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Photochemistry of *N*-Hydroxypyridine-2-thione Derivatives: Involvement of the 2-Pyridylthiyl Radical in the Radical Chain Reaction Mechanism

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Abstract: The primary and subsequent photochemistry of four *N*-hydroxypyridine-2-thione esters has been investigated by laser flash photolysis (λ_{exc} = 355 nm). A simple, high-yield synthetic method is given for their preparation with high purity. UV irradiation of these ester compounds was shown to lead specifically to the formation of benzyl, diphenylmethyl, *tert*-butyl, and benzoyloxyl radicals in addition to the 2-pyridylthiyl radical. In all cases, the initial photoinduced nitrogen–oxygen bond cleavage was found to occur in high quantum yield ($\Phi_{N-O} \approx 0.5$). The radical species generated by this process (2-pyridylthiyl radical and carbon-centered or oxygen-centered radicals) were characterized and their reactivity toward several radical scavengers has been studied. An efficient delayed depletion of the *N*-hydroxypyridine-2-thione esters was also observed, leading to overall bleaching quantum yields, Φ_{Bl}, close to unity. We have demonstrated that the delayed consumption of ground-state ester was due to the reaction of the 2-pyridylthiyl radical with its precursor, occurring with a rate constant, k_r, of 3–4 × 10^9 M^{-1} s^{-1}. This reaction, hitherto never proposed, leads to the formation of 2,2′-dipyridyl disulfide and further release of propagating radicals.

Introduction

There are many examples in the literature for both thermally[1,2] and photochemically[3,4] induced homolytic cleavage of nitrogen–oxygen bonds. A number of these studies concerned the ester derivative of *N*-hydroxy-2-pyridone developed by Taylor's group[5,6] and the closely related *N*-hydroxypyridine-2-thione esters developed by Barton and co-workers.[7,8]

Since their introduction, the latter compounds, also called thiohydroxamic esters (**2**), have been extensively used as a mild and convenient source of carbon-centered radicals which have been trapped in a variety of ways for synthetic purposes.[9] The tremendous flexibility in the controlled generation of radical species has also been extended to the production of oxygen-centered[10–14] as well as nitrogen-centered radicals.[15–20]

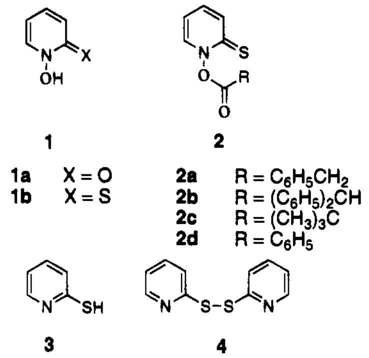

Figure 1. Chemical structures of *N*-hydroxy-2-pyridone (**1a**), *N*-hydroxypyridine-2-thione (**1b**) and its ester derivatives (**2a–d**), 2-mercaptopyridine (**3**), and 2,2′-dipyridyl disulfide (**4**).

N-Hydroxypyridine-2-thione esters (**2**) are known to undergo radical chain reactions.[7,21,22] Under continuous irradiation conditions, the main product was reported to be a 2-pyridyl thioether, formed by decarboxylative rearrangement. The reaction mechanism was proposed to involve homolytic cleavage of the N–O bond, initiated by light or heat, leading to the formation of a 2-pyridylthiyl radical (PyS$^\bullet$) and RCOO$^\bullet$ an acyloxy radical. When R is an aliphatic moiety, decarboxylation is expected to occur rapidly to give a carbon-centered radical

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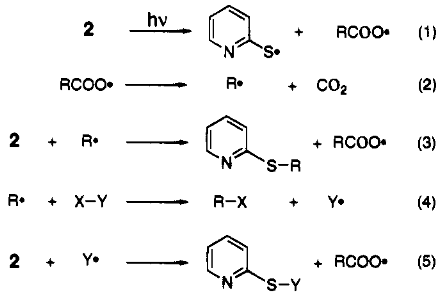
Scheme 1. Thermally or photochemically induced radical chain reactions undergone by *N*-hydroxypyridine-2-thione esters in the presence and absence of a radical trap (X−Y)



(R$^\bullet$) which then acts as a chain carrier by addition to the sulfur center of another molecule of starting compound (Scheme 1, reactions 1−3). However, in the presence of a radical trap X−Y (Scheme 1, reactions 4 and 5), the quenching of R$^\bullet$ by X−Y results in the formation of R−X, the trapped product bearing a new functional group, and Y$^\bullet$, a free radical capable of chain propagation by addition to the thiocarbonyl group of another molecule of precursor. For example, reductive decarboxylation occurs when X−Y is a tertiary thiol, introduction of a halogen atom takes place in the presence of $Cl-CCl_3$, $Br-CBr_3$, or $I-CHI_2$, and the use of disulfides, diselenides, and ditellurides as X−Y leads to the formation of thio-, seleno- and telluroethers, respectively (see review by Crich[9]).

Despite the profusion of successful synthetic applications[9] and their potential use as improved radical precursors for kinetic investigations,[23,24] surprisingly, little is known about the primary photochemistry and subsequent reactions of the *N*-hydroxypyridine-2-thione esters. To our knowledge, only two studies were concerned with this topic: EPR[25] and laser flash photolysis[26] have been used to detect the free radicals generated from thiohydroxamic esters.

We report here the results of a laser flash photolysis investigation of the photochemistry of four *N*-hydroxypyridine-2-thione esters in benzene and acetonitrile. The alkyl derivatives selected in this study (**2a**, **2b**, and **2c**) are expected to yield primary (benzyl), secondary (diphenylmethyl), and tertiary (*tert*-butyl) carbon-centered radicals, respectively, in addition to PyS$^\bullet$, the 2-pyridylthiyl radical, as decarboxylation of the initial RCOO$^\bullet$ should occur very rapidly.[8,22] The aryl thiohydroxamic ester (**2d**) is expected to form $C_6H_5COO^\bullet$, where decarboxylation to the phenyl radical is a much slower process[27] and may allow the benzoyloxyl radical to participate in subsequent reactions.[28,29] Our purpose was to (a) investigate the structural effects (nature of the R group) on the primary and subsequent photochemistry of these compounds, (b) spectroscopically characterize the radical species produced, (c) quantify their generation, and (d) study their reactivity and reaction mechanism in order to understand their role in the radical chain reactions of the thiohydroxamic esters.

Experimental Section

Chemicals. The starting compounds used in the syntheses described below, *N*-hydroxypyridine-2-thione sodium salt and 1-oxa-2-oxo-3-thiaindolizinium chloride, were supplied by Fluka Chemical Corp. (Ronkonkoma, NY) and Aldrich Chemical Co. (Milwaukee, WI), respectively. All other reagents were purchased from Aldrich except diphenylacetic acid which was obtained from Fluka. The NMR measurements were carried out using deuterated solvents (deuteriochloroform and deuteriobenzene, 99.8 atom %, from Aldrich) with a tetramethylsilane (TMS) internal reference. Methyl methacrylate, 1,3-cyclohexadiene, 2-mercaptopyridine, and 2′-acetonaphthone (Aldrich) were used as received. Benzhydrol (Aldrich) was recrystallized twice from aqueous ethanol in order to remove any contamination by benzophenone, 2,2′-Dipyridyl disulfide (Aldrich) was purified by recrystallization from methanol/water before use. For laser flash photolysis experiments, benzene and acetonitrile were of spectroscopic grade from Fisher Chemical (Pittsburgh, PA).

General Techniques. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were measured using a Varian XL 500 instrument or a Bruker AC 200 spectrometer. Chemical shifts are given in parts per million (ppm) relative to TMS as reference. Multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, and m = multiplet. Ground-state absorption spectra were measured with a Cary 2300 UV−visible spectrophotometer.

Syntheses and Characterization of *N*-Hydroxypyridine-2-thione Derivatives. Compounds **2a**, **2b**, and **2d** were prepared according to a method adapted from that described by Taylor and co-workers[5,6] for the synthesis of *N*-acyloxy-2-pyridones. The general procedure which we have applied includes (a) the conversion of *N*-hydroxypyridine-2-thione into its corresponding thallium(I) salt, (b) the preparation of an acid chloride from the appropriate carboxylic acid, and (c) the reaction of the thallium(I) salt of **1b** with the carboxylic acid chloride.

(a) Preparation of *N*-Hydroxypyridine-2-thione Thallium(I) Salt. *N*-Hydroxypyridine-2-thione sodium salt was first transformed into the free form (compound **1b**) according to the literature procedure.[30] Thallium(I) ethoxide (2.12 mL, 0.03 mol) was added to a stirred solution of *N*-hydroxypyridine-2-thione (3.81 g, 0.03 mol) in 75 mL of anhydrous ethyl ether resulting in immediate precipitation of the thallium(I) salt of **1b**. Stirring was continued for 10 min, and the solid was then collected, washed with ethyl ether, and dried *in vacuo*.

(b) Preparation of Acid Chlorides. Acid chlorides were prepared by reaction of the corresponding carboxylic acids (5 mmol, 681 mg of phenylacetic acid, 1.06 g of diphenylacetic acid, or 611 mg of benzoic acid) with an excess of oxalyl chloride (2.15 mL, 25 mmol) and one drop of *N,N*-dimethylformamide in dry benzene (10 mL). After 18 h of reaction, the residue obtained by evaporation of the solvent was redissolved in a small quantity of benzene which was then evaporated.

(c) Formation of *N*-Hydroxypyridine-2-thione Esters. To the thallium salt of **1b** (1.65 g, 5 mmol) suspended in 100 mL of anhydrous ethyl ether was added an equimolar quantity of acid chloride. The reaction mixture was stirred for 30 min at room temperature and filtered. The filtrate was evaporated to half its volume and petroleum ether added until the solution became cloudy. Refrigeration at 4 °C (from 1 to 3 h) resulted in precipitation of the product which was collected by filtration and recrystallized from petroleum ether/ethyl acetate. The overall yields for compounds **2a**, **2b**, and **2d** were higher than 95%. The ^{1}H-NMR spectrum of **2a** recorded in deuteriochloroform displays signals at 5.15 (2H, s), 6.60 (1H, dt), 7.19 (1H, dt), 7.37 (5H, m), 7.50 (1H, dd), and 7.70 ppm (1H, dd). The ^{1}H-NMR spectra of compounds **2b** and **2d** have been measured in deuterated benzene. They present signals at 5.25 (1 H, dt), 5.46 (1 H, s), 5.95 (1 H, dt), 6.25 (1 H, dd), 7−7.1 (6H, m), 7.39 (4 H, d), and 7.42 ppm (1 H, dd) for **2b** and at 5.4 (1 H, dt), 6.03 (1 H, dt), 6.46 (1 H, dd), 6.93 (2 H, dt), 7.0 (1 H, dd), 7.43 (1 H, dd), and 8.02 ppm (1 H, dd) for **2d**.

Compound **2c** was prepared by reaction of 1-oxa-2-oxo-3-thiaindolizinium chloride with trimethylacetic acid in the presence of

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trimethylamine as described by Barton *et al.*[31] and purified by recrystallization from *n*-hexane/dichloromethane. After purification, **2c** was obtained with an overall yield of 65%. Its ^{1}H-NMR spectrum determined in deuterated chloroform displays signals at 1.46 (9H, s), 6.61 (1H, dt), 7.18 (1H, dt), 7.49 (1H, dd), and 7.68 ppm (1H, dd).

The *N*-hydroxypyridine-2-thione esters were stored in powder form at −20 °C. Purity was checked by absorption spectroscopy and ^{1}H-NMR. No degradation with time was observed under these storage conditions. Solution samples were prepared immediately before use and were protected from light at all times.

Laser Flash Photolysis. Experiments were performed with either static cells or a flow system. Unless otherwise stated, samples were deaerated by bubbling nitrogen directly in the 10 × 10 mm quartz cuvette containing the solution or in a light-protected reservoir connected to the irradiation cuvette with tubing. Due to the photolability of the *N*-hydroxypyridine-2-thione esters and 2,2′-dipyridyl disulfide, a flow system was always used with a sufficiently high flow rate to ensure irradiation of a completely fresh volume of sample with each pulse.

The laser flash photolysis equipment has been described in detail elsewhere.[32] Briefly, experiments were carried out using either the frequency-tripled output of a Quantel YG660A Nd/Yag laser (Continuum, Santa Clara, CA) (355 nm, 8 ns duration pulse, up to 10 mJ/pulse) or a Lambda Physik EMG 103 MSC XeCl excimer laser (308 nm, 8 ns pulse duration, up to 20 mJ/pulse) as excitation source. Pulse energies were measured by a calibrated RJP-735 pyroelectric probe connected to an RJ-7610 energy meter (Laser Precision Corp., Utica, NY). Transient species were detected at right angles to the incident laser beam using a 75-W xenon arc lamp as monitoring beam (Photon Technology International, South Brunswick, NJ). The photomultiplier was powered from a remote-controlled high-voltage power supply (Venus Scientific, Farmingdale, NY) controlled by the analog output from a LAB/NB board (National Instruments, Austin, TX). Signal averaging was routinely performed to increase the signal-to-noise ratio. Kinetic analyses of transient decays were carried out using modified Levenberg-Marquardt nonlinear fitting programs on a Macintosh IIci computer. The transient absorption spectra were recorded point by point at intervals after pulsed laser excitation of the sample.

The quantum yields of initial N—O bond cleavage or photobleaching (Φ_{N-O}) of *N*-hydroxypyridine-2-thione esters were determined by the comparative technique using 2′-acetonaphthone (AN) in benzene as reference actinometer (at 430 nm, $\Phi_{T(AN)} = 0.84$[33] and $\epsilon_{T(AN)} = 10500$ M^{-1} cm^{-1} [34]). Φ_{N-O} was calculated for optically matched solutions of sample and reference (absorbance at 355 nm between 0.4 and 0.6) using the following relationship:

$$\Phi_{N-O} = \Phi_{T(AN)}(\Delta A_{N-O}/\Delta A_{T(AN)})(\epsilon_{T(AN)}/\epsilon_{GS}) \qquad (6)$$

where ϵ_{GS} is the molar absorption coefficient of the ground state of thiohydroxamic ester at 375 nm (the detection wavelength), and $\Delta A_{T(AN)}$ and ΔA_{N-O} are the maximum absorbance of the triplet state of 2′-acetonaphthone and the amplitude of ground-state photobleaching, respectively. Better accuracy was achieved by measuring transient absorbances as a function of laser energy. The resultant plots of ΔA *versus* laser energy were fitted and the measured initial slopes were substituted for the ΔA values. The assumption that negligible transient absorption occurs at 375 nm for the compounds studied has been verified (*vide infra*).

The reaction rate constant (k_s) of a particular radical with a substrate, S, was determined by monitoring the decay of the radical in the presence of several substrate concentrations. The experimental pseudo-first-order rate constant, k_{expt}, was plotted against the substrate concentration according to eq 7 to give k_s from the slope.

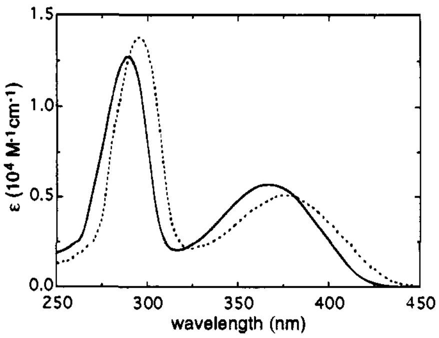

Figure 2. Absorption spectra of compound **2d** in benzene (- - -) and acetonitrile (—) reported as ϵ (the molar absorption coefficient) *versus* wavelength.

$$k_{expt} = k_0 + k_s[\text{substrate}] \qquad (7)$$

In this relationship, k_0 includes all reactions which the radical may undergo in a given solvent in the absence of substrate. The rate constant k_s includes all possible modes and sites of attack between the radical and the substrate considered.

Results

Syntheses of *N*-Hydroxypyridine-2-thione Derivatives. *N*-hydroxypyridine-2-thione esters were prepared using a method similar to that described by Taylor and co-workers[5,6] for the synthesis of *N*-acyloxy-2-pyridones. The key reaction involves the thallium(I) salt[35] of *N*-hydroxy-2-pyridone (**1a**) and the required acid chloride. This process, adapted to the transformation of **1b** (see Experimental Section), provides in short time the desired product with high yield (essentially quantitative) and high purity (a purification step by recrystallization is not always required). Compounds **2a**, **2b**, and **2d** were obtained using this simple synthetic pathway. We initially attempted to prepare our derivatives according to the procedure described by Barton.[8] This method is based on the reaction of the sodium salt of *N*-hydroxypyridine-2-thione (**1b**) with the appropriate acid chloride and generally aimed at producing thiohydroxamic esters for use as reagents *in situ*. In our hands, this method gave a reaction mixture containing the desired product. However, even after several consecutive purifications by liquid chromatography on silica gel, a complete elimination of the byproducts could not be reached. Both reported methods failed to synthesize compound **2c**, a tertiary ester derivative of *N*-hydroxypyridine-2-thione. Instead, direct reaction between the commercially available 1-oxa-2-oxo-3-thiaindolizinium chloride and trimethylacetic acid, as described by Barton *et al.*,[7,31] provided the expected product in good yield (see Experimental Section). The storage conditions chosen in this study (powder form at low temperature and protected from light) avoided any degradation of the derivatives with time.

Ground-State Absorption. The absorption spectra of the thiohydroxamic esters **2a–d** were recorded between 250 and 450 nm. As shown by the example presented in Figure 2, the spectrum displays two absorption bands with maxima around 300 and 375 nm, in benzene. These bands are blue-shifted ($\Delta\lambda \approx 8$ nm) in acetonitrile. The maxima and corresponding molar absorption coefficients (obtained from the slopes of Beer-Lambert plots of absorbance *versus* concentration in the range between 20 and 200 μM) are reported in Table 1 for both organic solvents.

Spectroscopic Characterization of Radicals. The transient absorption spectra formed on photolysis of the *N*-hydroxypy-

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[35] Due to their toxicity, the thallium salts should be manipulated with caution.

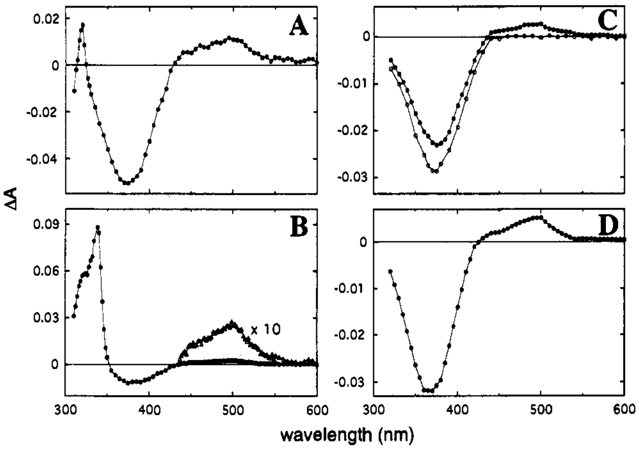

Figure 3. Spectra (●) recorded for compounds **2a** (A), **2b** (B), and **2c** (C) in deaerated benzene and compound **2d** (D) in N_2-saturated acetonitrile respectively 2.5, 2.6, 2, and 1.2 μs after laser flash excitation (λ_{exc} = 355 nm). In the case of compound **2b**, the part of the spectrum corresponding to the 2-pyridylthiyl radical has been expanded (△). Part C presents also the spectrum recorded 15 μs (○) after excitation of **2c**.

Table 1. Absorption Maxima (λ) and Corresponding Molar Absorption Coefficient (ε) of the Thiohydroxamic Esters (**2a–d**) in Benzene and Acetonitrile

	λ (nm) [ε (M^{-1} cm^{-1})]			
	benzene		acetonitrile	
2a	296 [13 300]	374 [5 200]	288	366
2b	296 [13 850]	374 [5 300]	288	366
2c	296 [13 500]	374 [5 100]	288	366
2d	296 [13 800]	374 [5 100]	288 [12 750]	366 [5 700]

ridine-2-thione esters (**2a–d**) were recorded after laser flash excitation (λ_{exc} = 355 nm) of deaerated solutions contained in a flow system. Benzene was used as solvent for compounds **2a**, **2b**, and **2c**. In the case of **2d**, acetonitrile was preferred, since $C_6H_5COO^\bullet$, the species expected to be formed by N–O cleavage, and $C_6H_5^\bullet$, the product of decarboxylation of the benzoyloxyl radical, are known to undergo addition reaction with aromatic systems.[6,36–38]

Figure 3 shows the spectra recorded for the four derivatives. Two spectral elements are common to all the thiohydroxamic esters studied. The first is the presence of an absorption band with a maximum at 500 nm. This transient absorption band, which has also been observed by Scaiano and co-workers,[26] was attributed to the 2-pyridylthiyl radical for the following reasons. (a) A similar spectrum with a maximum at 450–460 nm has been recorded for the closely related benzenethiyl radical formed either by laser flash excitation of diphenyl disulfide in cyclohexane[39] or by pulse radiolysis of thiophenol in the presence of *tert*-butyl sulfide or propan-2-ol.[40] (b) We have observed the same transient band at 500 nm by excitation (λ_{exc} = 355 or 308 nm) of 2-mercaptopyridine (**3**) in acetonitrile or benzene. In this case, the 2-pyridylthiyl radical is expected to be produced by S–H bond cleavage. (c) This absorption band with a maximum at 500 nm is also present in the spectrum recorded after laser flash photolysis (λ_{exc} = 308 nm) of a solution of 2,2′-dipyridyl disulfide (**4**) in acetonitrile or benzene. By analogy to the diphenyl disulfide, **4** should undergo a homolytic cleavage of the S–S bond.

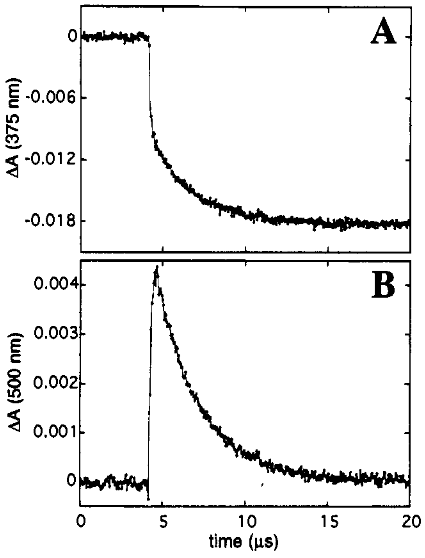

Figure 4. Parts A and B show respectively the bleaching signal at 375 nm corresponding to the ground-state depletion and the monoexponential decay of the 2-pyridylthiyl radical at 500 nm recorded after laser flash photolysis (λ_{exc} = 355 nm) of compound **2a** in air-saturated benzene. The concentration of precursor was 115 μM.

When $PyS^\bullet$ is generated from **3** or **4**, it decays with second-order kinetics suggesting a radical–radical process. The same behavior has been observed for the benzenethiyl radical formed by photolysis of diphenyl disulfide.[39] On the other hand, when produced from *N*-hydroxypyridine-2-thione esters, the 2-pyridylthiyl radical decays more rapidly with first-order kinetics. Under the general conditions used in these experiments (deaerated solutions with an absorbance at 355 nm ≈ 0.3, which corresponds to a concentration in precursor of 60–70 μM), the lifetime of $PyS^\bullet$ was found to be 3–5 μs.

The second characteristic present in all spectra is a marked negative band with a maximum at 375 nm due to ground-state depletion. The corresponding signal (Figure 4A) is composed of a fast step assigned to the photodecomposition of the starting ester by N–O bond cleavage and a slow bleaching process that we have identified as being caused by subsequent reactions which consume the precursor (*vide infra*).

The absorption band at 500 nm and bleaching at 375 nm are the only two features observable in the case of compound **2c** (Figure 3C), since the *tert*-butyl radical, $(CH_3)_3C^\bullet$, produced by reactions 1 and 2 of Scheme 1, is transparent at $\lambda \geq 320$ nm.[41]

The spectrum recorded for **2b** additionally displays a large absorption band with a maximum at 338 nm and a shoulder at 324 nm (Figure 3B). This transient absorption is assigned to the diphenylmethyl radical, $(C_6H_5)_2CH^\bullet$, since it is in full agreement with the spectrum reported in the literature[26,42,43] and with that which is observed by laser excitation (λ_{exc} = 308 nm) of 1,1-diphenylacetone in deaerated benzene. The excitation of compound **2a** leads to the formation of the benzyl radical, $C_6H_5CH_2^\bullet$, which has a smaller absorption band with a maximum at 318 nm (Figure 3A). The presence of the large bleaching band at 375 nm and thiyl radical absorption at longer wavelength masks the other weak transient absorptions at 422,

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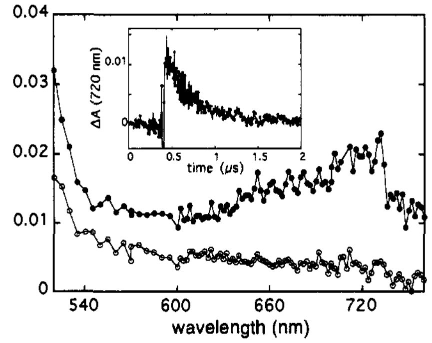

Figure 5. Spectra recorded 60 (●) and 820 ns (○) after laser flash excitation ($\lambda_{exc} = 355$ nm) of compound **2d** in N_2-saturated acetonitrile. The absorbance of the sample was 0.95 at 355 nm. The insert shows the monoexponential decay of the benzoyloxyl radical at 720 nm recorded for a solution of **2d** in deaerated acetonitrile at a concentration of 65 μM.

436, and 452 nm usually observed for $C_6H_5CH_2^\bullet$.[44] Under the conditions used in these experiments, $(C_6H_5)_2CH^\bullet$, the carbon-centered radical produced from compound **2b** decays with first-order kinetics and its lifetime was found to be 230 μs. Analysis of the signals recorded at 318 nm, the maximum absorption wavelength of $C_6H_5CH_2^\bullet$, generated from **2a**, is more difficult because of the interference presented by bleaching of the ground state. However, after correction for the depletion of the starting thiohydroxamic ester **2a**, the phenylmethyl radical was observed to decay with first-order kinetics and its lifetime was found to be 35 μs under the experimental conditions used to record the spectrum. In either case, there was no evidence of the presence of the initial $RCOO^\bullet$ species formed from compounds **2a** and **2b** by N–O bond cleavage, suggesting a fast decarboxylation occurring within the pulse duration.

Figure 3D presents the spectrum recorded after laser flash excitation of compound **2d** in deaerated acetonitrile, showing the ground-state depletion at 375 nm and the absorption band with a maximum at 500 nm due to the 2-pyridylthiyl radical. $C_6H_5COO^\bullet$, the expected product of N–O bond cleavage of **2d**, was detected on a time scale shorter than that used to observe the other free radicals. The spectrum at longer wavelength which is not masked by the transient absorption of $PyS^\bullet$ displays a broad structureless absorption which becomes visible at $\lambda \geq 550$ nm and presents a maximum located between 700 and 750 nm (Figure 5). This spectrum is very similar to that recorded after laser flash excitation ($\lambda_{exc} = 308$ nm) of dibenzoyl peroxide in CCl_4.[27] Under the experimental conditions used, the benzoyloxyl radical was found to decay with first-order kinetics and its lifetime, measured at 720 nm, was determined to be 310 ns. This value is close to that published for $C_6H_5COO^\bullet$, generated from dibenzoyl peroxide (250 ns in CCl_4 when studied by time-resolved EPR spectroscopic procedure,[45] 220 ns in CCl_4 and 270 ns in acetonitrile obtained by laser flash photolysis techniques[27]).

Kinetics of Radical/Molecule Reactions. (a) Reaction with Oxygen. The pseudo-first-order decay of the 2-pyridylthiyl radical formed by flash excitation of the *N*-hydroxypyridine-2-thione derivatives (**2a–d**) was found to be unaffected by the presence of oxygen in the solution. We also observed the same behavior when 2,2′-dipyridyl disulfide (**3**) and 2-mercaptopyridine (**4**) were used as thiyl radical precursors. This indicates a relatively low rate constant for the reaction of $PyS^\bullet$ with oxygen. An estimation[46] led to an upper limit of the quenching rate constant, k_{O_2}, of $\leq 4 \times 10^3$ M^{-1} s^{-1}. Similarly, Ito obtained an upper limit of 9×10^4 M^{-1} s^{-1} for the reaction between the *p*-chlorobenzenethiyl radical and oxygen.[47,48]

$C_6H_5CH_2^\bullet$ and $(C_6H_5)_2CH^\bullet$, produced by laser excitation of compounds **2a** and **2b**, respectively, were readily quenched by O_2, as expected for carbon–centered radicals.[49] The same is true for $(CH_3)_3C^\bullet$, generated from **2c**, since its abstraction of hydrogen from benzhydrol, according to eq 8, which leads to a diphenylketyl radical, easily detectable by its growth at 545 nm,[50] was only observed to take place under nitrogen-saturated conditions.

$$R^\bullet + (C_6H_5)_2CH{-}OH \rightarrow R{-}H + (C_6H_5)_2C^\bullet{-}OH \quad (8)$$

This also demonstrates that k_{O_2} for $(CH_3)_3C^\bullet$ (determined to be 4.93×10^9 M^{-1} s^{-1} in cyclohexane[49]) is much higher than the rate constant for hydrogen abstraction from benzhydrol (this was verified, as shown later).

Finally, the lifetime of $C_6H_5COO^\bullet$, the oxygen-centered radical produced from compound **2d**, was only slightly changed in the presence of oxygen in the solution (from 310 to 290 ns under nitrogen- and air-saturated conditions, respectively). Using the approximations of an oxygen concentration of 10^{-3} M in air-saturated acetonitrile and a complete deaeration under N_2-saturated conditions, an upper limit of 2×10^4 M^{-1} s^{-1} is obtained for the reaction between $C_6H_5COO^\bullet$ and O_2. The lack of reactivity toward oxygen has been noticed for several aroyloxyl radicals generated by photolysis of the corresponding diaroyl peroxides.[27]

(b) Quenching Reactions. The spectroscopic results reported above for the thiohydroxamic esters **2a–d** have shown that in the simplest case (**2c**), two events are observed: the ground-state depletion of starting ester, which takes place in two steps, and the decay of one absorbing radical species (the 2-pyridylthiyl radical). For the other compounds (**2a**, **2b**, and **2d**), the decay of a second absorbing radical ($R^\bullet$ or $RCOO^\bullet$) is also apparent. In order to elucidate the reaction pathways and determine the fate of the radical species produced, it is necessary to have means, such as specific quenchers, to simplify the system studied. As observed above, oxygen, which does not affect $PyS^\bullet$ and has only a small effect on $C_6H_5COO^\bullet$, can be used as an efficient quencher of carbon-centered radicals. Quenching experiments were undertaken to determine the effects of other specific radical scavengers which could be used to elucidate the reaction mechanism. Methyl methacrylate (MMA) and 1,3-cyclohexadiene (1,3-CHD) were selected as potential quenchers of $PyS^\bullet$ since by analogy to the benzenethiyl radical,[39,47] it is expected to undergo anti-Markovnikov addition to conjugated or nonconjugated unsaturated bonds. Benzhydrol and 1,3-cyclohexadiene were also chosen to test the ability for hydrogen abstraction of the radicals generated by the thiohydroxamic esters (**2a–d**). Tables 2 and 3 present the quenching rate constants (k_Q) measured for compounds **2a**, **2b**, and **2c** in benzene and **2d** in acetonitrile. The results concerning the 2-pyridylthiyl radical (Table 2) were obtained under air-saturated conditions. The quenching rate constants for $PyS^\bullet$ were determined by monitoring the decay of the 500 nm transient absorption for different substrate concentrations over the range

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(44) Huggenberger, C.; Fischer, H. *Helv. Chim. Acta* **1981**, *64*, 338–353.

(45) Yamauchi, S.; Hirota, N.; Takahara, S.; Sakuragai, H.; Tokumaru, K. *J. Am. Chem. Soc.* **1985**, *107*, 5021–5022.

(46) This value has been determined using the approximations of a complete removal of oxygen under N_2-saturated conditions and a concentration of 10^{-3} M in O_2 in air-saturated benzene. The value reported here corresponds to the highest value obtained for compounds **2a–d**.

(47) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1981**, *103*, 5871–5874.

(48) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 1815–1818.

(49) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095–5099.

Table 2. Reactivity of the 2-Pyridylthiyl radical (PyS$^\bullet$) produced by the Thiohydroxamic Esters (**2a–d**)[a]

	MMA	1,3-CHD	BH[b]	precursor[c]
2a	9.95×10^7	2.5×10^9	1.5×10^6	3.84×10^9 (3.05×10^9)
2b	1.05×10^8	2.0×10^9	1.3×10^6	3.00×10^9 (3.75×10^9)
2c	1.00×10^8	2.1×10^9	6.4×10^5	3.47×10^9 (4.28×10^9)
2d	8.55×10^7	3.0×10^9	1.2×10^6	3.77×10^9 (4.44×10^9)

[a] The determinations were carried out using solutions of **2a**, **2b** and **2c** in benzene and **2d** in acetonitrile. The quenchers are methyl methacrylate (MMA), 1,3-cyclohexadiene (1,3-CHD), and benzhydrol (BH). [b] The quenching constants for benzhydrol were obtained by monitoring the decay of the 2-pyridylthiyl radical at 500 nm in air-saturated solutions. [c] The bimolecular rate constants for the reaction of the thiyl radical with its precursor were determined by monitoring the decay of the 500 nm absorption band or by following the slow bleaching of the ground state at 375 nm under air-saturated conditions. The latter values are reported into parentheses.

Table 3. Reactivity of the Carbon-Centered (benzyl, diphenylmethyl and *tert*-butyl) and Oxygen-Centered (benzoyloxyl) Radical Produced by the Thiohydroxamic Esters (**2a–d**)[a]

	MMA	1,3-CHD	BH[b]
2a			4.0×10^6
2b	1.7×10^4	$<1.7 \times 10^4$	2.3×10^6
2c			2.8×10^6
2d	3.4×10^7	1.1×10^9	

[a] The determinations were carried out using deaerated solutions of **2a**, **2b**, and **2c** in benzene and **2d** in acetonitrile. The quenchers are methyl methacrylate (MMA), 1,3-cyclohexadiene (1,3-CHD), and benzhydrol (BH). [b] The quenching constants for benzhydrol were obtained by monitoring the growth at 545 nm of the ketyl radical formed. The signals were analyzed after correction for the absorption of the 2-pyridylthiyl radical at this wavelength.[52]

from 0.012 to 0.12 M in methyl methacrylate (MMA), from 0.25 to 10 mM in 1,3-cyclohexadiene (1,3-CHD), and from 0.025 to 0.25 M in benzhydrol. The results show that, for each scavenger, the k_Q values obtained using the different parent molecules (**2a–d**) are very similar. The quenching rate constants determined for PyS$^\bullet$ were also found to be independent of the presence of oxygen in the solution.

The carbon-centered radicals produced from compounds **2a**, **2b**, and **2c** abstract hydrogen from benzhydrol according to eq 8. The quenching rate constants presented in Table 3 were determined, under deaerated conditions, by monitoring the growth of the diphenylketyl radical formed at 545 nm at different concentrations of benzhydrol. The signals were analyzed after correction for the absorption of the 2-pyridylthiyl radical at this wavelength.[51] The quenching rate constant of the diphenylmethyl radical produced from **2b** was found to be 1.7×10^4 M^{-1} s^{-1} by monitoring the decay of the absorption band at 338 nm at different concentrations of methyl methacrylate. The k_Q value for the quenching of $(C_6H_5)_2CH^\bullet$ by 1,3-cyclohexadiene was observed to be even lower.

In the case of $C_6H_5COO^\bullet$, generated by compound **2d**, the decay of the 720 nm absorption band in air-saturated acetonitrile was monitored at various concentrations of 1,3-cyclohexadiene and methyl methacrylate. The oxygen-centered radical was observed to be scavenged very efficiently by 1,3-cyclohexadiene ($k_Q = 1.1 \times 10^9$ M^{-1} s^{-1}). The rate constant for the quenching of the benzoyloxyl radical by methyl methacrylate was found to be 3.4×10^7 M^{-1} s^{-1}. As already commented, benzene was not used as solvent for the investigation of compound **2d** because of the known reaction of $C_6H_5COO^\bullet$ with aromatic systems. In the presence of 0.1 M benzene, the transient absorption at 720 nm was found to be totally quenched (Chateauneuf reported a value of 7.8×10^7 M^{-1} s^{-1} for the reaction between the benzoyloxyl radical and benzene[27]).

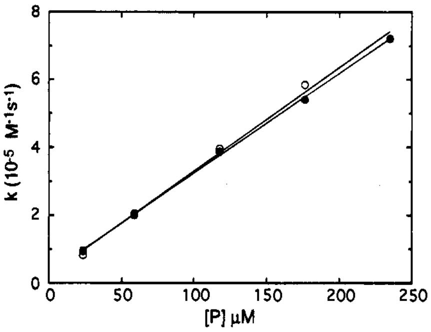

Figure 6. Concentration dependence of the decay of the 2-pyridylthiyl radical monitored at 500 nm (○) and of the slow bleaching process observed at 375 nm (●) for compound **2a** in air-saturated benzene. The observed rate constants (*k*) were plotted against the concentration of precursor ([P]) and the data were fitted by a first-order polynomial equation.

The specific radical scavengers studied here are used below to investigate the reaction mechanisms. The carbon-centered radicals, produced by the thiohydroxamic esters **2a**, **2b**, and **2c**, can be efficiently and specifically scavenged by oxygen. Quenching experiments have led to the conclusion that methyl methacrylate and 1,3-cyclohexadiene can play the same role for the 2-pyridylthiyl radical without interacting markedly with R$^\bullet$ (for example, for compound **2b**, the ratio between the quenching rate constants for PyS$^\bullet$ and R$^\bullet$ was found to be 6×10^3 in the case of MMA and $\geq 2 \times 10^5$ in the case of 1,3-CHD). Oxygen, methyl methacrylate, and 1,3-cyclohexadiene were observed to affect similarly $C_6H_5COO^\bullet$ and the 2-pyridylthiyl radical produced by compound **2d**. On the contrary, benzene appeared to quench the benzoyloxyl radical more efficiently than PyS$^\bullet$.

(c) Reaction with Precursor. In addition to the instantaneous photocleavage of the N–O bond, a slow bleaching process was also observed at 375 nm (Figure 4B). Two different hypotheses were considered: the slow process corresponds to either the decay of a transient species absorbing around 375 nm or the consumption of the starting thiohydroxamic ester due to a chemical reaction. The 2-pyridylthiyl radical and R$^\bullet$ (or RCOO$^\bullet$ in the case of compound **2d**), produced by initial photoinduced bond cleavage, are species which could be responsible for either transient absorption at 375 nm or reaction with the precursor molecule. A first indication that the thiyl radical rather than R$^\bullet$ (or RCOO$^\bullet$) is involved in the slow process results from the excellent correlation observed between the decay rate constant of PyS$^\bullet$ monitored at 500 nm and the rate constant of slow bleaching at 375 nm with the concentration of thiohydroxamic ester. Figure 6 shows an example of such a correlation obtained for compound **2a**. The observation that the signals recorded at 375 nm for compounds **2a**, **2b**, and **2c** are unchanged under air- or nitrogen-saturated conditions supports this idea since significant modifications would occur if the oxygen-sensitive carbon-centered radical were responsible for the slow process. Finally, a third argument in favor of the involvement of the 2-pyridylthiyl radical comes from the fact that in the presence of methyl methacrylate or 1,3-cyclohexadiene (shown to be efficient thiyl radical quenchers) the slow bleaching component is not observed.

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(50) Redmond, R. W.; Scaiano, J. C.; Johnston, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 9768–9773.

(51) Signals at 545 nm were recorded under air-saturated conditions for the same concentrations of benzhydrol. Under these experimental conditions, the oxygen-sensitive diphenylketyl radical is quenched and the observed absorption is only due to the 2-pyridylthiyl radical. The corrections were carried out by subtracting these signals from those recorded under deaerated conditions.

To determine whether the slow process was due to the presence of an absorption band of PyS• or to its reaction with the parent molecule, the absorption properties of the 2-pyridylthiyl radical were investigated independently. 2-Mercaptopyridine (**3**) and 2,2′-dipyridyl disulfide (**4**) were used as precursors of PyS•. In the case of **3**, no conclusion could be drawn because the same kind of signals presenting an instantaneous photobleaching and a slow process were observed around 370–380 nm (the absorption maximum of the ground state of **3**). The second compound allowed us to discard the hypothesis of a transient absorption at 375 nm due to PyS•, since the spectrum recorded after laser flash photolysis (λ_{exc} = 308 nm) of **4** in benzene or acetonitrile does not undergo any changes at 375 nm in the presence of methyl methacrylate or 1,3-cyclohexadiene in contrast to the 500-nm absorption band which disappears. We therefore conclude that the slow process observable at 375 nm corresponds to the reaction of the 2-pyridylthiyl radical with its precursor.

The bimolecular rate constants, k_r, for reaction of PyS• with the various parent compounds (**2a–d**) were determined in the usual way by monitoring the decay of the 500 nm transient absorption or the slow consumption of ground state at 375 nm for different substrate concentrations. The results obtained under air-saturated conditions are summarized in Table 2. The bimolecular rate constants determined under deaerated conditions were found to be identical to those reported in Table 2 within experimental error. The results show that these rate constants are high ($3-4 \times 10^9$ M^{-1} s^{-1}) and very similar for all *N*-hydroxypyridine-2-thione esters studied. This similarity suggests a reaction which involves the pyridine-2-thione ring which is common to all the thiohydroxamic esters rather than the RCOO– part of the parent molecule.

Attempts to directly determine the bimolecular rate constants for the reaction of $C_6H_5CH_2^•$ and $(C_6H_5)_2CH^•$ with their respective precursors **2a** and **2b** were unsuccessful. The decays of the absorption band at 318 nm (for the benzyl radial) and at 338 nm (for the diphenylmethyl radical) were monitored at different starting ester concentrations. In both cases, the decay of R•, which is originally first order, becomes increasingly second order in character, with increasing ground-state concentration, that is increasing R• concentration. As the self-quenching rate constants of carbon-centered radicals such as $C_6H_5CH_2^•$ and $(C_6H_5)_2CH^•$ are very high,[52] the radical recombination dominates and the reaction of R• with their parent molecules is not directly observable. However, since the signals recorded at 375 nm were found to be identical, under N_2-, air-, and O_2-saturated conditions, the consumption of thiohydroxamic ester due to the reaction with R•, an oxygen-sensitive species, cannot be very important. Using a low laser energy to reduce radical–radical processes, the ground-state depletion of compound **2a** has been monitored at 375 nm under deaerated conditions for different concentrations of starting ester between 27 and 270 μM. Except for the component corresponding to the reaction of the ground state with the 2-pyridylthiyl radical, no noticeable modification of the shape of the signals was observed with increasing concentration. This suggests a low rate constant for the reaction of the thiohydroxamic ester **2a** and $C_6H_5CH_2^•$.

A similar conclusion concerning the reactivity of $C_6H_5COO^•$ toward its precursor, compound **2d**, can be drawn from the bleaching signals observed at 375 nm. This result is consistent with the fact that by varying the concentration of thiohydroxamic ester **2d** from 20 to 200 μM, the decay rate constant of the benzoyloxyl radical monitored at 720 nm did not undergo any marked changes.

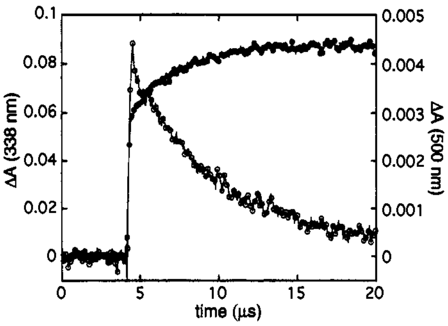

Figure 7. Formation of the diphenylmethyl radical (●) and decay of the 2-pyridylthiyl radical (○) produced by flash photolysis (λ_{exc} = 355 nm) of compound **2b** and monitored at 338 and 500 nm, respectively.

(d) Decarboxylation of RCOO• and Formation of R•. The lifetime of the benzoyloxyl radical generated from compound **2d** was found to be 310 ns in nitrogen-saturated acetonitrile. This short lifetime is due to the decarboxylation of $C_6H_5COO^•$ [27] according to reaction 2 in Scheme 1. Decarboxylation occurs on a much slower time scale than for the other RCOO• radicals.[53] The phenyl radical formed by this process was not detected because of its low molar absorption coefficient in the UV region.[54]

Using shorter time scales to investigate the kinetics of formation of the diphenylmethyl radical, we observed that the signal recorded at 338 nm (the absorption maximum of $(C_6H_5)_2CH^•$) is composed of two parts. The first shows that the diphenylmethyl radical, produced from the primary photochemical step of N–O bond cleavage of compound **2b**, is formed instantaneously (the decarboxylation of the corresponding initial RCOO• occurs within the pulse duration). The second part of the signal grows in with first-order kinetics. At low laser energies where radical–radical processes are reduced, we observed a correlation between this growth and the decay of the 2-pyridylthiyl radical monitored at 500 nm (Figure 7). We also found that in the presence of methyl methacrylate or 1,3-cyclohexadiene, the second part of the signal recorded at 338 nm disappears. We therefore conclude that the reaction of the 2-pyridylthiyl radical with its precursor **2b** leads to further formation of diphenylmethyl radical.

N–O Bond Cleavage and Bleaching Efficiencies. As discussed above, the assumption that negligible transient absorption occurs at 375 nm has been verified for the compounds studied. However, in order to determine precisely the quantum yields of initial photoinduced N–O bond cleavage, Φ_{N-O}, of the *N*-hydroxypyridine-2-thione derivatives, using the signals at 375 nm, it is necessary to get rid of the secondary bleaching process corresponding to the reaction of PyS• with the ground state of starting ester. To do so, the signals at 375 nm were recorded in the presence of a large excess of thiyl radical quencher (methyl methacrylate or 1,3-cyclohexadiene) (Figure 8A). Figure 8B shows an example of the energy dependence plots obtained for optically matched solutions of 2′-acetonaphthone (the actinometer) in deaerated benzene and of compound **2b** in the presence and absence of methyl methacrylate, in air- or nitrogen-saturated benzene.

The photobleaching quantum yields were determined using eq 6 (see Experimental Section) and were found to be 0.53,

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[52] The radical–radical self-reaction rate constant for the phenylmethyl radical was determined to be 4.1×10^9 M^{-1} s^{-1} in cyclohexane (see ref 57).

[53] The slower decarboxylation observed in the case of the benzoyloxyl radical is due to the stronger R–X bonds when R is an aryl rather than an alkyl group.

[54] Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609–3614.

0.50, 0.52, and 0.53 for compounds **2a**, **2b**, **2c**, and **2d**, respectively. These values were independent of the thiyl radical quencher used (methyl methacrylate or 1,3-cyclohexadiene). They were also unchanged in the presence and absence of oxygen (Figure 8B). These results show that the efficiency of the photoinduced N−O bond cleavage is independent on the nature of R and the corresponding radical type involved (primary, secondary, or tertiary carbon-centered or oxygen-centered radical).

The overall bleaching quantum yields (Φ_{Bl}) of the thiohydroxamic esters (corresponding to the depletion due to the photoinduced N−O bond cleavage and to the consumption by reaction with radicals) were determined according to eq 9

$$\Phi_{\mathrm{Bl}} = \Phi_{\mathrm{T(AN)}}(A_{\mathrm{Bl}}/A_{\mathrm{T(AN)}})(\epsilon_{\mathrm{T(AN)}}/\epsilon_{\mathrm{GS}}) \qquad (9)$$

where A_{Bl} and $A_{\mathrm{T(AN)}}$ are the initial slopes of the energy dependence plots of ΔA_{Bl}, the amplitude of total depletion of the ground state at 375 nm measured in the absence of thiyl radical quencher (Figure 8A), and $\Delta A_{\mathrm{T(AN)}}$, the maximum absorbance of the triplet state of 2′-acetonaphthone. Under the experimental conditions used (concentration of starting thiohydroxamic ester of 60−70 μM and low laser energy), the values of Φ_{Bl} were found to be close to 1 (0.92, 0.97, 1.02, and 0.83 for **2a**, **2b**, **2c**, and **2d**, respectively). This demonstrates that the N−O bond cleavage taking place in pulsed laser photolysis accounts for 50−60% of the total bleaching.

Molar Absorption Coefficient of Radicals. The molar absorption coefficient of the 2-pyridylthiyl radical at 500 nm, $\epsilon_{\mathrm{Thiyl}}$, was determined using the same comparative method as described previously. $\epsilon_{\mathrm{Thiyl}}$ was calculated using the following relationship:

$$\epsilon_{\mathrm{Thiyl}} = \epsilon_{\mathrm{GS}}(A_{\mathrm{max}}/A_{\mathrm{N-O}}) \qquad (10)$$

where A_{max} and $A_{\mathrm{N-O}}$ are the initial slopes measured for the energy dependence plots of ΔA_{max}, the maximum absorbance of PyS$^•$ at 500 nm, and $\Delta A_{\mathrm{N-O}}$, the amplitude of ground-state depletion due to photoinduced N−O bond cleavage (Figure 8A).

The experiments carried out with the four different *N*-hydroxypyridine-2-thione esters gave $\epsilon_{\mathrm{Thiyl}}$ values of 1400, 1580, and 1480 M^{-1} cm^{-1} for **2a**, **2b**, and **2c** in benzene, respectively, and 1800 M^{-1} cm^{-1} for **2d**, in acetonitrile. These data can be compared to the value of 2500 M^{-1} cm^{-1} obtained for the benzenethiyl radical at 460 nm.[39]

Using a mean value of 1500 M^{-1} cm^{-1} in benzene and 1800 M^{-1} cm^{-1} in acetonitrile, it is possible to determine the absorption coefficients of the different carbon-centered and oxygen-centered radicals generated simultaneously with the 2-pyridylthiyl radical. In the presence of thiyl radical quencher which inhibits subsequent reactions with the precursor, the photobleaching leads to the formation of PyS$^•$ and R$^•$ (or RCOO$^•$) in the proportion 1 to 1. After correction for the photobleaching due to N−O bond cleavage occurring at 338 nm,[55] the molar absorption coefficient of the diphenylmethyl radical in benzene at that wavelength was found to be 52 900 M^{-1} cm^{-1} (a value of 44 000 M^{-1} cm^{-1} at 331 nm has been reported by Bromberg *et al.*[43]). An estimation of the absorption coefficient of the phenylmethyl radical in benzene gave 4300 M^{-1} cm^{-1} at 318 nm (data reported in the literature for $C_6H_5CH_2^•$ are 8800 M^{-1} cm^{-1} at 316 nm in cyclohexane[44] and 5500 M^{-1} cm^{-1} at 317 nm in water[56]). Finally the absorption coefficient of $C_6H_5COO^•$ was found to be 395 M^{-1} cm^{-1} at 720 nm. This value is somewhat higher than that obtained by Chateauneuf (290 M^{-1} cm^{-1} in CCl_4[27]).

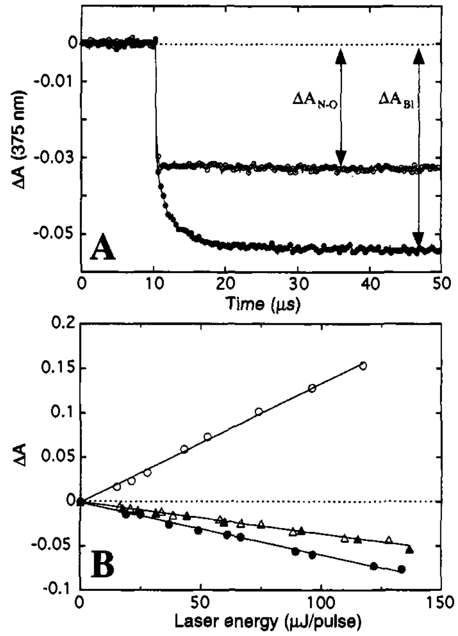

Figure 8. (A) Example of signals recorded at 375 nm for a deaerated solution of compound **2b** in the presence (○) and absence (●) of methyl methacrylate. (B) Determination of the N−O bond cleavage quantum yield ($\Phi_{\mathrm{N-O}}$). Laser energy dependence of ground-state depletion of **2b** monitored at 375 nm, in the presence of an excess of methyl methacrylate under N_2- (△) and air-saturated conditions (▲) and in the absence of thiyl radical quencher under deaerated conditions (●) compared to the triplet state formation of 2′-acetonaphthone monitored at 430 nm (○). All the samples were in benzene solution and optically matched at 355 nm (absorbance = 0.5). The data were fitted by a linear equation.

Discussion

In the present work, we have shown that the preparative method described by Taylor and co-workers can be successfully adapted to the synthesis of aroyl as well as alkyl ester derivatives of *N*-hydroxypyridine-2-thione (**1b**). The procedure developed by Taylor[5,6] to prepare *N*-hydroxy-2-pyridone esters is based on the reaction of the thallium(I) salt[35] of **1a** with an appropriate carboxylic acid chloride. The convenience, simplicity, and rapidity of Taylor's method, added to the high yields and high purity of the products obtained, make it the method of choice for the syntheses of thiohydroxamic esters when pure crystalline samples are needed, as in spectroscopic and kinetic studies.

The investigation of the *N*-hydroxypyridine-2-thione esters (**2a**−**d**) by laser flash photolysis has demonstrated that these compounds are specific precursors for free radicals. The fact that no long-lived excited states are produced alongside the generation of the radical species has also been reported by Bohne and co-workers in their exploratory study of the primary photochemistry of thiohydroxamic esters.[26] Irrespective of the R group in the precursor molecule, the quantum yield of photoinduced N−O bond cleavage, $\Phi_{\mathrm{N-O}}$, was found to be around 0.5. Despite the number of molecules known to undergo photochemical homolytic scission of a nitrogen−oxygen bond, to our knowledge, there are no other $\Phi_{\mathrm{N-O}}$ values reported in the literature. In the case of the thiohydroxamic esters, the

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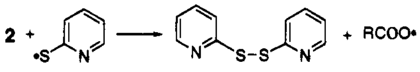
(55) The signals recorded at 338 nm under N_2-saturated conditions in the presence of enough methyl methacrylate to quench PyS$^•$ but not R$^•$ have been corrected by subtracting the corresponding signals recorded at the same wavelength for deaerated solutions containing an excess of MMA.

(56) Christensen, H. C.; Schested, K.; Hart, E. J. *J. Phys. Chem.* **1973**, *77*, 983−987.

similarity of the efficiencies of N−O cleavage is not surprising since the chromophore (the carbon−sulfur double bond conjugated to the pyridine ring) is identical for all the compounds studied (**2a**−**d**). Furthermore, in all cases, the cleavage step leads initially to the formation of similar species: the 2-pyridylthiyl radical and $RCOO^\bullet$, an acyloxy radical. The absence of long-lived excited states and the weak fluorescence displayed by the ester derivatives (data not shown) indicate that about half of the excitation energy is used in the bond cleavage ($\Phi_{N-O} \approx 0.5$) and the rest is mainly dissipated as heat in the system by internal conversion processes. As expected, the oxygen-centered radical $RCOO^\bullet$ was only observed in the case of compound **2d**. When R is an alkyl group (as in compounds **2a**, **2b**, and **2c**), decarboxylation of $RCOO^\bullet$ occurs within the laser pulse duration. Therefore, all the radicals generated by N−O bond cleavage of compounds **2a**−**d** and spectroscopically observable ($PyS^\bullet$, $C_6H_5CH_2^\bullet$, $(C_6H_5)_2CH^\bullet$, and $C_6H_5COO^\bullet$) were found to be produced instantaneously.

The high efficiency of N−O bond cleavage presented by the *N*-hydroxypyridine-2-thione esters allows the spectral characterization of the radicals generated and the investigation of their reactivity. The results obtained show that the species produced (2-pyridylthiyl radical, carbon- and oxygen-centered radicals) present very different reactivity patterns, which, in most cases, is explained by structural differences. In short, addition reactions (to methyl methacrylate or 1,3-cyclohexadiene) occur much more efficiently with $PyS^\bullet$ and $C_6H_5COO^\bullet$ than with the carbon-centered radicals, whereas the $R^\bullet$ species were found to abstract hydrogen from benzhydrol more rapidly than the 2-pyridylthiyl radical. The behavior of $PyS^\bullet$ (having a much higher capacity to add to double bonds (k_Q of 1×10^8 and $2-3 \times 10^9$ M^{-1} s^{-1} with methyl methacrylate and 1,3-cyclohexadiene, respectively) than to abstract hydrogen (k_Q of 1×10^6 M^{-1} s^{-1} with benzhydrol)) is similar to that observed for the benzenethiyl radical.[39,47] The order of magnitude of difference between k_Q for methyl methacrylate and k_Q for 1,3-cyclohexadiene may be explained by the fact that MMA has an electron-poor double bond while 1,3-CHD is an electron-rich conjugated diene which favors the reaction with the electrophilic thiyl radical. Such a difference in reactivity has also been noticed for the quenching of *para*-substituted and unsubstituted benzenethiyl radicals by methyl methacrylate and styrene[39] (having an electron-poor and electron-rich double bond, respectively) or by vinyl acetate and acrylonitrile[47] (nonconjugated and conjugated monomers, respectively). The absence of an oxygen effect on the rate constants determined for the quenching of $PyS^\bullet$ by methyl methacrylate and 1,3-cyclohexadiene and the range of these k_Q values (10^8-10^9 M^{-1} s^{-1}) differ considerably from the results observed for the benzenethiyl radical studied by Ito and co-workers.[39,47] They report that the *para*-substituted benzenethiyl radicals react reversibly with the double bond of the scavenger leading to the formation of a carbon-centered radical species which is rapidly quenched by oxygen. The rate of the addition reaction was shown to increase while its dependence on the concentration of oxygen decreases with increasing electron-withdrawing ability of the *para* substituent. The behavior of the 2-pyridylthiyl radical, produced from the *N*-hydroxypyridine-2-thione esters studied here, was found to be closer to the behavior of the *para*-nitro-substituted than that of the unsubstituted benzenethiyl radical. The higher electrophilicity of $PyS^\bullet$, compared to the unsubstituted benzenethiyl radical, which results from the electron-withdrawing inductive effect of the electronegative nitrogen atom, explains the observed difference. The reaction of the carbon-centered radicals ($C_6H_5CH_2^\bullet$, $(C_6H_5)_2CH^\bullet$, and $(CH_3)_3C^\bullet$) with benzhydrol was found to occur with a rate constant of $2-4 \times 10^6$ M^{-1} s^{-1} depending on the radical involved. These values are in the range of those reported for hydrogen abstraction by various carbon-centered radical species.[57] As expected,[57] the different $R^\bullet$ did not undergo efficient addition reaction with unsaturated systems: the k_Q values were found to be lower than 2×10^4 M^{-1} s^{-1} for both methyl methacrylate and 1,3-cyclohexadiene in the case of compound **2b**. On the contrary, the oxygen-centered radical, $C_6H_5COO^\bullet$, was seen to be quenched very efficiently by 1,3-cyclohexadiene ($k_Q = 1.1 \times 10^9$ M^{-1} s^{-1}, which is close to the value of 9.6×10^8 M^{-1} s^{-1} determined by Chateauneuf[27]). The addition rate constant of the benzoyloxyl radical to methyl methacrylate was determined to be 3.4×10^7 M^{-1} s^{-1} (this value is comparable to 5.1×10^7 M^{-1} s^{-1} measured for the quenching of $C_6H_5COO^\bullet$ by styrene[27]).

The reactivity of the different radical species toward their precursor is dramatically different. The spectroscopic investigation of the reaction between the free radicals and their respective parent molecule has demonstrated that the most rapid process which subsequently consumes the starting ester derivatives involves the 2-pyridylthiyl radical (bimolecular rate constant, k_r, of $3-4 \times 10^9$ M^{-1} s^{-1}). Ground-state depletion due to reaction with $R^\bullet$ or $RCOO^\bullet$ was found to be negligible on these time scales. Because of the similarity of the k_r values obtained for the different *N*-hydroxypyridine-2-thione esters, the reaction with $PyS^\bullet$ must take place on the pyridine-2-thione part of the precursor molecule, which is common to all compounds. Finally, the correlation observed between the decay of the 2-pyridylthiyl radical monitored at 500 nm and the slow formation process of the carbon-centered radical (Figure 8) suggests that the reaction of $PyS^\bullet$ with its precursor leads to further production of $R^\bullet$. These conclusions allow us to propose reaction 11 as a participant in radical chain reaction mechanisms undergone by *N*-hydroxypyridine-2-thione esters.



(11)

The addition of the 2-pyridylthiyl radical to the carbon−sulfur double bond of the parent molecule gives the 2,2′-dipyridyl disulfide (**4**) and $RCOO^\bullet$ which can then decarboxylate, depending on the nature of R.

As demonstrated by our results, the depletion of starting ester is due to the initial photoinduced N−O bond cleavage and to the reaction of the 2-pyridylthiyl radical with its precursor. A contribution resulting from the reaction of $R^\bullet$ (or $RCOO^\bullet$ in the case of compound **2d**) with the parent molecule was not observed and must be negligible on these time scales. The values of overall bleaching quantum yields (Φ_{Bl}) measured for the *N*-hydroxypyridine-2-thione esters (**2a**−**d**) all were determined to be close to unity. This similarity is explained by the fact that for the four compounds studied, the efficiencies of N−O bond cleavage as well as the rate constants for the reaction of $PyS^\bullet$ with its precursor were found to be identical within experimental error. The values of Φ_{Bl}, measured in these pulsed photolysis experiments, are indicative of efficient photocleavage and then scavenging of $PyS^\bullet$ by precursor. Under pulsed irradiation conditions, transient radical concentrations can be orders of magnitude higher than in continuous irradiation studies and the radical−radical recombination products (termination) are more probable and, consequently, chain lengths shorter. However, our investigation shows that the formation of the 2,2′-dipyridyl disulfide (**4**), identified as a product in continuous

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(57) Lusztyk, J.; Kanabus-Kaminska, J. M. In *CRC Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1989; Vol. 2, pp 177−210.

irradiation studies[58] and postulated to arise from the recombination of two 2-pyridylthiyl radicals, is in fact due to reaction 11, which effectively removes PyS• from the system. This process will be even more dominant under continuous irradiation conditions where steady state radical concentrations are lower and the concentrations of starting esters generally much higher (>0.1 M) than used here. This explains the relatively high chemical yield of compound **4** determined by product studies under continuous irradiation in the absence of radical trap.[58]

We did not observe efficient reaction of any of the carbon-centered radicals with their parent molecule. In part, this is due to the unreactive nature of the radicals produced in our study, although even for more reactive alkyl radicals the reaction rates are orders of magnitude lower than for the corresponding reaction of PyS• with its precursor.[23,57,59] Following the rapid reaction 11, the only remaining radical species is R•. In continuous irradiation experiments, one of the major reaction products is the 2-pyridyl thioether formed through addition of R• to the parent molecule (Scheme 1, reaction 3). This reaction is more likely in the reported continuous irradiation studies due to the use of higher precursor concentrations and more reactive R• radicals used.[58]

When continuous irradiations are carried out in the presence of a radical trap (X−Y), long radical chains for formation of R−X are observed.[58] In this case, once initiated, the radical chain is carried effectively by the propagating Y• radicals, which are initially formed through the trapping of the carbon-centered radical (R•) by X−Y (Scheme 1, reaction 4). Thus, one observes much lower relative yields of 2-pyridyl thioether and 2,2′-dipyridyl disulfide to the trapped product, R−X, when the radical trap is present,[58] resulting from the efficient chain propagation due to Y• reacting with the starting *N*-hydroxypyridine-2-thione ester and the relative concentrations of these species (an excess of X−Y is always used).

Scaiano and co-workers[26] have noted that for two of the three thiohydroxamic esters which they studied ($\lambda_{\text{exc}} = 308$ nm), the ground-state depletion was only due to photoinduced N−O bond cleavage. In one case, some delayed bleaching has been observed. These results led them to the conclusion that chain reactions play only a minor role in the time scale of their laser experiments. The discrepancy between these observations and ours (where ground-state depletion caused by chemical reaction with the 2-pyridylthiyl radical was present for all compounds studied) cannot be explained by a concentration effect since both investigations were carried out using a similar concentration range. On the other hand, using an excitation wavelength of 355 nm, where the absorbance of the diphenylmethyl radical produced by photolysis of compound **2b** is weak (see Figure 3B), we have not observed any evidence of the excitation of $(C_6H_5)_2CH^\bullet$, which is not the case when the photolysis is carried out with $\lambda_{\text{exc}} = 308$ nm.[26]

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[58] Barton, D. H. R.; Blundell, P.; Jaszberenyi, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 6937−6942.

[59] Newcomb, M.; Kaplan, J. *Tetrahedron Lett.* **1987**, *28*, 1615−1618.