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PHOTO-PK OF INDOLINE-2-THIONE

ARAYA-HERNÁNDEZ, C.G[a]*. AND STEINER, U.E.*[b*]

[a]Laboratorio de Luminiscencia y Estructura Molecular, Facultad de Ciencias,
Universidad de Chile, Las Palmeras 3425, Ñuñoa, Santiago, Chile
[b]Fachbereich Chemie, Universität Konstanz, D-78457 Konstanz, Germany

ABSTRACT

The photochemistry and photokinetics of indoline-2-thione (1) has been investigated by continuous illumination at 334 nm and flash photolysis in aqueous solutions as a function of pH. The photokinetic behaviour and product distribution were almost independent on the presence of oxygen in the solution. Whereas indole is formed as the main product in acidic solutions biindolyl was found as the main product in unbuffered solution. For the quantum yield ϕ of photodegradation of 1 a marked increase was observed in acidic solutions. The pH dependence follows a Henderson-Hasselbalch relation with a pKa of 2.2. This photo-pK does note correspond to a pK_a in the ground state. It is tentatively assigned to the protolytic equilibrium $^{3}1 + H+ \rightarrow {}^{3}1H^{+}$ in the excited triplet state, evidence for which is found in the pH-dependence of transient absorption observed in laser flash photolysis experiments. Our findings support the intermediacy of a 2-mercapto-indole tautomer of 1 in the photochemical desulfurization mechanism as suggested previously by Nishio.11

1. INTRODUCTION

Although not comparable to the rich photochemistry of carbonyl compounds, the photochemistry of thiocarbonyl compounds has been widely explored[1-3] . Most work in this area is dealing with thioketones, a prominent feature being photo-oxidation reactions with molecular oxygen, whereby the corresponding ketones and, in some cases, sulfoxides are formed in varying amounts.[4-6] The photochemistry of thioamides has also found some interest in the literature.[7-9] Thus, for example, after UV irradiation of primary thioamides[7] in a nitrogen atmosphere, nitriles, amides, carboxylic acids and thiadiazoles were identified together with sulphur, SO_2 and SO_4^{2}-, while secondary and tertiary thioamides were stable under these conditions. Thiourea and its substituted derivatives[9] do not undergo photolysis under nitrogen or photooxidation under oxygen. Singlet oxygen produced by dye sensitization reacts with thioureas to form cyanamides, ureas, heterocyclic condensation products and sulfur-containing fragments.

The photochemistry of cyclic thioamides, or thiolactames, is of particular interest because such compounds are members of two interesting classes of substances thioamides and heterocycles. A nice study of the pH dependence of photo-oxidation of mercaptolumazine type thiolactames has been reported by Heckel and Pfleiderer.[10] These compounds undergo photo-oxidations to different reaction products depending on the protolytic form in the excited state. In other words, the pH dependence of the photoreaction is governed by the pK_a^* of the molecules.[10]

In this paper we will deal with new aspects of the photochemistry of indoline-2-thione (1), another member of the class of cyclic thioamides or thiolactames. Previous studies on the photochemistry of substituted indoline-2-thiones have been reported by Nishio et al.[11-14] According to these authors, indole is formed when 1 is irradiated in benzene under oxygen atmosphere. For this reaction an amino episulfide as an intermediate was suggested.[11] The desulfurized indolines as products are also formed upon photoreaction of indoline-2-thiones with tertiary amines[12,13] or with dienes14. In a recent photokinetic study of 2-mercaptobenzothiazole, Malouki et al.[15] also described the observation of photodesulfurization, which in this case was observed under aerobic as well as unaerobic conditions, albeit with largely different quantum yields. They also investigated the pH-dependence and found the anionic form of 2-mercaptobenzothiazole much more reactive than the neutral form. Our interest in the photochemistry of 1 arose from our search for new UV-actinometers. As we found out, indoline-2-thione is very UV-sensitive in acid aqueous solution. A pronounced change in the UV-absorption spectrum is going along with its photoreactions. This prompted us to investigate the photo-oxidation of 1 in aqueous solution in a quantitative manner with a particular focus on the pH-dependence of the quantum yield. Since all the investigations were done with dilute solutions on a small scale, various methods of instrumental analysis were employed, but no product isolation attempted.

2. EXPERIMENTAL

Reactant: Indoline-2-thione (1) was synthesized according to Cava and Levinson[16] by reaction of Lawesson´s Reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide) (7.82 g) with oxindole (3.28 g) in 200 mL toluene. The final product was characterized by means of ^{1}H-NMR and ^{13}C-NMR spectroscopy, UV/Vis absorption spectra and elemental analysis.

Solutions: Aqueous sample solutions were prepared using distilled water and, for pH adjustment, 3N H_3PO_4 (85%, Merck) and 1N NaOH (Merck GR). pH measurements were carried out with a Metrohm 713 pH meter using a combined LL pH glass electrode.

Irradiation and analysis of solutions: Sample solutions were irradiated at room temperature in a 1-cm quartz cell with an ILC Technology 300 W Xe lamp as a radiant source. The lamp was part of a photon-counting spectrofluorimeter model PC1 (ISS) with its slit width adjusted to 8 nm such as to yield an optimum combination of high light intensity and minimal band width. For photokinetic measurements absorption spectra were taken with a Perkin Elmer Lambda 11 UV/Vis Spectrometer after appropriate time intervals of irradiation. For quantum yield measurements, the photon irradiance of the sample was measured using a tris(oxalate) ferrate (III) solution according to Parker[17] as an actinometer. For photochemical product analysis by GC-MS the photoproducts were extracted from the irradiated aqueous solutions in

1 ml of CH2Cl2 (Aldrich, 99.6% A.C.S. spectrophotometric grade). A probe volume of 1.0 mL was injected (HP 6890 Series Injector) in a chromatographic column (HP 19091S-433) with a constant carrier gas flux of 2.0mL/min. MS-spectra were recorded in a Hewlett Packard 5973 Mass Selective Detector. HPLC analysis of the photolyzed solutions was performed on a Merck-Hitachi L 7000 HPLC system with a LiChropsher 100 RP-18 (5mm) column. Sample volumes of 20 µL were injected and separated using a H_2O/MeCN solvent gradient protocol. For NMR-analysis, the samples were irradiated in NMR tubes and measured in situ on a Bruker 600 MHz NMR spectrometer after irradiation.

Laser flash spectroscopy: Transient absorption spectra were recorded by using the frequency-tripled output (355 nm) of an Nd-YAG Laser as pump light, and a pulsed Xe lamp (XBO 150) as probe light. For these measurements a cylindrical quartz cell was used, and the solution was pumped with a flow rate adjusted such that no photoproducts were accumulated in the probe cell during a series of laser shots applied for signal accumulation.

3. RESULTS

3.1 Tautomeric and protolytic equilibria

As a secondary thioamide, indoline-2-thione could exist in different tautomeric forms and, depending on pH, exhibit various acid-base equilibria. Since these aspects will be important for its photochemical reactivity they shall be considered here in the first place.

Regarding the possible tautomerism

(1)

1a 1b

Hino et al.[18,19] reported evidence that only the thiolactam tautomer 1a is present in ethanol. Our own NMR-spectroscopic results lead to the same conclusions for CH_3CN and DMSO as solvents. The ^1H-NMR signal of the N-H proton appears at 10.4 ppm in CH_3CN (cf. Table 1) and at 12.6 ppm in DMSO. These results agree very well with published data for N-H proton in peptides[20]. On the other hand, the typical peak for an aromatic S-H proton at 3-4 ppm[20] was not observed. The ^{13}C-NMR spectrum shows a peak at 203.1 ppm in DMSO and at 205.4 ppm in CD_3CN, the typical range for the C=S carbon[20], a signal in the region 50 -70 ppm for the carbon in a thioimidic acid function[20] was not observed. The UV/Vis spectra of indoline-2-thione in the polar solvents mentioned above are very similar to the compound's spectrum in water at pH values below 6. The absorption spectrum of tautomer 1b, however, should be distinctly different which is a clear indication that in water too, indoline-2-thione essentially exists as tautomer 1a.

Table 1: ^1H- and ^{13}C- chemical shifts for indoline-2-thione (1) and its photoproducts in CD_3CN and CD_3CN/D_3PO_4

Compound	Chemical shift, ppm	
	CD_3CN	
	^1H (J, Hz)	^{13}C
Indoline-2-thione (1)		
	3.98(s, 2H, CH_2)	49.90 (CH_2)
	7.02(d, 1H, J=7.76Hz)	110.80 (arom)
	7.10 (dd, 1H, J=7,32Hz)	124.52 (arom)
	7.26 (dd, 2H, J=8.52Hz)	125.08 (arom)
	10.32 (shoulder, NH)	128.77 (arom)
		131.94 (arom)
		145.93 (arom)
		205.37 (C=S)
Photoproduct assigned to 2,2´-Biindolyl	6.81(s, 1H; -CH=)	99.57
	7.06(dd, 1H; J=7,2Hz)	111.92
	7.16(dd, 1H; J=7,02Hz)	112.85
	7.43(d, 1H; J=7,80Hz)	116.92
	7.59(d, 1H; J=8,40Hz)	120.92
	9.74(s, 1H; NH)	121.21
		121.39
		121.59
		123.24
		125.91
	CD_3CN/D_3PO_4 0.15 M	
	^1H (J, Hz)	^{13}C
Indoline-2-thione (1)	3.96(d, 2H; J=14.4Hz)	110.80
	7.013(d, 1H; J=7.8Hz)	124.54
	7.095(dd, 1H; J=7,8Hz)	125.14
	7.256(ddd, 2H; J=7.73Hz)	128.80
	10.49(s, 1H)	
Photoproduct assigned to indole	6.805(s, 2H)	111.88
	7.112(ddd, H; J=7.2Hz)	120.17
	7.422(d, H; J=8.1Hz)	120.90
	7.574(ddd, 2H; J=7.8Hz)	121.18
	9.78(s, NH)	123.20

In order to determine any protolytic equilibria of 1a in aqueous solution, we dissolved the compound in 0.1N H_3PO_4 and titrated this solution with 0.1N NaOH while simultaneously measuring the pH and the absorption spectrum. The pH-dependence of the absorbance at λ_{max} = 318 nm (corrected for the dilution due to the addition of NaOH) is shown in Figure 1. From a Henderson-Hasselbalch analysis of

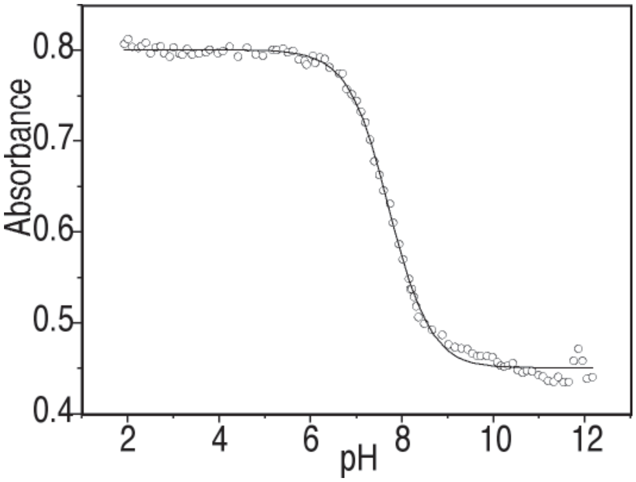
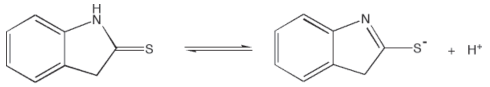


Fig.1. Photometric titration curve of a 5.6 × 10^{-5} M aqueous solution of 1. Data points represent absorbance values at 318 nm, corrected for the volume change during titration. The solid line represents the best fit using the Henderson-Hasselbalch equation.

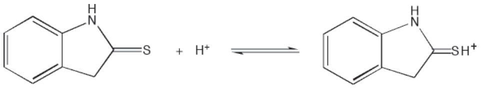
these results a pK_a value of 7.69 was estimated. This pK_a corresponds to the equilibrium



(2)

1a 2

Protonation of 1a according to



(3)

1a 3

does not occur in the pH range investigated.

Dealing with photoreactions, the acid-base properties in the excited state are also of interest. From the change in the absorption spectra associated with the protolytic process (2) we can infer on the pK_a^* in the S_1 state of compound 1a by applying the Förster cycle[21] which yields the following equation

$$pK_a^* = pK_a - \frac{hc}{\ln(10)kT}(\tilde{\nu}_{HA} - \tilde{\nu}_{A^-}) \qquad (4)$$

where $\tilde{\nu}_{HA}$ is the wavenumber of the absorption maximum of the acid HA and $\tilde{\nu}_{A^-}$ of the absorption maximum of the conjugated base A-. With a pK_a value of 7.69 and $\tilde{\nu}_{HA}$ = 31496.1cm-1 (317.5 nm) and $\tilde{\nu}_{HA}$ = 32310.2cm^{-1} (309.5 nm), and considering room temperature T=298K, a pK_a^* value of 9.4 was obtained for equilibrium (2) in the excited S_1 state.

3.2 Photochemical products

Under UV-illumination of compound 1, a gradual change of the absorption spectrum reflects the occurrence of a photoreaction. As can be seen for the spectral series taken in pure water as a solvent and in 3N aqueous H_3PO_4 (cf. Figure 2), the pH of the solution has a strong effect both on the rate (quantum yield) and on the product(s) of the photoreaction.

Analysis of the irradiated solutions by HPLC confirms that different products are formed in acidified and in unbuffered solution. In Figure 3, the change of the different HPLC peak areas as a function of irradiation time is shown. The main product peaks show different retention times (17.1 min in plain

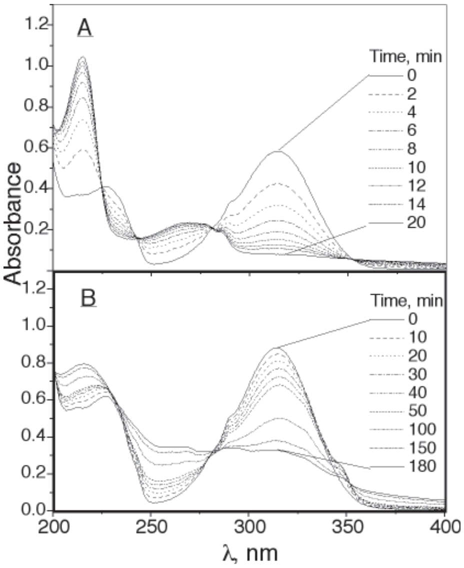
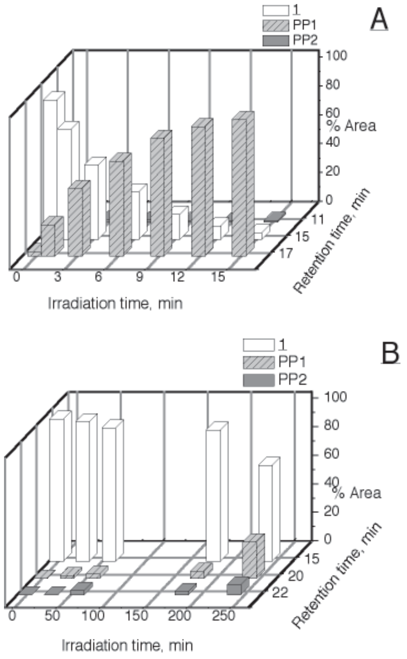


Fig. 2. Photochemically induced change of absorption spectra of 1 during irradiation at 334 nm in (A) 3 N aqueous H_3PO_4 solution and (B) plain aqueous solution (pH = 6.0) as a function of the irradiation time



Fig, 3. Evolution of HPLC peaks of 1 and the two main photoproducts (PP1 and PP2) during irradiation of a 10^{-4} M solution of 1 : (A) in 3 N aqueous H_3PO_4 and (B) in plain aqueous solution.

aqueous solution, 20.4 min in acidic solution) indicating that different main products are formed. The UV/Vis absorption spectra corresponding to the main chromatographic product peaks have been recorded by means of the diode array detector of the HPLC equipment. As will be further evidenced in the following, the main product can be assigned to 2,2'-biindolyl in neutral solution and to indole in acidic solution. The spectra of the product peaks shown in Figure 4A and 4B are in agreement with literature spectra of these compounds.[22,23]

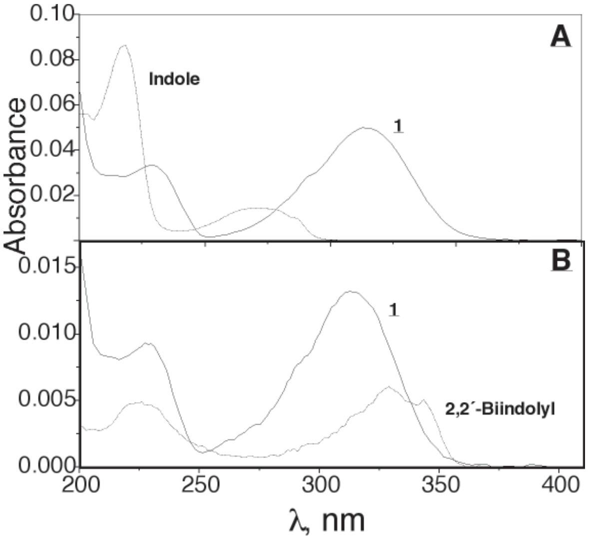


Fig. 4. Absorption spectra of 1 and the main photoproduct (PP1) in (A) aqueous 3 N H_3PO_4 solution and (B) in plain aqueous solution.

The irradiated solutions were also analysed by GC/MS. The pertinent mass spectra for samples from neutral and acidic solutions are shown in Figure 5. In neutral solution we found the main photoproduct (97.1% relative yield in air-saturated solution, 93.2% relative yield under nitrogen) with m/z= 232 (M^+) corresponding to the dimer 2,2‘-biindolyl.[24,25] In acid solution we found a peak with m/z = 117 (M^+) for the main photoproduct (97.3% relative yield in air-saturated solution, 97.4% relative yield under nitrogen), which corresponds to indole.[26]

Finally, also ^{1}H- and ^{13}C-NMR spectra of irradiated solutions of compound 1 in CD_3CN and in CD_3CN acidified with D_3PO_4 were measured. CD_3CN was used instead of D_2O in order to achieve higher sample concentrations to facilitate NMR detection. Judging from the UV/Vis absorption spectra, solutions in neutral and acidic CD_3CN behave very similar to the corresponding aqueous solutions. In neutral as well

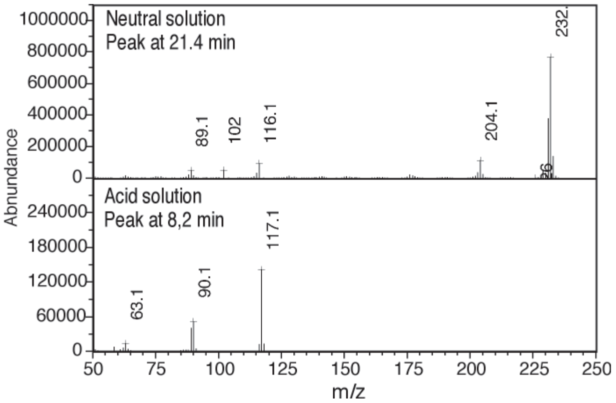


Fig. 5. Upper panel: mass spectrum of the main photoproduct in unbuffered aqueous solution (pH=6.0), lower panel: mass spectrum of the main photoproduct in aqueous acid solution (pH=1.0).

as in acidic CD_3CN the spectra of 1 before irradiation are almost identical. Only the peak of the NH-proton appears a little shifted between these situations. As mentioned above, the peaks due to the CH_2- and NH-protons indicate the predominant existence of the thiolactame form 1a. The NMR-signals of the main photoproducts obtained after 21 h of irradiation in neat CD_3CN in an NMR-tube are consistent with NMR data from the literature[25,27] for 2,2'-biindolyl. The changes of NMR signals observed upon irradiation in the acidic solution are consistent with the formation of indole as the main primary photoproduct.

Thus, altogether, there is convincing evidence from different analytical methods for the photochemical formation of 2,2'-biindolyl in neutral solution and of indole in acidic solution.

Finally, it must be pointed out that in both neutral and acidic solution the products formed are independent on whether the solutions are photoirradiated in N_2- or in air-saturated solutions.

3. 3 Photochemical quantum yields

The quantum yield of the photoreaction of 1 was determined for an irradiation wavelength of 334 nm. The experiments were carried out with solutions at concentrations in the range 3 – 4 $\times 10^{-4}$ $M^{-1}cm^{-1}$ such that close to total absorption of the photolysis light by 1 was achieved. The photoinduced change of the concentration of 1 was corrected for a broad background absorption (cf. Figure 2, long wavelength end) originating during the photoreaction probably because of light scattering due to the formation of colloidal sulfur. In a first approach, the necessary background correction at 340 nm was estimated by assuming that the apparent absorption at 390 nm is entirely due to Rayleigh-type light scattering according to which a λ^{-4} dependence of the scattered intensity should be assumed.[28] The corrected absorption change of 1 was converted into a corresponding concentration change using an absorption coefficient of 6553 $M^{-1}cm^{-1}$. The light intensity required to calculate the quantum yield was determined using the Fe(III)oxalate actinometer according to Parker.[17] On the basis of this evaluation, it was found that the photochemical quantum yield at low pH reaches a value as high as 1.3. A quantum yield greater than 1 would imply that more than one reactant molecule per absorbed photon is involved in the reaction. But the absolute quantum yield values obtained as described above should be taken with care since they critically depend on the background correction at 340 nm. The correction on the basis of the Rayleigh scattering law implies that the background ratio between 340 nm and 390 nm corresponds to $(390/340)^4 = 1.73$. The conditions for this law to be valid require that the scattering particles are smaller than λ/20 which in our case correspond to about 20 nm. If they are larger, Mie scattering predicts a less pronounced wavelength dependence,[29] which could well bring the observed limiting quantum yield from 1.3 to below 1.0. To estimate a lower limit of the absolute photochemical quantum yield ϕ, the wavelength-dependence of the scattered light intensity may be completely neglected and the observed value of attenuation of transmitted light at 390 nm adopted for 340 nm. This yields a limiting quantum yield of 0.75 at the lower pH-limit investigated. Since the true value should be somewhere in the middle between the estimated extremes of 1. 3 and 0.75 it probably comes close to 1. Therefore, the quantum yield values obtained with the correction following the λ^{-4} dependence were linearly corrected such as to yield a limiting low-pH value (cf. section 4) of 1.0.

The quantum yields of photo-induced disappearance of 1 as a function of pH are plotted in Figure 6. A marked sigmoidal pH-dependence is observed characterized by a high quantum yield in the region of low pH, a low quantum yield at higher pH, and an inflection point around pH 2. As reported in the last section, the main product at pH 1 – 5 is indole. At pH 6, the nature of the main photo product (indole or biindolyl) is still dependent on the buffer. However, the rate of the photoreaction at pH 6 does not show large differences. At pH > 8 solutions of 1 decompose already in the dark. Therefore, a quantitative study of the photoreaction of the anion of 1 was not attempted.

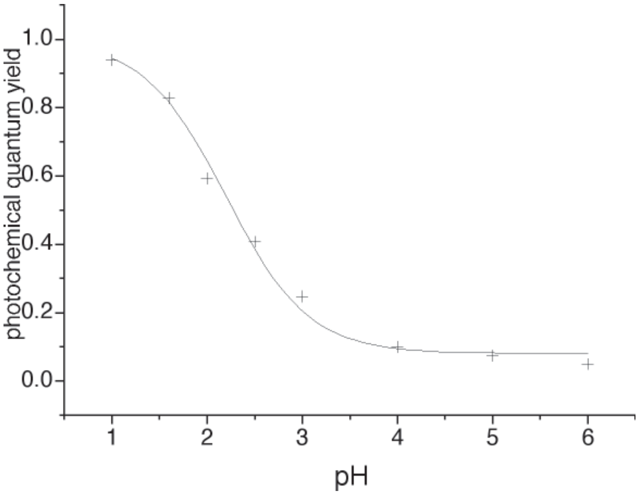


Fig. 6. Quantum yield ϕ (for calibration of absolute values cf. text) of photodecomposition of 1 at 334 nm as a function of pH. The smooth line represents a best fit according to the modified Henderson-Hasselbalch equation wherein the quantum yield replaces the absorbance.

3.4 Evidence of intermediate triplet state

In order to observe short-lived intermediates of the photoreaction of 1, laser flash spectroscopy experiments were performed. Figure 7 shows pertinent transient absorption spectra observed at various delay times after the laser pulse. Immediately after the laser pulse, a broad absorption band with a maximum at about 600 nm is observed. Below 390 nm the transient absorption is negative which is due to the intermediate bleaching of the ground state of 1a. The spectra decay with a time constant of about 100 ns without a change of the spectral profile. The life time of the transient decreases only slightly if air-saturated instead of N_2-saturated solutions are used. On the other hand, laser flash experiments with sodium benzoate show that the benzoate triplet is quenched by 1. In a 0.7 mM aqueous solution of sodium benzoate (pH = 6.6) the life time of the benzoate triplet is reduced from 16 µs in quencher-free solution to 10 µs at a concentration of 1a of 4×10^{-5} M. This corresponds to a quenching constant of about 10^9 $M^{-1}s^{-1}$.

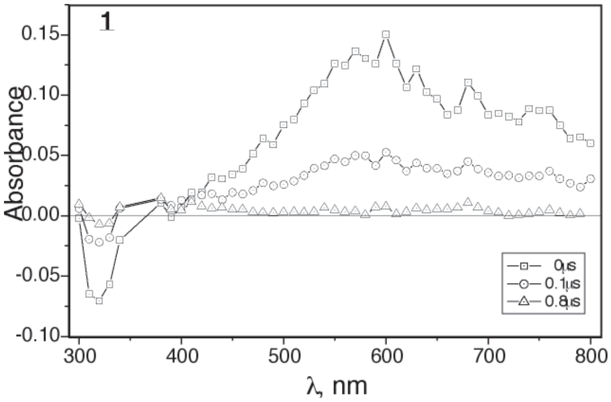


Fig. 7. Transient absorption spectra of 1 (1.12×10^{-4} M) in aqueous solution (pH = 6.0) at various delay times after the laser pulse.

It is worth of note that the life time of the observed transient shows a significant decrease in acidified solutions (cf. Figure 8). At pH 1 the signal is hardly detectable and its decay time is around 10 ns. Unfortunately, due to the weakness of the signal, it cannot be decided whether the spectral profile of the transient is changed in acidic solution.

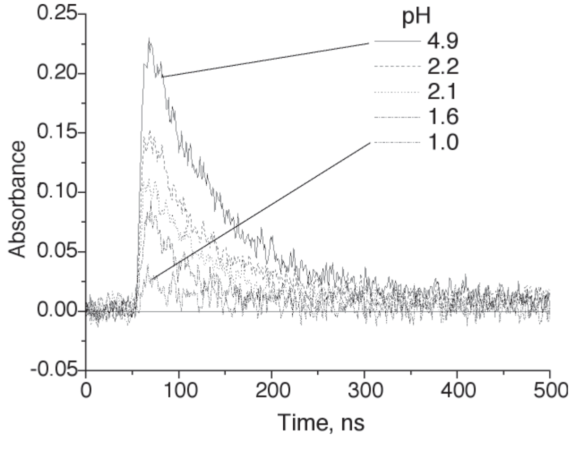


Fig. 8. Transient absorption decay of 1 (8.7×10^{-5} M) observed at 600 nm as a function of pH, adjusted with 3 N H_3PO_4 and 1N NaOH in aqueous solution

In order to find out whether the short-lived transient observed upon flash photolysis might be assigned to the triplet state of 1, independent evidence of the population of the T_1 state of 1 was sought by phosphorescence spectroscopy. At 77 K in EPA glass, a phosphorescence spectrum has indeed been observed (cf. Figure 9). The phosphorescence excitation spectra at 77 K closely resemble the absorption spectrum of 1 at room temperature although they are somewhat more structured and they exhibit stronger Franck-Condon factors for higher vibrational transitions. The blue edge of the phosphorescence emission is located at about 430 nm which corresponds to a triplet energy of 280 kJ mol^{-1} (2.9 eV).

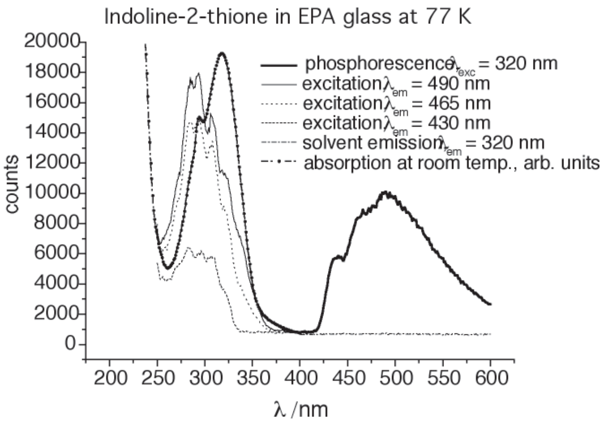


Fig. 9. Phosphorescence spectrum and phosphorescence excitation spectra of 1 in EPA glass at 77 K, absorption spectrum at room temperature (arbitrary units).

4. DISCUSSION

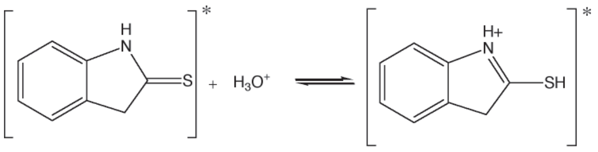
In this work, a remarkable pH-dependence of the photochemical quantum yield of the photodecomposition of a heterocyclic thioamide has been found. In fact, the pH-dependence shown in Figure 6 can be fitted by a type of Henderson-Hasselbalch equation:

$$\phi = \frac{(\phi_{\max} - \phi_{\min})}{1 + \exp((pH - pK) * \ln 10)} + \phi_{\min} \qquad (5)$$

containing two limiting quantum yields ϕ_{max} (1.0) and ϕ_{min} (0.08) and a pK (2.2) as parameters. Such a behaviour justifies the introduction of the term "photo-pK". It should be related to the protolytic equlbrium of an intermediate responsible for the change in ϕ as a function of pH in the range 1 to 4.

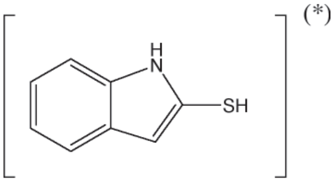
From our titration in the ground state we obtain just one pK_a (7.69). It implies that in neutral aqueous solution this compound is present in its neutral form. The dramatic change of ϕ in acidic solutions between pH 1 and 4 cannot be related to a protolytic dissociation of 1 given that the pK_a value is 7.69 and its pK_a* corresponds to 9.39 (cf. 3.1). Rather, a pK in the acidic range would be related to an acid-base equilibrium where 1 reacts as a base according to equation 3.

The increase of ϕ in the pH range from 4 to 1 cannot be due to a protolytic reaction in the ground state since there is no change of the absorption spectra in this range. However, the strong change in the reaction rate could be related to an acid-base equilibrium in the excited state (equation 6):



1^* $(1H^+)^*$

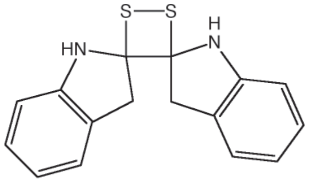
A pH-dependence of some thioamide photoreactions has also been observed by Heckel and Pfleiderer.[10] They found that illumination of 6- or 7-mercapto lumazine leads to a disulfide-coupled dimer at pH <1, whereas sulfinic and furtheron sulfonic acid derivatives are formed at neutral pH. These photoreactions take place only under aerobic conditions. In contrast, the photoproducts and reaction rates of indoline-2-thione 1 investigated in this work do occur under anaerobic conditions and are very little affected by the presence of oxygen, a fact that was not described by Nishio.[11] At present, we can only speculate about the mechanism according to which the observed desufurized products indole and 2,2-bisindolyl are formed without molecular oxygen in the system. From the photo-pK observed it seems likely that the excited protonated state $(1H^+)^*$ is a reactive intermediate. It might undergo photo-tautomerization to 2-mercaptoindole $1c^{(*)}$ (perhaps still electronically excited).



$1c^{(*)}$

from which reaction steps with final formation of indole might start with an episulfide as an intermediate as suggested by Nishio.[11] Of course, another possible reaction of $(1H^+)$* is the formation of the photo-tautomer $1b^{(*)}$. However, a transformation of the thioindole $1c^{(*)}$ to the episulfide intermediate suggested by Nishio[11] seems more feasible than of $1b^{(*)}$.

The formation of 2,2-biindolyl prevails in solutions of low acidity. Disulfide formation, as described by Nishio[11] was not observed to a significant extent under our experimental conditions. However, as was postulated for the formation of the disulfide, a coupling step to a dimer is needed for biindolyl, too. A primary dimer structure formed between an excited and a ground-state molecule could be the spiro-1,2-dithietane 2:



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which, in subsequent steps, would have to desulfurize to yield 2,2-biindolyl.

Finally, we address the issue of the electronic nature of the photoreactive state and of the role of the intermediate observed by laser flash photolysis. As a thiocarbonyl compound with the possibility of spin-orbit-favoured nπ* - π * conversion enhanced by the heavy-atom effect of the sulfur atom, photoexcited 1 is expected to undergo efficient S* → T intersystem crossing. This expectation is supported by the observation of only a very weak fluorescence of 1 but of phosphorescence at low temperature. From the band edge at short wavelengths of the phosphorescence spectrum at 425 nm, a triplet energy of 281 kJ mol^{-1} (2.9 eV) is obtained. Such a value is supported by our quantum chemical calculations[30] and by the observation that 1 can act as a triplet quencher of benzoate which has a triplet energy of about 320 kJ mol^{-1} (3.31 eV).[31]

It is reasonable to assign the transient absorption observed at room temperature to the T_1-state of 1. The transient absorption observed by us has a similar spectrum to what has been identified as the triplet of the related 2-mercaptobenzothiazole by Malouki et al.[15] In unbuffered aqueous solution, our transient has a life time of 73 ns which is almost insensitive to the exposition of the solution to air. Molecular oxygen is known to quench triplets that are higher in energy than the energy of $O_2(^1\Delta_g)$ (96 kJ mol^{-1}) at close to diffusion-controlled rates. In aqueous solutions a typical quenching constant of 5×10^9 M^{-1}s^{-1} can be reasonably assumed. Based on a solubility of molecular oxygen of 2.5×10^{-4} M when water is in equilibrium with air of 1 bar, an effective first order rate constant of 1.5×10^5 s^{-1} of triplet decay due to quenching by molecular oxygen is estimated. This quenching should decrease the life time of a triplet from 73 ns to 71 ns which is a small effect and not incompatible with our observations.

Thiocarbonyl compounds have also been reported to undergo efficient self-quenching[32] with rate constants between 10^9-10^{10} M^{-1}s^{-1}. For concentrations up to 10^{-4} M, as employed in our experiments, a maximum value of an effective first-order rate constant of 10^6 s^{-1} would ensue which is much lower than that observed, so that the main decay mechanism must be of intramolecular nature.

A feature most interesting in relation to the pH-dependent quantum yield of the photoreaction of 1 is the pH-dependent life time and intensity of the transient absorption signal. As the pH is decreased the initial intensity and the life time of the observed transient decreases. Such a behaviour correlates well with the increase of the quantum yield with the acidity of the solution. If it is assumed that the protonated triplet undergoes a fast chemical reaction, the shift of the protolytic equilibrium in the excited triplet state would result in a decrease of the concentration of the neutral triplet and a shortening of its life-time which is just the behaviour of the transient observed.

4. CONCLUSION

In this work the formation of the desulfurization product indole as the main photoproduct in the photoconversion of indoline-2-thione, reported by Nishio[11] to occur in benzene, is also confirmed for aqueous solutions buffered at acid pH. The study of the role of oxygen, which has no significant effect on photoproducts and photokinetics, and of the photochemical quantum yield as a function of pH with the detection of a photo-pK not corresponding to a protolytic equilibrium in the ground state, has provided further evidence for a reaction mechanism wherein 2-mercaptoindole as a phototautomer of 1 might be involved.

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