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Quantitative Description of the Deactivation Channels of the First Excited Singlet State of 2- and 4-Thiosalicylic Acids

Yasser M. Riyad, Ralf Hermann, and Ortwin Brede*

University of Leipzig, Interdisciplinary Group Time-Resolved Spectroscopy, Permoserstr. 15,
D-4303 Leipzig, Germany

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On the bases of picosecond and nanosecond laser flash photolysis with detection by emission and absorption spectroscopy, a quantitative description is given of all of the deactivation channels of the first excited singlet state of 2- ands 4-thiosalicyclic acids (TS) such as fluorescence, intersystem crossing (ISC), chemical dissociation into radicals, and radiationless internal conversion (IC). For this purpose, the investigated compounds were studied in solvents of increasing polarity: 1-chlorobutane, acetonitrile, ethanol, and water. As an exception for thiols, and in contrast to recent findings on thiophenol and its methyl- and methoxy-substituted derivatives, the photoinduced first excited triplet state of the thiosalicyclic acids was directly observed by its T_1-T_n absorption spectra and characterized by sensitization experiments. According to the direct determination of the quantum yields of all deactivation channels of the first excited singlet state of 2- and 4-thiosalicylic acid isomers, it was found that the compounds studied have small fluorescence quantum yields ($\Phi_F = 0.003-0.009$) and higher ones for triplet formation ($\Phi_T = 0.10-0.35$) and S−H photodissociation ($\Phi_D = 0.05-0.15$). As a difference to the total, the radiationless internal conversion ($\Phi_{IC} = 0.6-0.8$) was found to be the dominating process.

1. Introduction

Aliphatic as well as aromatic thiols are known as efficient antioxidants[1,2] of organic matter ranging from polymers to living systems. In biological systems, the widespread thiols play a prominent role. Because of their low ionization potential and the relatively weak S−H bond, they are active in radical repair and deactivation as well as in cellular redox processes.[3,4] Thiols are often thought to act as protectors against ionizing radiation via their radical scavenging activity. In addition, it was found that thiyl radicals also cause biologically important chemical changes such as the efficient cis−trans isomerization of mono- and polyunsaturated fatty acid residues in model membranes via a catalytic action.[5,6]

Generally, it is known that photoexcitation of aromatic thiols results in the formation of phenylthiyl radicals.[7−9] Information does not exists on the mechanism of the radical formation nor does any quantitative data of the deactivation channels of the first excited singlet state of the thiols. In a previous paper,[10] we reported on laser flash photolysis of thiophenol and its methyl derivatives. Surprisingly, after flashing thiophenols with 266 nm photons, no directly photogenerated triplets could be found. Therefore, the observed phenylthiyl radicals should result from the homolytic S−H bond cleavage of the first excited singlet state. Triplet states of thiophenols, however, were found in pulse radiolytic sensitization experiments.[10]

Introducing a strong electron-withdrawing substituent such as the carboxyl group could change the photophysical parameters; they differ from the parent thiophenol molecule parameters. In this paper, we report on the photophysical and photochemical properties of monophotonic-excited thiosalicylic acids (2-TS, or 4-TS). By different time-resolved methods such as ps- and ns-laser photolysis supplemented by pulse radiolysis, all of the deactivation channels of the first excited singlet state of the thiosalicylic acids were characterized quantitatively, see eqs 2−6. Under our experimental conditions, self-quenching (6) does not play any significant role because of the concentration chosen. Indeed, for the thiolsalicyclic acids we found the triplet states 2-TS^{T1} and 4-TS^{T1}.

$$\mathrm{TS} + h\nu_1 \rightarrow \mathrm{TS(S_1)} \tag{1}$$

$$\mathrm{TS(S_1)} \rightarrow \mathrm{TS(S_0)} + h\nu_2,\ \text{fluorescence} \tag{2}$$

$$\rightarrow \mathrm{TS(S_0)} + \mathrm{E},\ \text{internal conversion} \tag{3}$$

$$\rightarrow \mathrm{TS(T_1)},\ \text{intersystem crossing} \tag{4}$$

$$\rightarrow \mathrm{TS}^{\bullet} + \mathrm{H}^{\bullet},\ \text{fragmentation} \tag{5}$$

$$+\ \mathrm{TS} \rightarrow 2\ \mathrm{TS(S_0)},\ \text{self-quenching} \tag{6}$$

TS = thiosalicylic acid isomers, E = excess heat.

2. Experimental Section

2.1. Materials. Water, acetonitrile (AN), ethanol (EtOH), and 1-chlorobutane (1-BuCl) of the highest spectroscopic grade were chosen as solvents (99.9%, VWR). Benzophenone (99.9%), naphthalene (99%), and β-carotene (95%) were obtained from Aldrich. Phenol (99.5%) was of high grade from Riedel-de Haen. Water treated in a Millipore milli-Q plus system was used for the experiments in aqueous solutions. 2-Thiosalicylic acid (98%, VWR) and 4-thiosalicylic acid (98%, Aldrich) were used after recrystallization in alcohol−water mixture (1:2). The structures of the investigated compounds in the present study are shown below.

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* Corresponding author. Fax: +49-341-235-2317. E-mail: brede@mpgag.uni-leipzig.de.

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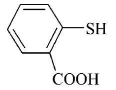
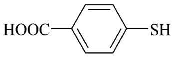


2-Thiosalicylic acid



4-Thiosalicylic acid

2.2. Apparatus and Methods. The ground-state optical absorption and fluorescence spectra were recorded with an UV−Vis spectrophotometer (UV-2101 PC, Shimadzu) and a FluoroMax-2 (Instruments S. A., Jobin Yvon-Spex), respectively.

ps-Laser Photolysis. The fluorescence lifetimes were measured with an amplified (CPA) 10 Hz Ti:sapphire femtosecond-UV laser system. After excitation of thiosalicylic acids with a 250 fs (fwhm) UV laser pulse at 253 nm, a highly sensitive streak camera C5680/M5676 (Hamamatsu Photonics) recorded the fluorescence kinetics. A time resolution of 1ps was achieved for the emission studies by applying the deconvolution technique.[11]

ns-Laser Flash Photolysis. To investigate spectral and kinetic data of the carboxyphenylthiyl radicals and thiosalicylic acid triplet states, the real-time nanosecond laser photolysis with detection by absorption spectroscopy was applied. The solutions were photolyzed by the fourth harmonics (266 nm) of a Quanta-Ray GCR-11 Nd:YAG laser (Spectra Physics). Pulses of <3 ns duration (fwhm) with energies of 0.5 mJ were used. The optical detection system consisted of a pulsed Xenon lamp (XBO 150, Osram), a monochromator (SpectraPro-275, Acton Research), a R955 photomultiplier tube (Hamamatsu Photonics) or a fast Si-photodiode with 1 GHz amplification, and a 500 MHz digitizing oscilloscope (DSA 602 A, Tektronix). Every pulse of the laser power was monitored using a bypath with a fast Si photodiode. The laser flash photolysis setup is reported elsewhere in more detail.[12]

Electron Pulse Radiolysis. The liquid samples were irradiated with high energy electron pulses (1 MeV, 12ns 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 setup consisting of a pulsed Xenon lamp (XPO 450), a SpectraPro-500 monochromator (Acton Research Corporation), a R4220 photomultiplier (Hamamatsu Photonics), and a 1 GHz digitizing oscilloscope (TDS 640, Tektronix). Further details of this equipment are given elsewhere.[13]

All experiments were performed at room temperature. Freshly prepared solutions were used flowing continuously through a 5 or 10 mm quartz sample cell in laser photolysis or in pulse radiolysis, respectively. Prior to the laser photolysis and the pulse radiolysis experiments, the solutions were deoxygenated by bubbling with purest grade N_2 or saturated with the desired gas for 15 min and were used within 1 h. The pH of the solutions was the one obtained with thiosalicylic acid isomers; in aqueous solutions, the pH generally ranged from 3.8 to 4.0 (unless specified otherwise).

3. Results and Discussion

3.1. Fluorescence Kinetics and Quantum Yield. *3.1.1. Steady-State Fluorescence Study*. The fluorescence spectra of 2-thiosalicylic acid were studied in polar (water, acetonitrile, ethanol) and nonpolar surroundings (1-chlorobutane), see Figure 1A. In each of the solvents, the fluorescence spectrum consists of a broad and unstructured band. The fluorescence maximum, λ_F(max), and the intensity are dependent on the solvent type. The fluorescence maxima generally exhibit a red shift with increasing polarity of the solvent used. This is particularly pronounced for 2-TS with λ_{max}= 355 nm in 1-BuCl which shifts to 370, 375, and 390 nm in AN, EtOH, and water, respectively (see Figure 1A).

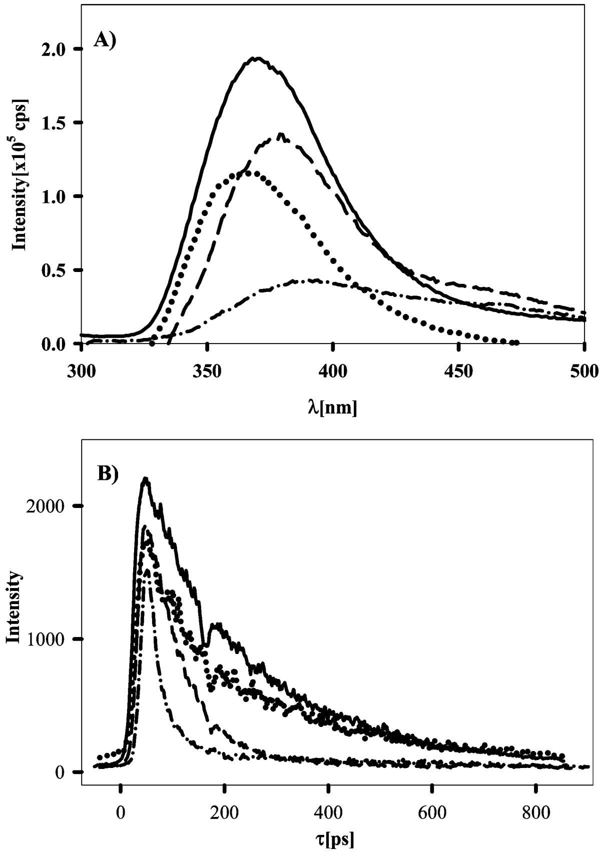


Figure 1. (A) Fluorescence spectra of 2-TS (0.4 mmol dm^{-3}) in 1-chlorobutane (•••) × 2, ethanol (− −), acetonitrile (—), and water (—•—) solutions at room temperature. (B) Time-resolved fluorescence for 2-TS in various solvents.

For 4-thiosalicylic acid, the fluorescence spectra taken in different solvents are shown in Figure 2A. The fluorescence maximum shifts from 320 nm (1-chlorobutane, ethanol) to 325 and 360 nm in acetonitrile and water, respectively.

3.1.2. Picosecond Fluorescence Measurements. The fluorescence lifetimes, τ_F, were determined by recording the fluorescence decay using a streak camera for the S_1−S_0 transition of 2- and 4-thiosalicylic acids in the solvents mentioned above. For 2-TS, the kinetic analysis of the traces (see Figure 1B) has revealed a monoexponential decay function in all solvents. The fluorescence lifetimes, τ_F, thus obtained are given in Table 1. The fluorescence lifetime measured in aprotic acetonitrile (τ_F = 175 ps) is longer than the one in the nonpolar 1-chlorobutane (τ_F = 130 ps). In contrast, the lifetimes are extremely short in protic solvents, such as ethanol (τ_F = 60 ps) or water (τ_F = 40 ps).

For 4-TS, the kinetic analysis of the traces in EtOH and AN has revealed a monoexponential function, whereas in water and 1-chlorobutane, the kinetic analysis has revealed only a biexponential-function, see Figure 2B. It was found that one component decays in a few tens of picoseconds, and the other one is of the order of several hundreds of picoseconds. The short component of nonsingle-exponential decay behavior is either attributed to the spectral shifts across the detection

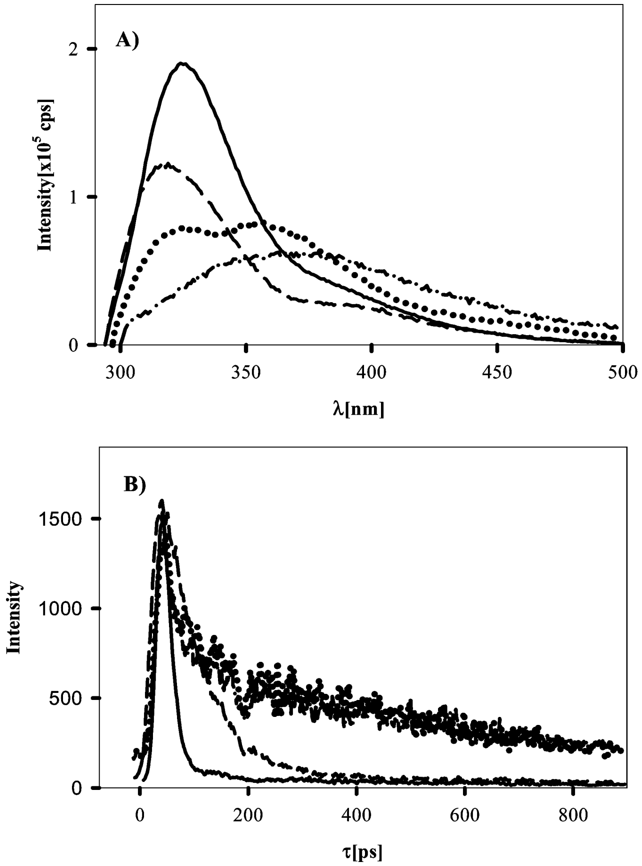


Figure 2. (A) Fluorescence spectra of 4-TS (0.02 mmol dm^{-3}) in 1-chlorobutane (•••) x 2, ethanol (— —) × 3.8, acetonitrile (—)/1.25, and water (—•—) × 2.3 solutions at room temperature. (B) Time-resolved fluorescence for 4-TS in various solvents.

TABLE 1: Fluorescence Kinetics and Quantum Yields of All Deactivation Channels of the First Excited Singlet State of 2- and 4-Thiosalicylic Acids in 1-Chlorobutane (1-BuCl), Ethanol (EtOH), Acetonitrile (AN), and Water at Room Temperature[a]

compound	solvent	τ_F[b] [ps]	k_r [10^7 s^{-1}]	Φ_F	Φ_T	Φ_D	Φ_{IC}
2-TS	1-BuCl	130	5.4	0.007	0.10	0.10	0.80
	EtOH	60	6.7	0.004	0.10	0.10	0.80
	AN	175	4.0	0.007	0.10	0.15	0.75
	water	40					
4-TS	1-BuCl	$\tau_1 = 200$ $\tau_2 = 30$	4.5	0.009	0.20	0.05	0.75
	EtOH	60	5.0	0.003	0.35	0.10	0.55
	AN	15	60.0	0.009	0.35	0.10	0.55
	water	$\tau_1 = 400$ $\tau_2 = 15$					

[a] The yields are within ±10% accuracy. [b] The error is about ±10%.

wavelength[14] or to a $S_0 \leftarrow S_2$ transition. The spectral shifts apply when the time-scales for vibrational relaxation and emission are comparable which causes time-dependent spectral shifts. This point, however, was not further investigated. The fluorescence data are summarized in Table 1. Generally, the long time behavior is used for the evaluation of fluorescence quantum yield data.

Under the protic conditions, the fluorescence lifetimes are shorter than in nonpolar and aprotic solutions. This might be caused by the low stability of the first excited singlet state S_1 and it points to a more efficient nonradiative relaxation. In EtOH, the shortening of the fluorescence lifetime is probably caused by the presence of the carboxylic group which facilitates hydrogen-bonding interactions.[15] In water, it is probably interpreted by the more intense overtones of the OH-vibrations than in EtOH (as expressed by the corresponding OH-vibrational bands at around 3100 cm^{-1} obtained by IR spectroscopy[16]). Such influences may increase the yield of the nonradiative IC-deactivation route considerably.

3.1.3. Fluorescence Quantum Yield (Φ_F). Fluorescence quantum yields of thiosalicylic acids were determined by steady-state fluorescence measurements using phenol in cyclohexane, acetonitrile, and ethanol as standards ($\Phi = 0.083$, 0.19, and 0.16, respectively[17]). Under optically matching conditions at $\lambda_{exc} = 266$ nm, i.e., $OD_{266\ nm}$ (ArOH) = $OD_{266\ nm}$ (TS), Φ_F was determined for diluted solutions ($\leq 5 \times 10^{-4}$ mol dm^{-3}) with the method of comprising the integrals of reference and sample substance over the whole emission range.[18,19] The fluorescence quantum yield values determined in 1-BuCl, EtOH, and AN are given in Table 1. It is obvious that both TS isomers fluoresce with a low quantum yield and, generally, the emissions do not show a pronounced solvent dependence. Using the fluorescence quantum yield, the radiative constant could be determined by $k_r = \Phi_F/\tau_F$, see Table 1. Moreover, it was found that the radiative lifetimes ($\tau_0 = 1/k_r$) were in the range from 15 to 25 ns. Therefore, in all cases there are large differences between the experimental fluorescence (τ_F) and radiative lifetimes (τ_0). Consequently, this emphasizes that radiationless (ISC or IC) and/or photodissociation channels play the main role in the deactivation process of the first excited singlet state of thiosalicylic acids.

A thorough analysis of the deactivation mechanism of the first excited singlet state entails a detailed study of all nonradiative processes (3−5). According to whether the transition is spin-allowed or spin-forbidden, the radiationless transitions are known as internal conversion (IC) or intersystem crossing (ISC), both in connection with vibrational relaxation (VR). In the next sections, the radiationless processes as well as the fragmentation will be characterized from the kinetic and spectral point of view.

3.2. ns-Laser Flash Photolysis. *3.2.1. 2-Thiosalicylic Acid (2-TS).* In oxygen-free saturated solution, the transient absorption spectra obtained in the 266 nm laser flash photolysis of 2-TS (0.3 mmol dm^{-3}) are shown in Figure 3. The spectra exhibit three bands, a sharp and intense band with a maximum at 280 nm, a weak band at 340 nm, and a broad and moderate one in the range between 460 and 500 nm. The decay monitored at 500 nm (Figure 3d) showed a first-order kinetics corresponding to a lifetime of 300 ns. In contrast, the decay kinetics monitored at 280, 340, and 460 nm showed mixed first and second-order kinetics which may arise from the existence of more than one transient.

In the presence of oxygen, the absorption band observed at 500 nm was markedly quenched as shown in Figure 3. Furthermore, the saturation of the solution with oxygen enabled the separation of the long-lived transient absorbing at λ_{max} = 290 and 460 nm; it was found to be insensitive toward oxygen, see Figure 3. Moreover, it is evident that in the presence of oxygen the decay of the short-lived transient becomes faster. Because of this typical behavior, we assign the short-lived transient to be the 2-thiosalicylic acid triplet, 2-TS(T_1) (λ_{max} at 290 and 460−500 nm). The long-lived transient is attributed to the 2-carboxyphenylthiyl radical as found in a former study.[20] Indeed, the thiyl radicals decay by recombination according to the second-order kinetics close to the diffusion-controlled process (7).[21]

Hence, the absorption spectra consist of the thiol-derived species such as 2-TS(T_1) (λ_{max} at 290, 510 nm), and 2-TS$^\bullet$ (λ_{max}

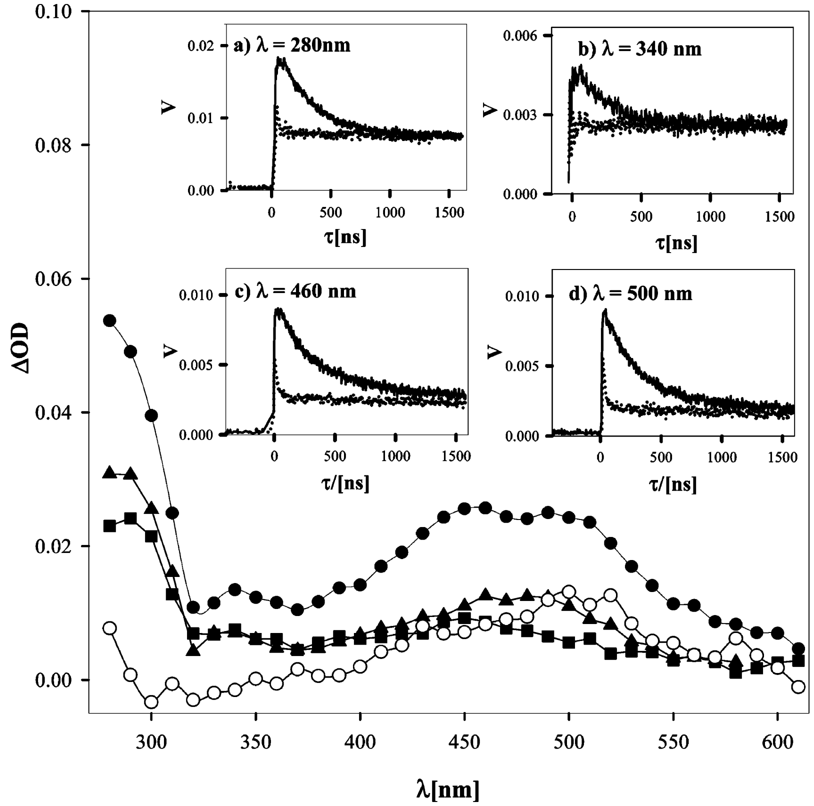


Figure 3. Transient absorption spectra of acetonitrile solution of 0.3 mmol dm^{-3} 2-TS: purged with N_2 taken 50 (●), 1000 ns (▲) after the pulse, (■) purged with O_2 taken 50 ns, and (○) difference spectrum between former and later spectra (laser power = 4 mJ). The insets (a−d) show time profiles of N_2 (—) and O_2 (···) saturated solutions at different wavelengths.

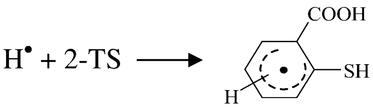
TABLE 2: Kinetic and Spectral Parameters of the Triplet State and Thiyl Radicals of 2- and 4-Thiosalicylic Acids

		TS(T$_1$)			TS$^\bullet$ [b]	
substance	solvent	λ_{max}(T$_1$) [nm]	triplet deactivation[a] [$\times 10^6$ s^{-1}]	k_{10} [$\times 10^9$ dm^3 mol^{-1} s^{-1}]	λ_{max}(TS$^\bullet$) [nm]	$\epsilon_{TS}{}^\bullet$ [$\times$ dm^3 mol^{-1}cm^{-1}]
2-TS	1-BuCl	500	3.5			
	EtOH	500	5.0	4.4 (with β-C)	470	2500 ± 200
	AN	510	3.5			
4-TS	1-BuCl	390	0.2	7.5 (with β-C)		
	EtOH	400	0.2			
	AN	380	0.15	1.7 (with N)	480	2700 ± 200

[a] Values are within ±10%. [b] The spectral data of the thiyl radicals were measured in N_2O-purged aqueous alkaline solutions at pH 12 in the visible region by pulse radiolysis.

at 290, 460 nm). As an additional and minor effect, the cyclohexadienyl radical of 2-thiosalicylic acid (low yield, λ_{max} = 340 nm) was formed upon the reaction of the dissociative hydrogen radicals (cf. equation 5) with the benzene ring of 2-TS as shown by eq 8.[22,23]

$$2\ \text{2-TS}^\bullet \rightarrow \text{product} \qquad k_7 \approx 2 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \quad (7)$$



(8)

The triplet lifetimes of 2-TS vary in the range from τ_T = 200 to 300 ns, depending on the type of the solvent. The absorption bands of 2-TS(T$_1$) decay according to the first-order kinetics with a rate of 3.3 × 10^6 s^{-1} as shown in the insets of Figure 3a-c. As already mentioned, 2-TS(T$_1$) is efficiently quenched in the presence of oxygen, as indicated by a reduction in lifetime (to about 25 ns) and yield (9). The corresponding kinetic and spectral data of 2-TS(T$_1$) are given in Table 2. Subtracting the

$$\text{2-TS(T}_1) + O_2 \rightarrow \text{2-TS} + O_2 \qquad k_9 = 4 \times 10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \quad (9)$$

radical background absorption measured in oxygen-containing sample from the overall absorption measured in nitrogen purged solution; enables the separation of the triplet spectrum of the 2-TS(T$_1$), see Figure 3.

3.2.2. 4-Thiosalicylic Acid (4-TS). In the same manner as described above, laser photolysis of oxygen-free acetonitrile solution of 4-TS (0.02 mmol dm^{-3}) was carried out (see Figure 4). The obtained absorption spectra exhibit maxima at λ = 310 and 390 nm, a broad band between 460 and 520 nm, and a shoulder at 360 nm. The decay monitored at 390 nm (Figure 4d) showed a first-order kinetics corresponding to a lifetime τ = 7 μs. In the presence of oxygen, the absorption band observed at 390 nm was markedly quenched, whereas the absorption with λ_{max} = 300 nm was found to be insensitive toward oxygen, as shown in Figure 4. In the oxygen containing solution, the

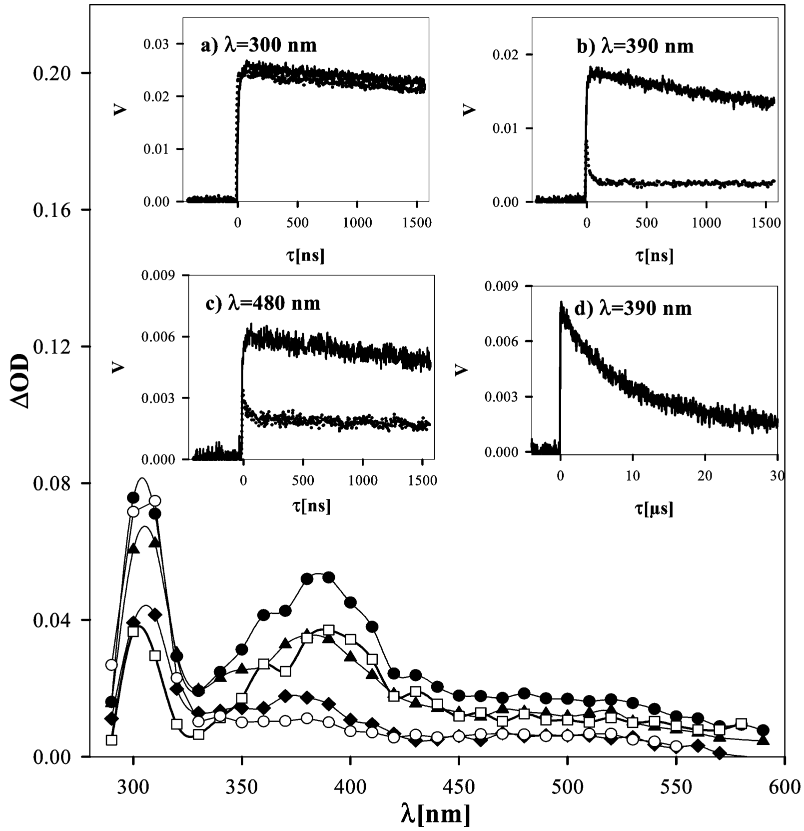


Figure 4. Transient absorption spectra of acetonitrile solution of 0.02 mmol dm^{-3} 4-TS: purged with N_2 taken 0.1 (●), 2 (▲), and 10 μs (◆) after the pulse, (□) difference spectrum between (●) and (◆), (○) purged with O_2 taken 0.1 μs (laser power = 3 mJ). The insets (a−c) and (d) show short and long time profiles of N_2 (—) and O_2 (•••) saturated solution at different wavelengths.

insensitive transient absorbing at λ_{max}= 300 and partially in the range from 460 to 520 nm is assigned to be 4-TS$^{\bullet}$. However, the transient which is efficiently quenched by oxygen (up to $\tau \sim$ 30 ns) is assigned to be 4-TS(T_1) (λ_{max}=390 nm). The shoulder peaking around λ = 360 nm is supposed to be caused by the cyclohexadienyl radical, as mentioned before for 2-thiosalicylic acid.

The absorption of 4-TS(T_1) decays much slower than that of 2-TS(T_1). The triplet lifetimes of 4-TS vary in the range from τ_T = 4.5 to 7.0 μs, depending on the type of the solvent. The corresponding spectral and kinetic data are given in Table 2.

3.2.3. Triplet Energy Transfer. To characterize the thiosalicylic acid triplets TS(T_1) further, we carried out sensitization experiments with β-carotene (β-C, E_{T1} = 88 kJ mol^{-1}) and naphthalene (N, E_{T1} = 253 kJ mol^{-1}).[24] Because of the relatively high triplet energy differences between donor and acceptor (in particular for β-C), a diffusion-controlled rate is assumed for the energy transfer formulated in eq 10.[25, 26]

$$\mathrm{TS(T_1) + A \rightarrow TS + A(T_1)} \text{ where } \mathrm{A} = \beta\text{-C or N} \quad (10)$$

Flashing a deaerated solution of 0.2 mmol dm^{-3} 4-TS in acetonitrile containing 0.06 mmol dm^{-3} β-C, we got the pronounced triplet absorption of β-carotene formed in a time-resolved manner, see Figure 5A. The time profile given as inset (a) shows the kinetics of β-C(T_1) formation well. Using different concentrations of β-C, the rate constant of the energy transfer was determined to be $k_{10} = 7.5 \times 10^9$ dm^3 mol^{-1} s^{-1} as derived from the Stern−Volmer plot (inset (b)), see Table 2.

In the analogous manner, laser photolysis of N_2-saturated solution of 4-TS (1 mmol dm^{-3}) in the presence of naphthalene (0.2 mmol dm^{-3}) resulted in an absorption band with an absorption maximum at 410 nm, which is characteristic of the N(T_1), see Figure 5B. The N(T_1) formation can also be seen from the time profile given as inset of Figure 5B(b). Consequently, the 4-TS(T_1) decay at 390 nm became faster in the presence of naphthalene (inset (a) of Figure 5B), whereas at λ = 410 nm an indication of the time-resolved formation of N(T_1) arose (inset (b)). The rate constant in the case of N as a quencher amounts to $k_{10} = 1.7 \times 10^9$ dm^3 mol^{-1} s^{-1}. Therefore, we conclude that the energy of the first excited triplet state of 4-TS(T_1) is above those of N(T_1), i.e., $E_{T1} >$ 253 kJ mol^{-1}. Flashing samples of 2-TS (0.3 mmol dm^{-3}) in the presence of β-carotene (0.2 mmol dm^{-3}) gave quite analogous results (not shown here), and the data are given in Table 2.

3.2.4. Triplet Quantum Yield (Φ_T). To determine the quantum yields of the thiosalicylic acids triplets, we performed a sensitization experiment using the triplet energy transfer from thiosalicylic acids to β-carotene (11). Since this triplet spectrum is superimposed with the red self-absorption of β-carotene, we adjusted the β-C triplet extinction coefficient in a further sensitization experiment with benzophenone (BP) (12), (Φ_T = 1).[24,27] Monitoring the experiment at λ = 515 nm, the immediately formed BP(T_1) decays under the formation of the β-C(T_1) enableing a direct comparison of the absorptions under the required conditions.

The experiments were carried out under optically matching conditions (13) at low laser energy, ~0.6 mJ per pulse. The comparably low self-absorption of β-C at the laser wavelength (266 nm) was compensated by using constant concentrations. Furthermore, it should be remembered that its direct excitation does not result in triplet-excited molecules. Therefore, in a solution of 1 mmol dm^{-3} 2-TS or 0.05 mmol dm^{-3} 4-TS and a constant amount of 0.1 mmol dm^{-3} β-carotene (β-C), the 266 nm laser photolysis excites primarily thiosalicylic acid molecules

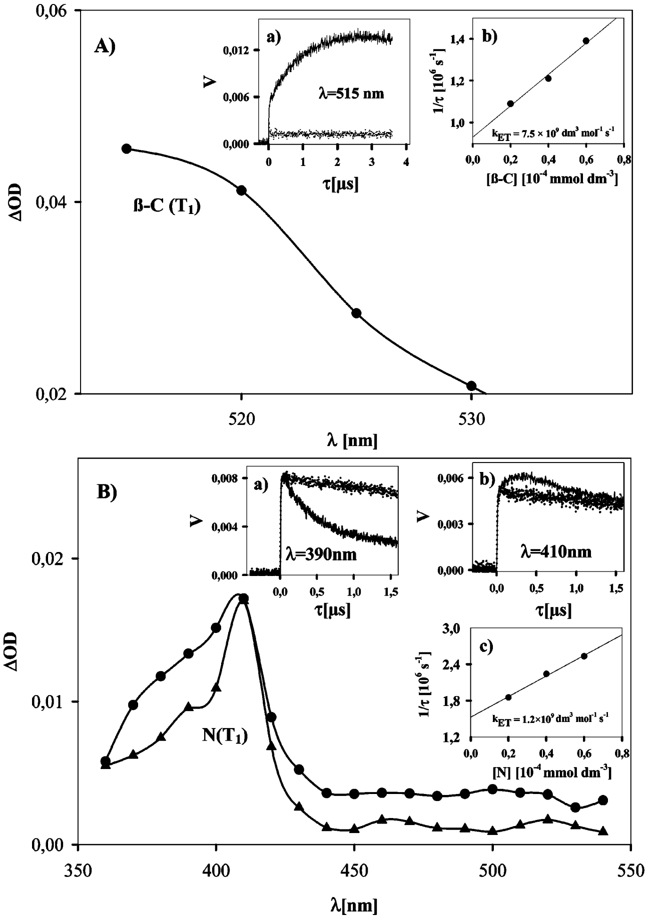


Figure 5. Transient absorption spectra of N_2-purged acetonitrile solution of (A) 0.2 mmol dm^{-3} 4-TS in the presence of 0.06 mmol dm^{-3} β-C taken 500 ns after the pulse and (B) 1 mmol dm^{-3} 4-TS in the presence of 0.2 mmol dm^{-3} N taken 100 (●) and 500 ns (▲) after the pulse (laser power = 0.7 mJ). The insets (a) and (a, b) in A and B show the time profiles of N_2 saturated acetonitrile solutions without (···) or with (—) triplet quencher at different wavelengths, respectively. The insets (b) and (c) in A and B show the Stern−Volmer plot of observed rate constants (k_{obs}) against quencher concentrations.

and transforms them to triplets. Subsequently, we observed the time-resolved formation of β-C(T_1) according to eq 11.

$$\mathrm{TS(T_1)} + \beta\text{-C} \rightarrow \beta\text{-C(T_1)} + \mathrm{TS} \qquad (11)$$

$$\mathrm{BP(T_1)} + \beta\text{-C} \rightarrow \beta\text{-C(T_1)} + \mathrm{BP},\ \Phi_T\,(\mathrm{BP})_{525\ \mathrm{nm}} = 1 \qquad (12)$$

$$\mathrm{OD}_{266\ \mathrm{nm}}(\mathrm{BP}) = \mathrm{OD}_{266\ \mathrm{nm}}\,(\mathrm{TS}) \qquad (13)$$

The thiosalicylic triplet quantum yields Φ_T(TS) were obtained by the ratio of the ΔOD_{515} values of β-carotene triplet formed via the energy transfer (eqs 11 and 12) under the conditions mentioned above (13):

$$\phi_T(\mathrm{TS}) = \frac{\Delta \mathrm{OD}_{515\mathrm{nm}}(\mathrm{TS} \rightarrow \beta\text{-C}_{\mathrm{reaction\ 11}})}{\Delta \mathrm{OD}_{515\mathrm{nm}}(\mathrm{BP} \rightarrow \beta\text{-C}_{\mathrm{reaction\ 12}})} \qquad (14)$$

Triplet quantum yields of thiosalicylic acids Φ_T were thus determined for solutions in 1-chlorobutane, ethanol and acetonitrile (see Table 1). The data showed that the triplet quantum yields of 4-TS are apparently larger than those of 2-TS, and generally, only minor or no solvent effects were observed for the intersystem crossing of the first excited singlet states of the thiosalicylic acids.

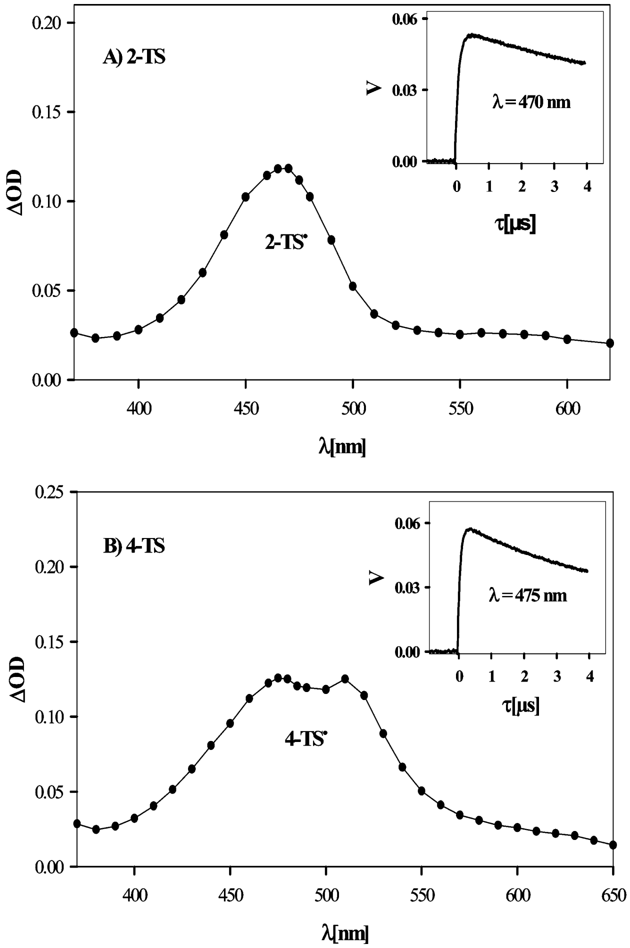


Figure 6. Maximum transient optical absorption spectra recorded on pulse radiolysis of N_2O purged aqueous solutions of thiosalicylic acids (2 mmol dm^{-3}) in the presence of 0.02 mol dm^{-3} NaN_3 at pH = 12. The insets show time profiles of N_2-saturated solutions λ maxima.

Surprisingly, direct photoexcitation of thiophenol and its substituted (methyl, methoxy or chloro) compounds formed the thiyl radicals as the only intermediate, while triplet formation could not be observed.[10] Nevertheless, the triplet states of those aromatic thiols could be identified and characterized by radiation chemical sensitization using the triplet state of the solvent benzene.[10] This can be explained by the selection criteria for ISC known as El-Sayed's rule, where transitions $^1(\pi,\pi^*) \leftrightarrow {}^3(\pi,\pi^*)$ are forbidden. Compared with the other thiophenols, the thiosalicylic acids represent an exception caused by the electronic structure of the carboxylic group. Details will be discussed in a subsequent paper which will be concerned to the majority of aromatic thiols.

3.3. Quantum Yield of the Photodissociation of the S−H Bond of TS (S_1). *3.3.1. Extinction Coefficient of the Thiyl Radical (ϵ_R).* To verify the spectra of 2- and 4-carboxyphenylthiyl radicals (TS•) as well as for the calculation of their yields, pulse radiolysis studies of the thiosalicylic acids were performed in aqueous alkaline (pH 12) solution under N_2O atmosphere in the presence of sodium azide. Under these conditions, the solvated electrons are converted to •OH, reaction 16, with the subsequent generation of azide radicals, reaction 17. The azide radicals then react with the thiolate anions leading to the quantitative formation of thiyl radicals and azide anions (18) (Figure 6). The rate constants k_{18} at pH 12 were calculated to be in the range from (4−6) × 10^9 dm^3 mol^{-1} s^{-1} for thiosalicylic acids. In the kinetic analysis, we had no indication of the formation of disulfide radical anions, as observed for aliphatic thiols.[28,29]

$$H_2O \rightarrow H^\bullet, OH^\bullet, e_{solv}^- \tag{15}$$

$$e_{solv}^- + N_2O \rightarrow OH^\bullet + OH^- + N_2 \tag{16}$$

$$OH^\bullet + N_3^- \rightarrow OH^- + N_3^\bullet \tag{17}$$

$$TS^- + N_3^\bullet \rightarrow TS^\bullet + N_3^- \qquad k_{18} = 5 \times 10^9\ dm^3\ mol^{-1}\ s^{-1} \tag{18}$$

Pulse radiolysis of a N_2O-saturated alkaline solution containing 0.02 mol dm^{-3} sodium azide leads to the production of the azide radical ($N_3^\bullet$, $\lambda_{max} = 275$ nm). As expected, the transient absorption spectrum monitored by pulse radiolysis of such a solution containing 2 mmol dm^{-3} of 2-TS at pH = 12 (Figure 6A) exhibits a pronounced band at 470 nm. According to laser photolysis results, we ascribe the spectrum in Figure 6A to the 2-carboxyphenylthiyl radical obtained according to eq 18. The value of the extinction coefficient of the 2-carboxyphenylthiyl radical, ϵ_R, given in Table 2 was determined from the comparison of the 2-carboxyphenylthiyl and azide absorptions (measured separately) using $\epsilon(N_3^\bullet)_{275\ nm} = 2300\ dm^3\ mol^{-1}\ s^{-1}$.[30]

In the same manner as for 2-TS and under similar experimental conditions described above, the transient absorption spectrum of the 4-carboxyphenylthiyl radical, see Figure 6B, which exhibits two peaks at 475 and 510 nm, was observed. This agrees with the laser photolysis observation and with the data of Grodkowski and Neta.[31] Furthermore, the ϵ_R of the 4-carboxyphenylthiyl radical was calculated to be 2700 dm^3 mol^{-1} cm^{-1}, see Table 2.

3.3.2. Quantum Yield of the Thiyl Radicals (Φ_D). The radical quantum yields of the S−H bond photodissociation of the $TS(S_1)$ were determined by time resolved ns-laser photolysis using the benzophenone triplet, $BP(T_1)$, as an external standard. Under optically matched conditions at 266 nm, i.e., $OD_{266\ nm}$ (BP) = $OD_{266\ nm}$ (TS), the Φ_D values were derived for N_2-purged diluted solutions (≤ 0.5 mmol dm^{-3}) by comparing the concentration of reference (BP^{T1}) and sample radical ($TS^\bullet$) transients. The process was performed at low laser energy ~0.6 mJ per pulse to avoid two-photon ionization. The data are given in Table 1 for the three solvents 1-chlorobutane, ethanol, and acetonitrile.

Surprisingly, the radical quantum yields of thiosalicylic acids are much smaller than those of thiophenol and most of its isomers. This could be attributed to the efficient influence of the carboxyl group on the dissociation process. In other words, the dissociation process seems to be influenced by the electronic structure of the substituent on the aromatic ring. Thus, carboxyl as an electron-withdrawing group would increase the strength of the S−H bond more than thiophenol itself.[32,33] Hence, the bond dissociation energy of the S−H bond of thiosalicylic acids seems to be higher than those of thiophenol itself.

Finally, the question remains whether the thiosalicylic triplet states contribute to the formation of the thiyl radicals. For 4-TS, the absorption time profile at 300 nm given in Figure 4 belongs only to the thiyl radical. In the presence of O_2, the 4-$TS(T_1)$ was efficiently quenched, whereas the yield of the thiyl radical observed at 300 nm remains unchanged. Therefore, there seems to be no evidence for thiyl radical formation via dissociation of 4-$TS(T_1)$.

3.4. Deactivation of the First Excited Singlet States by Internal Conversion (IC). The remaining process is the radiationless deactivation from the first excited singlet (S_1) to the singlet ground state (S_0) which occurs via internal conversion (IC). Here the excitation energy is consumed by changes in the molecular geometry or it is dissipated into the surroundings. The overall IC process can be understood in terms of the rate controlling resonance interaction (RI) between the S_1- and the S_0-vibration levels followed by rapid vibration relaxation (VR). In contrast to the other deactivation channels studied, there is no direct measure of the internal conversion efficiency (3). Using the directly determined data of the other competing $TS(S_1)$ deactivation processes (2,4,5), the quantum yield difference to the total gives the fraction of the internal conversion (19).

$$\Phi_{IC} = 1 - (\Phi_F + \Phi_{ISC} + \Phi_D) \tag{19}$$

The data are given in Table 1 together with the experimentally determined quantum yields of the deactivation channels studied described in the previous sections and estimated for 1-chlorobutane, ethanol, and acetonitrile solutions. Generally, the approach used cannot distinguish between the RI and VR contribution, for physical reasons the vibration relaxation is nearly unaffected by the influences considered, whereas relaxation by resonance interaction depends on the overlap of the corresponding vibration levels (Franck−Condon factors).

In all cases, however, Φ_{IC} values are larger than 0.5. For 2-TS, the quantum yield of internal conversion is estimated to be around $\Phi_{IC} = 0.8$, whereas the value for 4-TS amounts to $\Phi_{IC} = 0.6-0.8$. For both thiosalicylic acids studied, the internal conversion is unaffected by the nature (dielectric constant) of the surrounding molecules within the experimental errors. Therefore, vibrational relaxation determines the IC channel of nonradiative relaxation to a large extent. Relaxations from $S_n \rightarrow S_1$ appear with rate constants $10^{-11}-10^{-14}\ s^{-1}$, whereas the $S_1 \rightarrow S_0$ relaxation shows slower rates.

When the influence of the carboxyl group position at the aromatic moiety on the deactivation mechanism of the first excited singlet state is analyzed, it should be noted that 2-$TS(S_1)$ exhibits considerably lower Φ_F, Φ_T, and Φ_D quantum yields than 4-TS. As a consequence, Φ_{IC} values of 2-TS are higher than those of 4-TS. This reveals that both isomers, particularly 2-TS, decay mainly by IC.

4. Conclusion

As initially indicated by the general competition mechanism (reactions 1−6), the deactivation channels of the first excited singlet state of the thiosalicylic acids are summarized in Table 1. Excitation brings the molecule from the ground-state S_0 into any vibrationally excited level of S_1. Besides fluorescence, intersystem crossing, and dissociation, the first excited singlet state of the two thiosalicylic acid molecules is mainly deactivated by internal conversion.

Applying different spectroscopic methods (steady-state and time-resolved fluorescence as well as absorption spectroscopy), we obtained a comprehensive picture of the spectral and photophysical properties of the 2- and 4-thiosalicylic acids.

The main point in this study is the first observation of a directly photogenerated triplet state of an aromatic thiol, i.e., for the thiosalicylic acids. In contrast, the triplets of thiophenol and its methyl derivatives could not be generated directly by photoexcitation but can be generated only indirectly via pulse radiolysis by sensitization experiments with species of higher triplet energy.[10]

Further, it should be mentioned that the dissociation reaction 5 of the TS(S_1) state is of minor importance. Instead, the internal conversion, which is unaffected by the solvent nature, plays a dominant role. The efficient vibrational relaxation could be a reason.

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