



Invited paper

Thioanisole triplet: Laser flash photolysis and pulse radiolysis studies

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ARTICLE INFO

Article history:

Received 19 September 2016

Received in revised form 25 November 2016

Accepted 10 December 2016

Available online 14 December 2016

Keywords:

Thioanisole excited triplet state

Triplet quantum yield

Triplet lifetime

Energy transfer

Laser photolysis

Pulse radiolysis

ABSTRACT

Direct photogeneration of excited triplet states of thiophenol and its derivatives is substantially influenced by substitutions and structural changes. In this study the impact of the methyl substituent of thioanisole (a derivative of thiophenol, denoted as PhS-Me) relative to the basic molecular structure (PhS-H) on the dynamics of thioanisole triplet and its features has been explored by direct excitation ($\lambda_{exc.} = 266$ nm) and by sensitization. The T_1 - T_n absorption spectrum is characterized by three bands peaking at 320 nm, 360 nm and 490 nm. The triplet reactivity with triplet quenchers was determined and the triplet energy level was identified by sensitization with beta-carotene, naphthalene, and benzophenone using laser photolysis as well as solvent benzene using pulse radiolysis. The results indicate that the replacement of the hydrogen atom by the methyl substituent leads to a significant change in the thioanisole triplet properties ($\tau_{(PhSMe(T_1))} = 1.20 \mu s$, $\Phi_{T(PhSMe)} = 0.35$, $353 \text{ kJ mol}^{-1} > E_{(PhSMe(T_1))} > 287 \text{ kJ mol}^{-1}$) compared with those of thiophenol ($\tau_{(PhSH(T_1))} = 40$ ns, $\Phi_{T(PhSH)} = 0.00$, $E_{(PhSH(T_1))} = 248 \text{ kJ mol}^{-1}$).

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1. Introduction

Owing to the relatively low ionization potential and weak carbon-sulfur bond in general, sulfur compounds are used as antioxidants for organic matter ranging from polymers to living systems [1,2]. The antioxidant action of sulfur compounds is understood in terms of electron and hydrogen atom donor ability [3,4]. Indeed, they are active in many biochemical processes, including those connected with biological aging [5], pathologies such as Creutzfeldt-Jacob and Alzheimer's diseases [6,7], radical repair mechanisms [8], *cis-trans*-isomerisation of mono- and polyunsaturated fatty acid residues [9], and with oxidative stress [10].

Generally, intersystem crossing process (ISC) is expected to be enhanced by heavy atom substitution (such as the sulfur atom) which affects spin-orbit coupling interaction. It has been previously reported that direct photogeneration of excited triplet states of thiophenols is substantially influenced by substitutions and structural changes [11–15]. Triplets of thiophenol (PhSH) and its derivatives (e.g. methyl, methoxy, and chloro substituents) [11]

were not observed either by direct photoexcitation with 266 nm or by photosensitization experiment, but rather by pulse radiolysis via triplet energy transfer with solvent benzene [12]. On the other hand, triplets of thiosalicylic acids and thionaphthols were directly generated by photoexcitation [13–15]. These studies emphasized that sulfur substitution in aromatic thiophenols results in promotion of the radiationless processes over the radiative pathway.

Now an obvious question arises as to whether these dynamical behaviours can be extended to structural systems such as thioanisole (a derivative of thiophenol, in which the thiyl hydrogen is replaced by the methyl group, denoted as PhSMe) where the leaving species is a methyl group instead of a hydrogen atom. The knowledge regarding light-induced transient reaction behaviour of thioanisole remains limited [16–20]. In fact the excited singlet state of PhSMe has been characterized to some extent. To the best of my knowledge, thioanisole triplet or other possible transients, such as radicals and radical ions, generated by direct photoexcitation of PhSMe in solution have not yet been studied.

The aim of this paper is to study the effect of the structural changes of PhSMe, compared to the parent thiophenol molecule (PhSH), on the dynamic of the excited triplet state of thioanisole (PhSMe(T_1)) and its properties such as absorption spectrum, lifetime, quantum yield, energy level, and reactivity with triplet

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quenchers. Indeed, it is of particular interest to identify the other possible transients, such as radicals and radical ions, generated by direct excitation of PhSMe. This approach has been performed by laser flash photolysis and complemented by electron pulse radiolysis. The results show that the substitution of the methyl group for the S–H hydrogen in thiophenol results in an essential change on the triplet parameters of the thioanisole molecule.

2. Experimental

2.1. Chemicals

Thioanisole (PhSMe, purity $\geq 99\%$) was purchased from Sigma-Aldrich and used as received. Acetonitrile (MeCN) was purchased from VWR and was of highest spectroscopic grade (purity $\geq 99.9\%$, VWR). Benzene (purity $\geq 99.8\%$) was obtained from VWR too. Other chemicals including ferrocene (purity $\geq 98\%$), benzophenone (BP, purity $\geq 99.9\%$), naphthalene (Np, purity $\geq 99\%$) and β -carotene (β -C, purity $\geq 95\%$) were obtained from Aldrich.

2.2. Apparatus and methods

2.2.1. Nanosecond-laser flash photolysis

Spectral and kinetic data of the triplet state of PhSMe were measured with the 266 nm 4th harmonic of a Quanta-Ray GCR-11 Nd:YAG laser (Spectra Physics). Pulse widths of 3 ns and energies between 0.5 and 3.0 mJ/pulse at 266 nm were selected. The optical detection is based on a pulsed xenon lamp (XBO 150, Osram), a monochromator (Spectra Pro 275, Acton Research), R955 photomultiplier tube (Hamamatsu Photonics) or a fast Si-photodiode and a 1 GHz digital oscilloscope (TDS 684A, Tektronix). The laser power of every laser pulse was registered using a bypath with a fast Silicon photodiode. A more detailed description is reported elsewhere [21].

2.2.2. Electron pulse radiolysis

The liquid samples were irradiated with high energy electron pulses (1 MeV, 12 ns duration) generated by a pulse transformer type accelerator ELIT (Institute of Nuclear Physics, Novosibirsk, Russia). The dose delivered per pulse was measured with an electron dosimeter and was usually between 50 and 100 Gy. Detection of the transient species was performed using an optical absorption set-up consisting of a pulsed xenon lamp (XPO 450), a SpectraPro-500 monochromator (Acton Research Corporation), a R4220 photomultiplier (Hamamatsu Photonics) and a 1 GHz

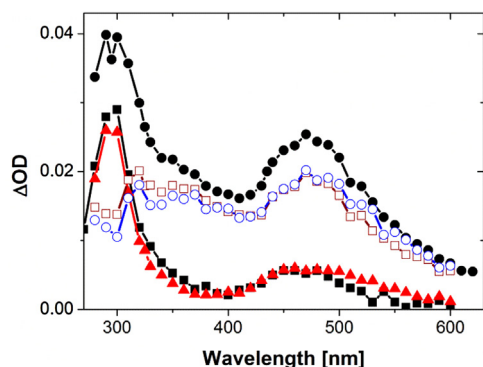


Fig. 1. Nanosecond transient absorption spectra of PhSMe ($0.04 \text{ mmol dm}^{-3}$) in MeCN: purged with N_2 taken 150 ns (filled circles), 8 μs (filled boxes), and purged with O_2 taken 150 ns (filled triangles) after the pulse. The spectrum shown by open circles or open squares; is obtained from the difference between spectra of 150 ns and 8 μs or 150 ns in the N_2 - or O_2 -containing sample, respectively; represents the T_1 - T_n absorption spectrum of PhSMe ($\lambda_{\text{exc.}} = 266 \text{ nm}$, laser energy = 3 mJ).

digitizing oscilloscope (TDS 640, Tektronix). Further details of this equipment are given elsewhere [22].

All experiments were performed at room temperature. Freshly prepared solutions were used flowing continuously through a 5 mm or 10 mm quartz sample cell in laser photolysis or in pulse radiolysis, respectively. Prior to the experiments, the solutions were bubbled with purest grade N_2 or O_2 for 15 min, and were used within one hour.

3. Results and discussion

3.1. Nanosecond-laser flash photolysis

In nitrogen saturated MeCN solution, the transient absorption spectra obtained after excitation of PhSMe ($0.04 \text{ mmol dm}^{-3}$) at 266 nm is shown in Fig. 1. The spectrum taken 150 ns after the pulse displayed two broad absorption bands in the 300–320 nm and 450–500 nm regions as well as a shoulder in the range between 350 nm and 375 nm. After 8 μs the shoulder completely disappeared, the absorption intensity of other bands was decreased, and the absorption spectrum which became narrow exhibited only two bands; a sharp and intense one centered at

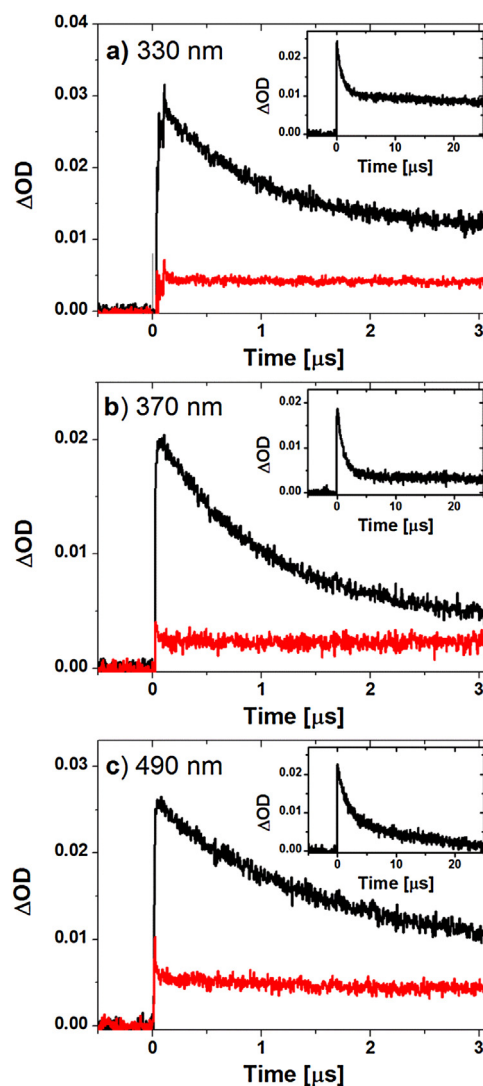


Fig. 2. Experimental time profiles of PhSMe ($0.04 \text{ mmol dm}^{-3}$) in N_2 (black lines) and O_2 (red lines) saturated MeCN solutions at different wavelengths ($\lambda_{\text{exc.}} = 266 \text{ nm}$, laser energy = 3 mJ). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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