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Electron Spin Polarization by Intramolecular Triplet Quenching of a Nitroxyl Radical Labeled Thioxanthonedioxide

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Time-resolved electron spin resonance (TR-EPR) has been used to investigate the chemically induced dynamic electron polarization (CIDEP) generated by the interaction between a stable free radical (TEMPO) and the triplet states of thioxanthonedioxide derivatives. The intensity of CIDEP for intermolecular triplet quenching (thioxanthonedioxide methylester triplets with TEMPO) and intramolecular triplet quenching were compared using a covalently linked TEMPO–thioxanthonedioxide molecule. It is shown that at equivalent concentrations of TEMPO, the CIDEP is much larger in the case of intramolecular triplet quenching than for intermolecular quenching. The CIDEP intensity for intermolecular triplet quenching is limited to a maximum TEMPO concentration of ∼4 mM (at which point spin–spin interactions become dominant) and reaches only 1/8 of the intensity for intramolecular quenching. Laser flash photolysis experiments at room temperature showed that the intramolecular triplet quenching is fast (τ_t < 20 ns). This quenching reaction is also dominant at low temperatures in organic glasses (77 K), which was demonstrated by low-temperature phosphorescence and EPR analysis.

Introduction

The quenching of the triplet states of ketones[1–10] and aromatic hydrocarbons[2,3,5,8–15] by nitroxides has been the subject of considerable attention. For sensitizers with triplet energies higher than 225 kJ/mol, quenching rate constants close to the diffusion limit were found.[8,11,13] Chemically induced dynamic electron polarization (CIDEP) of the nitroxides has been observed as a result of this quenching process. Among the strongest spin polarization reported for these processes was that observed for the quenching of triplet benzophenone with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO).[8,10] The strong net polarization in the case of benzophenone was explained by its high magnitude of the triplet splitting parameter ($|D|$) compared to that of aromatic hydrocarbons.[16]

To the best of our knowledge, with one exception,[8] spin polarization of the nitroxyl radicals was obtained by intermolecular quenching of triplet sensitizers. If the nitroxide is directly linked to the ketone, triplet quenching of ketones by the nitroxide should be much faster and spin polarization of the nitroxide more intense. Jenks showed that, upon irradiation, intramolecular spin polarization of TEMPO can be achieved by linking TEMPO to benzophenone through an ester bridge.[8] In this work, we report a TEMPO-labeled thioxanthonedioxide (**1**), which showed high spin polarization produced by intramolecular quenching of the thioxanthonedioxide triplet by the TEMPO moiety. We compared the results to an intermolecular quenching system of similar structure (**2** and **3**).

1   **2**   **3**
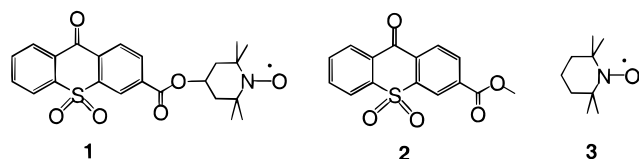
Experimental Section

Materials and Solvents. Benzene (Aldrich spectrophotometric grade) and methylcyclohexane (Aldrich spectrophotometric grade) were used as received. The TEMPO-labeled thioxanthonedioxide (**1**) was synthesized by a procedure analogous to that described by Hassner.[17] 9-Oxo-9*H*-thioxanthene-3-carboxylic acid 10,10-dioxide (Aldrich) was esterified with 4-hydroxy-TEMPO (Aldrich) in the presence of 1,3-dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine in THF under argon for 10 h. After removal of the THF, the residue was dissolved in methylene chloride, washed with water and 5% acetic acid, and chromatographed over silica gel (hexane/ethyl acetate gradient from 9:1 to 8:2) to obtain the ester in 85% yield. The structure and purity of **1** was determined by NMR and EPR. Methylester **2** was synthesized analogously to **1**, using methanol instead of 4-hydroxy-TEMPO, and was characterized by NMR.

General Methods. UV–vis absorption spectra were recorded on a Hewlett-Packard HP8452A UV spectrometer. Low-temperature phosphorescence spectra were recorded on a SPEX Fluorolog 1680 0.22 m double spectrometer. The phosphorescence lifetimes at 77 K were measured on a Perkin-Elmer LS-50 spectrofluorimeter.

Laser Flash Photolysis Experiments. Laser flash photolysis experiments employed the pulses from a Spectra-Physics GCR 100 Nd:YAG laser (266 nm, 8 ns) or a Lambda Physik Lextra 50 excimer laser (308 nm, 10 ns) and a computer-controlled system which has been described elsewhere.[18] Solutions of **1** and **2** were prepared at concentrations such that the absorbance was ∼0.3 at the excitation wavelength employed. Transient absorption spectra were recorded employing a Suprasil quartz flow cell (1 × 1 cm) to ensure that a fresh volume of sample was irradiated by each laser pulse. Quenching rate constants were measured using argon-saturated static samples contained in 1 × 1 cm Suprasil quartz cells. Fresh solutions were prepared at each quencher concentration.

Electron Spin Polarization by Triplet Quenching

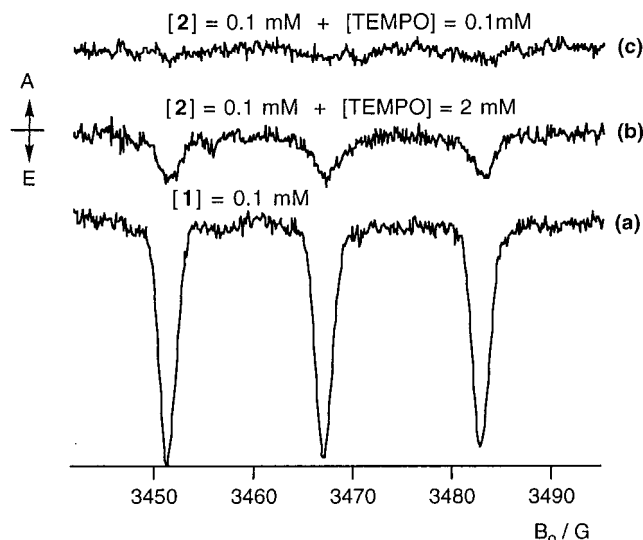*J. Phys. Chem. B, Vol. 103, No. 43, 1999* **9127**

Figure 1. TR-EPR spectra recorded from 200 to 500 ns following laser excitation (308 nm, 20 ns) of **1** (0.1 mM) (a), **2** (0.1 mM) + TEMPO (2 mM) (b), and **2** (0.1 mM) + TEMPO (0.1 mM) (c) in argon-saturated acetonitrile solutions at 23 °C.

Figure 2. Intensity of the TR-EPR signal of TEMPO depending on the TEMPO concentration. TR-EPR was recorded from 200 to 500 ns following laser excitation (308 nm, 20 ns) of **2** (1 mM) at various TEMPO concentrations in argon-saturated acetonitrile solutions at 23 °C.

Figure 3. Phosphorescence emission spectra (λ_{ex} = 308 nm) of **1** and **2** in ethanol glass at 77 K.

EPR Experiments. TR-EPR experiments employed the pulses (308 nm, 10 ns) from a Lambda Physik LPX 100 excimer laser, a Bruker ER 100D X-band EPR spectrometer, and a PAR boxcar averager and signal processor (models 4420 and 4402). Argon-saturated solutions were passed through a quartz flow cell (~0.3 mm thick) in the rectangular cavity of the EPR spectrometer. Further details are described elsewhere.[19,20] The cw-EPR experiments were performed on a Bruker ER 100D X-band EPR spectrometer. The low-temperature EPR experiments at 77K employed a liquid nitrogen Dewar inside the EPR cavity.

Results

TR-EPR. Laser flash photolysis (308 nm excitation) of argon-saturated acetonitrile solutions of **1** affords an intense TR-EPR spectrum shown in Figure 1a. The spectrum displays an emissive triplet with a ^{14}N hyperfine splitting of 15.8 G, which is typical for TEMPO. The experimental proof that spin polarization was produced by intramolecular triplet quenching of the thioxanthonedioxide moiety by the linked TEMPO moiety and not by intermolecular quenching of two molecules of **1** was carried out in the following way. A thioxanthonedioxide derivative (**2**) possessing a similar structure to **1**, but without a covalently linked TEMPO, was irradiated with laser flashes at 308 nm in the presence of an equimolar amount of TEMPO (**3**). A very weak TR-EPR signal of polarized TEMPO was observed (Figure 1c), even though the concentrations of **1**, **2**, and **3** were identical in both experiments (1×10^{-4} M) and the extinction coefficients of **1** and **2** at 308 nm were similar. Intermolecular quenching of triplets of **2** was clearly observed at higher concentrations of **3** (see Figure 1b; [**3**] = 2 mM) which is consistent with the bimolecular quenching rate constant $k_{TEMPO} = 8.8 \times 10^9$ M^{-1} s^{-1} measured by laser flash photolysis (see below).

We then attempted to quantify the increase in spin polarization for intramolecular quenching (**1**) vs intermolecular quenching (**2** + **3**). For this experiment, higher concentrations of **1** and **2** were used (1 mM) to improve the signal-to-noise ratio in the TR-EPR experiments. The TR-EPR spectra of solutions containing **2** and different amounts of **3** (0−4 mM) were measured. Figure 2 shows that the EPR signal intensity increases with increasing concentrations of **3** and reaches a plateau at about 2
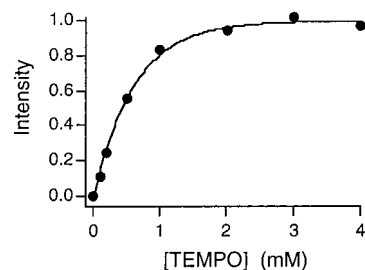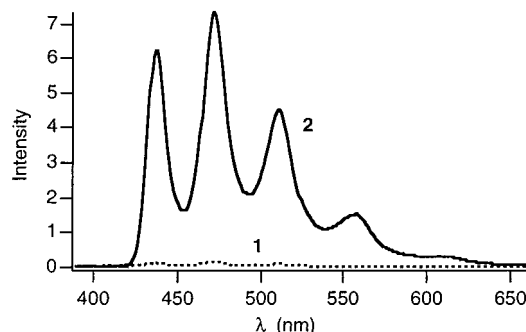
mM of **3**, indicating that triplet quenching of **2** with **3** is quantitative. In contrast, an EPR signal approximately 8 times larger than that in the intermolecular case was observed for the intramolecular triplet quenching, using **1**. A further increase in the concentration of **3** above 4 mM is not useful for EPR measurements, because at higher concentrations spin−spin interactions produce a change in the shape of the EPR signal from a triplet to a single broad peak, vitiating comparison of the intermolecular and intramolecular systems.

Phosphorescence Spectroscopy. The thioxanthonedioxide derivative **2** exhibits a phosphorescence emission with resolvable vibrational fine structure in ethanol glass at 77 K upon excitation with 308 nm light (see Figure 3). From the (0,0) emission band at 438 nm, the triplet energy was estimated ($E_T \approx 273$ kJ/mol). The vibrational progression is ca. 1700 cm^{-1}, which is typical for n,π^* emission from ketones. The phosphorescence quantum yield at 77 K is at least 0.2 or higher, as determined by comparison with the phosphorescence of benzophenone. The phosphorescence possesses a lifetime of 1.9 ms, and together with the relatively high phosphorescence quantum yield, suggests a n,π^* nature of the lowest triplet state. In contrast, **1** showed only a weak phosphorescence at 77 K, with an intensity of about 2% of **2** (see Figure 3) and a lifetime of 1.6 ms. The spectral shapes of both compounds were almost identical. The weak phosphorescence intensity of **1** could be caused by minor contamination of thioxanthonedioxide derivatives which do not contain the TEMPO tether. That could also explain the almost identical phosphorescence lifetimes between solutions containing **1** and **2**.

Nanosecond Laser Flash Photolysis. Laser flash photolysis (266 nm excitation) of argon-saturated acetonitrile solutions of **2** affords a readily detectable transient absorption spectrum (see Figure 4), which decays obeying first-order kinetics ($\tau = 22$ μs). This transient was assigned to the triplet state of **2**, since this triplet is efficiently quenched by naphthalene ($E_T = 255$ kJ/mol[21]) with a rate constant of 1×10^{10} M^{-1} s^{-1}. In addition,
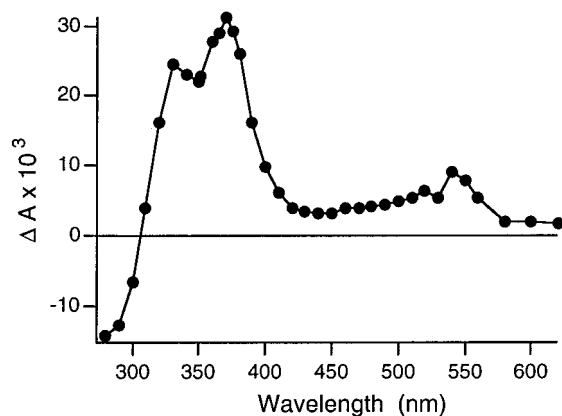
Figure 4. Transient optical absorption spectrum recorded 50−2000 ns following laser excitation (266 nm, 8 ns) of **2** in argon-saturated acetonitrile solution at 23 °C.
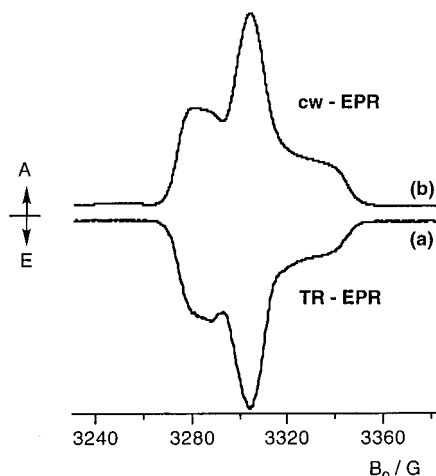

Figure 5. TR-EPR (a) and cw-EPR (b) spectra of **1** in ethanol/toluene glass (1:1 by volume) at 77 K. TR-EPR spectrum (a) was recorded 0.1−1.1 μs following 308 nm laser excitation. The cw-EPR spectrum (b) is displayed in its integrated form.

a grow-in of the naphthalene triplet at 412 nm[22] was observed. This is a strong indication of the triplet nature of the observed transient. For the experiments involving naphthalene, an excitation wavelength of 308 nm was chosen to minimize the absorbance of laser light by naphthalene. The triplets of **2** were effectively quenched by TEMPO. The rate constant was determined by pseudo-first-order treatment of the decay of the triplet absorption at 370 nm ($k_{TEMPO} = 8.8 \times 10^9$ M^{-1} s^{-1}). This high rate constant is in good agreement with values published for other ketone triplets with similar triplet energies.[6]

Laser flash photolysis of **1** did not show any detectable transient absorption spectrum within the time limit of our instrument (20 ns). Therefore, we conclude that the intramolecular triplet quenching of thioxanthonedioxide by TEMPO is very fast ($k > 5 \times 10^7$ s^{-1}).

Low-Temperature cw- and TR-EPR. Since almost no phosphorescence of **1** was observed at 77 K, TR-EPR was performed at 77 K to determine if intramolecular triplet quenching is effective in an organic glass matrix. Figure 5a shows the TR-EPR spectrum recorded 0.1−1.1 μs following 308 nm laser excitation in ethanol/toluene glass. Similar to the TR-EPR spectra at room temperature, emissive polarized spectra were observed. The spectrum obtained by TR-EPR (Figure 5a) shows the same absorptive features as the spectrum obtained by cw-EPR spectroscopy (Figure 5b). Note that the cw spectrum is shown in its integrated form.

Discussion

Laser flash photolysis and TR-EPR experiments showed that triplets of **1** were quenched effectively by TEMPO via an intramolecular process resulting in emissive spin polarized TEMPO ($k > 5 \times 10^7$ s^{-1}). Interestingly, this quenching reaction is even dominant at low temperatures in organic glasses (77 K), which was demonstrated by low-temperature phosphorescence and EPR analysis.

Intermolecular triplet quenching of **2** by TEMPO, resulting in emissive spin polarization of TEMPO, was also observed by TR-EPR (Figure 1b). A radical−triplet pair mechanism (RTPM) has been proposed as the polarization mechanism to explain the bimolecular quenching of triplet ketones by nitroxyl radicals.[2,3,16,23] This mechanism involves the interaction of nonpolarized triplets and doublets, involving the zero-field splitting of the triplet and the hyperfine interaction-mediated mixing of quartet and doublet states.[1,9]

Electron spin polarization transfer (ESPT) is another mechanism that can explain the observation of spin-polarized TEMPO upon quenching by triplets.[7,8,24,25] Spin-polarized triplet states, produced by triplet sublevel selective intersystem crossing, could transfer their polarization to nitroxides by exchange or dipole−dipole interactions.[23] Since the lifetime of the spin polarization of the triplet state of ketones is usually short (several nanoseconds),[23] the bimolecular triplet quenching with nitroxides must be very fast to be efficient. Since the rate is limited by diffusion, high concentrations of nitroxides are necessary. But TEMPO concentrations higher than 4 mM could not be used, because spin exchange interactions between the nitoxides would then modify the EPR signal. Therefore, ESPT is unlikely to occur under our experimental conditions for intermolecular quenching of triplet states of **2** by TEMPO. Since laser flash photolysis demonstrated that the intramolecular triplet quenching of **1** is fast ($\tau_t < 20$ ns), ESPT could contribute to the observed polarization of TEMPO. However, at this juncture, we do not have any direct evidence that ESPT is involved.

It has been shown by TR-EPR that the CIDEP is much larger in the case of intramolecular triplet quenching than for intermolecular quenching. A concentration of approximately 2 mM of **3** is necessary for a quantitative quenching of triplets of **2** (see Figure 2). But under these optimal conditions for intermolecular quenching, the CIDEP intensity is only 1/8 compared to the intensity for intramolecular quenching (compound **1**) at a concentration of 2 mM of **1**, **2**, and **3**. At lower concentrations (under an equimolar condition of **1** and **2** + **3**), the intramolecular enhancement effect can reach orders of magnitude larger than that observed for the intermolecular cases. At a concentration of 0.1 mM, an intramolecular enhancement of 20 was observed (compare spectra a and c in Figure 1). At concentrations of 1×10^{-5} M, no polarization for intermolecular quenching (**2** + **3**) was detected under our experimental conditions. However, spin polarization produced by intermolecular quenching of **1** was readily observed with a signal-to-noise ratio of approximately 4:1, demonstrating that even in minute concentration nitroxides can be detected intramolecularly.

Because TR-CIDEP intramolecular photosensitized detection of nitroxides has been shown to be considerably more sensitive than conventional (cw-EPR) detection, a novel method for detection of nitroxides, key intermediates in the photostabilization of polymers, may be possible.

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