (D) is usually studied by measuring the lifetime of the excited state as a function of concentration. Values of the excited state decay constant at infinite dilution (k_0) and the bimolecular self-quenching rate constant (k_{sq}) can be obtained from the following Stern–Volmer-type equation [18]

$$\tau^{-1} = k_0 + k_{sq} \times [\mathrm{D}] \qquad (1)$$

For thioketones, for which the self-quenching process is an efficient method of triplet state decay, the formation of a T_1 excimer has been postulated on the basis of the quantum yields of photodecomposition [13,14,17]. In particular, Kozłowski et al. [17], in recent work on the photochemistry of xanthione, 4-H-1-benzopyran-4-thione and 4-pyran-4-thione, have assumed, among other things, that "the fraction of $T_1 \cdots S_0$ encounters which yields product via the postulated triplet excimer increases in the order xanthione ≪ 4-H-1-benzopyran-4-thione < 4-pyran-4-thione. This may help to explain the previous failure to observe triplet excimers of xanthione spectroscopically". However, the earlier studies of the photophysical and photochemical properties of xanthione in the triplet state carried out by Brühlmann and Huber [15,19], a recent investigation of the photophysical properties of 4-H-1-benzopyran-4-thione (BPT) [20] in the triplet

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state and the studies of Eisenberger et al. [21] devoted to BPT failed to confirm the existence of a triplet state excimer which was postulated for the above compounds. Similarly, no direct evidence has been obtained for the formation of triplet state excimers for any other aromatic thioketone. The present study of 2,6-dimethyl-4H-1-benzothiopyran-4-thione (DMBTPT) is analogous to the classic investigation by Brühlmann and Huber [15] for xanthione and the recent investigation of BPT [20]. This time, as the subject of study, we have chosen a thioketone which has, in addition to a thiocarbonyl group, a sulphur atom in its aromatic ring and two methyl groups in positions 2 and 6. Our work concerns the intramolecular and intermolecular decay processes of the lowest triplet state of DMBTPT.

2. Experimental details

DMBTPT was synthesized and purified as described in Refs. [3] and [5]. *n*-Hexane and *n*-hexadecane (spectral grade, Aldrich) were used as received. 3-Methylpentane (3-MP) (purum, Fluka AG) was further purified by fractional distillation.

The study was carried out using cells of 1.5–2.0 mm thickness and an optical quartz Dewar tube containing a quartz cell (thickness, 1–2 mm) for low temperature measurements. In order to deoxygenate the solutions, argon bubbling was used. No emission or absorption was detected for any of the solvents under the excitation conditions used in our experiments.

The laser flash photolysis apparatus based on an XeCl excimer laser (308 nm) has been described in detail elsewhere [20].

Rate constants were calculated by a standard non-linear least-squares method with an accuracy of 10%. Transient spectra were measured point-by-point and normalized to the measured relative laser pulse energy.

3. Results

The transient absorption spectrum of DMBTPT in *n*-hexane is given in Fig. 1. The triplet decay kinetics of DMBTPT, monitored using the phosphorescence decay at about 700 nm, were measured in *n*-hexane, *n*-hexadecane and 3-MP solutions at room temperature. The triplet decay lifetimes τ were measured as a function of the ground state DMBTPT concentration in the limit of low laser intensities. Within the DMBTPT concentration range of $(0.8\text{–}12.0)\times10^{-5}$ M, the plot was found to be linear. Exponential decays were observed under these conditions. The results of the concentration dependence of the DMBTPT triplet lifetime are shown in Fig. 2. Values of the triplet state decay constant at infinite dilution (k_0) as well as the self-quenching rate constants (k_{sq}) for DMBTPT at room temperature were determined from Eq. (1). The values of k_0 and k_{sq}, obtained from the curves, are summarized in Table 1.

Fig. 3 shows the temperature dependence of $\log(\tau^{-1})$ for two concentrations of DMBTPT in 3-MP. The temperature effect increases with increasing DMBTPT concentration. The

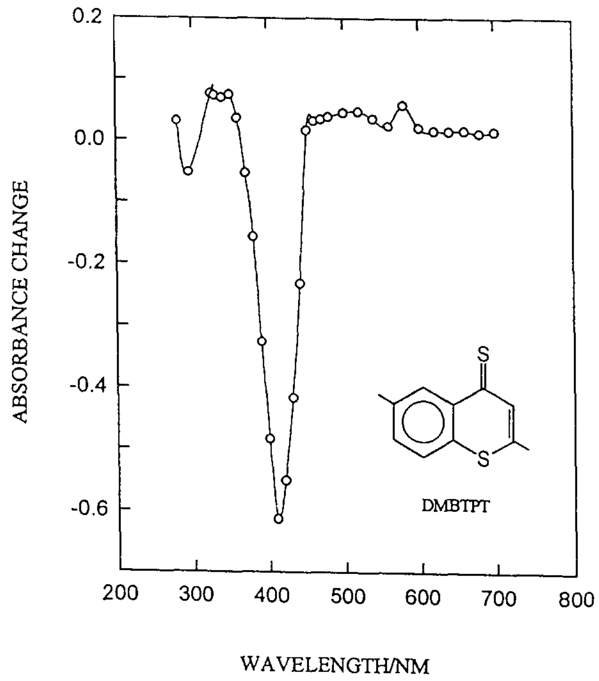

Fig. 1. Difference absorption spectrum of DMBTPT triplet observed on 308 nm laser flash photolysis of 10^{-5} M DMBTPT solution in degassed *n*-hexane (at 0.2 μs following laser flash, $T=198$ K).

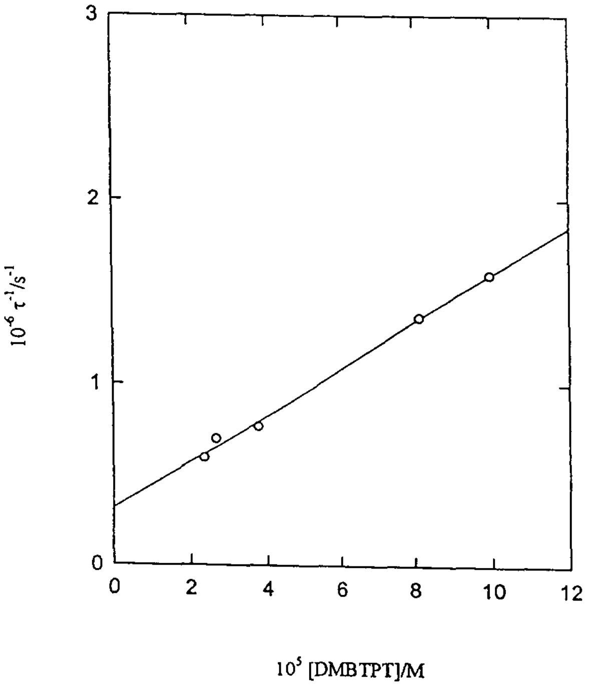

Fig. 2. Plot of τ^{-1} vs. concentration of DMBTPT in *n*-hexane at room temperature. Linear regression yields $k_0=3.1\times10^5$ s^{-1} and $k_{sq}=1.3\times10^{10}$ M^{-1} s^{-1}.

Table 1
Values of the triplet state decay constant at infinite dilution (k_0) and the bimolecular rate constant (k_{sq}) of DMBTPT at 22 ± 2 °C

Solvent	$k_0 \times 10^{-5}$ (s^{-1}) [a]	$k_{sq} \times 10^{-10}$ ($M^{-1} s^{-1}$)	Viscosity (cP)
3-MP	2.3	1.5	0.31
3-MP	1.7 [b]	1.8 [b]	
n-Hexane	3.1	1.3	0.31
n-Hexadecane	2.8	0.41	3.34
Perfluoro-1,3-dimethylcyclohexane	1.18 [b]	0.7 [b]	1.88

[a] Extrapolated to infinite dilution.
[b] Ref. [8].

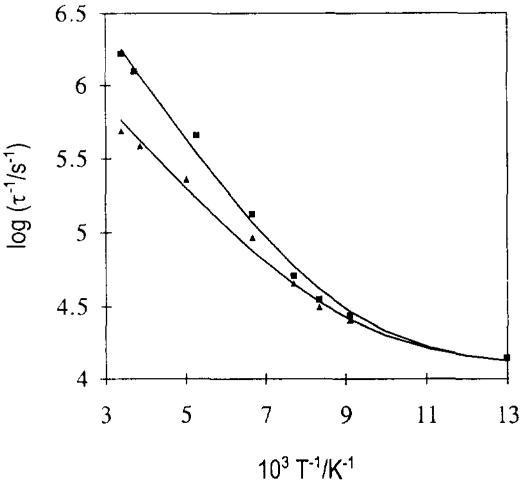

Fig. 3. Temperature dependence of log(τ^{-1}) of DMBTPT triplet at different DMBTPT concentrations (■, 6.67×10^{-5} M; ▲, 0.83×10^{-5} M) in 3-MP. The model used to calculate the theoretical curves is explained in the text.

model used to calculate the theoretical curves will be discussed later.

4. Discussion

The various photophysical and photochemical processes of thioketones contributing to the decay of the triplet state are solvent dependent. We have chosen as solvents 3-MP, *n*-hexane and *n*-hexadecane, the first for low temperature measurements, and the other two due to their considerable difference in viscosity. 3-MP is relatively unreactive towards T_1 thioketones and the photophysical and spectral properties of DMBTPT were measured in this solvent [7,8]. The quantum yield of DMBTPT phosphorescence in 3-MP, determined on primary excitation to the S_2 state, is 0.04. For comparison, it is worth mentioning that the yield of this process, as determined for BPT under similar conditions, is close to the above value being equal to 0.03 [7]. On the other hand, the quantum yields of DMBTPT and BPT fluorescence in 3-MP differ significantly, being equal to 0.0002 and 0.0018 respectively. The mechanism of thioketone S_2 state deactivation is as yet unknown, including the mechanism of S_2 state deactivation of DMBTPT. As shown in Ref. [3], for rigid aromatic thioketones characterized by a large difference in energy between the S_1 and S_2 states in perfluoroalkane solvents, a linear correlation exists between the logarithm of the rate constant of radiationless deactivation from the S_2 state (k_{nr}) and the energy gap between the S_1 and S_2 states, $\Delta E(S_2–S_1)$. High rates of radiationless deactivation from the S_2 state, a linear dependence between the logarithm of the rate constant of radiationless deactivation and the energy gap between the S_2 and S_1 states and the absence of such a dependence between k_{nr} and $\Delta E(S_2–S_0)$ or $\Delta E(S_2–T_1)$, indicate, according to Maciejewski et al. [3], a dominant role played by $S_2 \rightarrow S_1$ radiationless processes in the decay of the second excited singlet state of thioketones, including DMBTPT. The yield of the $S_2 \rightarrow S_1$ radiationless transition is, however, slightly smaller (although still quite large) in alkanes than in perfluoroalkanes [22]. It should be noted that, in our experiment, the DMBTPT molecules were excited to the S_2 state (308 nm). According to Maciejewski et al. [3], the energy gap between S_1 and T_1 states is very small for aromatic thioketones, being equal to 890–760 cm^{-1} for DMBTPT [3,6] and only 690 cm^{-1} for BPT. Thioketones excited to the S_2 or S_1 states generally have high yields of intersystem crossing [2,6,10,11,16]. In our studies, the phosphorescence decay time of DMBTPT was always equal to the decay time of transient absorption of this thioketone in all the solvents. This shows that the T_1 state is responsible for the observed transient absorption. Fig. 1 shows the transient absorption spectrum of DMBTPT (plotted as the change in optical density vs. wavelength) in *n*-hexane obtained using laser flash photolysis. In the spectral region in which the ground state absorption of DMBTPT dominates, negative absorbance changes due to ground state depletion constitute a mirror image of the absorption band system due to the $S_0 \rightarrow S_2$ transition. Similar spectral and decay properties were found in other thioketones [16,20,23]. As for BPT [20], we attempted to detect T_1 excimer absorption or emission, but did not succeed at room temperature.

Values of the triplet state decay constant at infinite dilution obtained for DMBTPT in 3-MP, *n*-hexane and *n*-hexadecane are similar and of the same magnitude as the k_0 values determined for other thioketones in aprotic solvents. Comparison between the k_0 value determined for DMBTPT in an inert solvent, such as perfluoro-1,3-dimethylcyclohexane ($k_0 = 1.18 \times 10^5$ s^{-1}) [8], and the k_0 values obtained for DMBTPT in the three alkane solvents used here (Table 1) point to an important role of solvent interactions in the deactivation process. As shown for BPT and xanthione, the values of the triplet state decay constant at infinite dilution determined in protic solvents are considerably greater than in aprotic solvents. A much larger k_0 value in ethanol than in aprotic solvents indicates a significant contribution of hydrogen abstraction to the deactivation. The importance of the hydrogen abstraction process for thioketones was noted previously by Brühlmann and Huber [15] and Kemp and de Mayo [24]. For DMBTPT in 3-MP, *n*-hexane and *n*-hexadecane, we did not observe a large change in the determined k_0 values, which suggests that the rate constants of the hydrogen abstraction process for DMBTPT in these solvents are either the same or low compared with those of other deactivation processes.

The previously determined self-quenching and triplet decay constants for DMBTPT in 3-MP at infinite dilution are 1.8×10^{10} M^{-1} s^{-1} and 1.7×10^5 s^{-1} respectively [7], and are in good agreement with the k_{sq} and k_0 values determined here (see Table 1). The value of the bimolecular rate constant k_{sq} indicates a nearly diffusion-controlled interaction between the T_1 and S_0 states of DMBTPT molecules. Moreover, an analysis of the temperature dependence of τ^{-1} at different concentrations of DMBTPT in 3-MP provides further evidence for a viscosity-controlled deactivation process. As Brühlmann and Huber [15] showed, assuming that an Arrhenius-type temperature dependence holds for each individual rate constant, the difference between the τ^{-1} values at two different concentrations is given by

$$\tau_1^{-1} - \tau_2^{-1} = ([\mathrm{DMBTPT}]_1 - [\mathrm{DMBTPT}]_2) \times A_{sq} \times \exp(-E_{sq}/RT) \quad (2)$$

Values of the activation energy of the self-quenching process ($E_{sq} = 2.03$ kcal mol^{-1}) and the frequency factor ($A_{sq} = 5.2 \times 10^{11}$ s^{-1}) obtained here are similar to those reported in Ref. [15], but we must keep in mind the approximate character of the above equation resulting from simplifications made during its derivation. The activation energy is in good agreement with that of the solvent viscosity ($E_D = 2.07$ kcal mol^{-1}) and with that obtained for xanthione in 3-MP ($E_{sq} = 2.09$ kcal mol^{-1} [15]) (and for BPT in 3-MP ($E_{sq} = 2.1$ kcal mol^{-1} [20]).

Further, we have also attempted to calculate the parameters of the excited state decay process at infinite dilution according to the model proposed by Eisenberger et al. [21]

$$k_0(T) = [k_t + (k_s/3)\exp(-E_{st}/RT)] / \times [1 + (1/3)\exp(-E_{st}/RT)] \quad (3)$$

which presumes fast equilibration between the S_1 and T_1 states. The parameters obtained are $k_t = 1.2 \times 10^4$ s^{-1}, $k_s = 1.2 \times 10^7$ s^{-1} and $E_{st} = 1.24$ kcal mol^{-1} (430 cm^{-1}). Here k_t and k_s are the triplet and singlet state decay rates and $E_{st} = E(S_1) - E(T_1)$ is the energy gap between the two states. Similar values for BPT were obtained in Ref. [21] between 218 and 300 K. Using published triplet and singlet state energies for DMBTPT [3,6], and estimating the E_{st} value from the energy difference between the $T_1 \rightarrow S_0$ and $S_1 \rightarrow S_0$ transitions from the typical values published for the difference between the "up" and "down" transition energies for thiones [9], we obtain the value $E_{st} = 530$ cm^{-1}, which compares very well with the value obtained from the temperature dependence, given the uncertainty (100 cm^{-1}) in the published values of the respective energies and the implicit assumptions made in the above treatment, e.g. neglecting completely the hydrogen abstraction reaction by triplet DMBTPT from 3-MP, which should have a low but noticeable reaction (compare with the xanthione data [19]). The model curves presented in Fig. 3 represent the kinetics resulting from simultaneous intermolecular and intramolecular decay processes. The general trend is reproduced correctly; however, the deviations of individual points (30% of the respective rate constant value) mean that the model in its present form is incomplete.

On the basis of the τ^{-1} measurements as a function of concentration in the temperature range 110–296 K, we conclude that the self-quenching (depending on the thioketone concentration) and/or intramolecular reactions are the primary processes responsible for the changes in the apparent triplet state lifetime. However, below about 110 K, the observed lifetime of the triplet state is practically independent of the thioketone concentration. In addition, the solvent viscosity below 110 K is sufficiently high to suggest that, in this temperature range, the intramolecular channel of triplet state decay is responsible for the observed changes in τ^{-1} of DMBTPT. Thus we conclude that at least two different mechanisms are responsible for the observed decay of the T_1 state of DMBTPT in the temperature range 110–296 K, but below 110 K the intramolecular mechanism is responsible for the triplet decay of DMBTPT. This conclusion is in agreement with the model calculations assuming an intramolecular decay path via a (fast) thermal equilibrium between the S_1 and T_1 states, which is feasible given the very small distance between these states. Similar conclusions may be drawn from measurements carried out earlier for xanthione [15] and BPT [20].

The mechanism of self-quenching in thioketones is not yet fully understood. A thioketone triplet state quenching mechanism by the ground state of the same or another thione has been put forward [25,26] in terms of orbital overlap in the collision complex, i.e. interaction of the singly occupied n orbital of the S atom in the triplet state with the lone pair of the ground state. The excited state thioketone acts as an acceptor, while the ground state thioketone behaves as a donor. Turro and Ramamurthy [27] have studied the quenching of the triplet state of xanthione by a number of olefins. From the relationship between the quenching rate constant and the ionization potentials of the olefins, they suggest that the contribution of charge transfer interactions is low.

For a series of thioketones, such as xanthione, BPT and 4-pyran-4-thione, a mechanism of triplet state deactivation has been proposed based on the contribution of the T_1 excimer formed [13–15,17,26]. Maciejewski and coworkers [13,14,17] report that, in aromatic thioketones, the probability of T_1 excimer formation in the self-quenching process is particularly high. In contrast, Nickel and Rodriguez Prieto [28] have questioned the possibility of T_1 excimer formation by aromatic hydrocarbons and some of their derivatives in solution. Studies of the photophysical and photochemical properties of xanthione in its triplet state, carried out by Brühlmann and Huber [15,19], our investigation of the photophysical properties of BPT [20], the results reported in the paper by Eisenberger et al. [21] who studied BPT in its triplet state and the results presented in this paper for DMBTPT have failed to indicate the formation of a T_1 excimer postulated for thioketones. We chose DMBTPT as the subject of study in the hope that the introduction of a sulphur atom into the aromatic ring would produce a more interesting transient absorption spectrum compared with other aromatic thioketones [10,11,16,20,23]. On the other hand, it was important to compare the kinetics of DMBTPT T_1 state decay over a wide range of temperatures with similar results obtained for xanthione and BPT. It should be noted that the ability to detect optically the excimers depends on their lifetime. Thus fast non-radiative decay could make the excimers unobservable both in transient absorption and emission on the timescale of our measurements (cf. the very short-lived transient with picosecond lifetimes observed in the cycloaddition reactions of triplet excited aromatic thiones with allenes [29]).

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