

Possible singlet oxygen generation from the photolysis of indigo dyes in methanol, DMSO, water, and ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate

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Abstract—We suggest that singlet molecular oxygen [¹O₂ (¹Δ_g)] is formed upon irradiation of indigo **1** [in air or O₂-saturated DMSO and DMSO (0.5% H₂SO₄)] and indigo carmine **2** [in air or O₂-saturated CH₃OH, D₂O, and 1-butyl-3-methylimidazolium tetrafluoroborate (BmIm–BF₄)]. The quantum yield for production of ¹O₂ is estimated to be 0.6 for **1** and 0.3–0.5 for **2**. The rates of reaction of ¹O₂ with **1** and **2** were determined by monitoring the emission of ¹O₂ at 1270 nm over time. Low molar absorptivities (at 532 nm) and rapid physical quenching caused by **1** and **2** limit their utility as ¹O₂ photosensitizers in solution. Compounds **1** and **2** degrade slowly during the photolysis due to a self-sensitized (type I or II) photooxidation reaction. Oxidative cleavage of **1** by singlet oxygen and superoxide, and **2** by superoxide has been noted before (Kuramoto, N.; Kitao, T. *J. Soc. Dyers Color.* **1979**, *95*, 257–261; Kettle, A. J.; Clark, B. M.; Winterbourn, C. C. *J. Biol. Chem.* **2004**, *279*, 18521–18525).

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1. Introduction

Indigo (**1**) possesses a blue color, and has been of scientific interest given its historic provenance and esthetic hue. Indigo is a naturally derived dye that comes from a variety of plant species.^{1,2} Biosynthetic and laboratory preparations of **1** have been reported.^{3–6} Indigo **1** and indigo carmine **2** represent stable dyes and colorants, and are composed of a central carbon double bond with two imine nitrogens and two carbonyl groups affixed (Chart 1).⁷

Both **1** and **2** are quite photostable⁸ and this led us to raise the following question: *How efficiently might they generate*

¹O₂ by photosensitization? The yield of ¹O₂ formed by irradiation of triplet O₂ plus sensitizer varies depending on the structure of the photosensitizer, the nature of the photosensitizer's excited state, and on the solvents used. Studies of indigo dye spectroscopy,^{8–12} excited state chemistry,^{13–24} and photofading^{25,26} date back to the 1950s. The mechanism of quenching of electronically excited states of thioindigo dyes (S replacing NH) by triplet molecular oxygen has been studied.^{27–35} Wyman and co-workers observed that dissolved oxygen quenched the photoisomerization of **3** without diminishing the intensity of the fluorescence.³⁶ This suggested that the trans–cis isomerization of **3** may involve the excited triplet state. The triplet energy of **3** was determined to be 27–32 kcal/mol,^{16,17} which is greater than the 22.5 kcal/mol required to excite O₂ from its ground state to its first excited singlet state. The triplet state energies of **1** and **2** have not yet been reported.

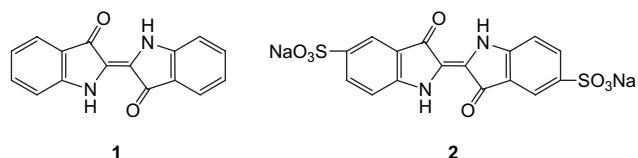
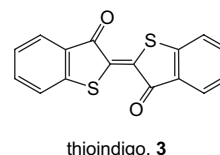


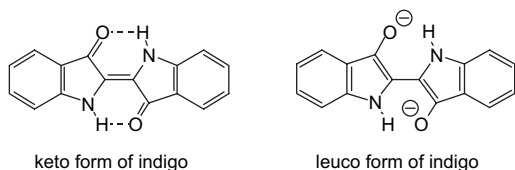
Chart 1. Structures of indigo and indigo carmine in their keto forms.



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The photostability of indigo **1** has been attributed by Kobayashi and Rentzepis to the high internal conversion from excited singlet state S_1 to ground singlet state S_0 rather than trans to cis isomerization.¹⁴ The internal conversion process may be enhanced by excited state intramolecular proton transfer. However, Elsaesser et al. have concluded that the internal conversion is related to the vibrations of the N–H bonds, which are part of the intramolecular hydrogen bonds.¹³

Despite the importance of indigo dyes, little information is available about whether they may serve as 1O_2 sensitizers.³⁶ Recent work by Seixas de Melo and co-workers showed that the fluorescence efficiency Φ_F is favored by the leuco, but not keto forms, e.g., Φ_F of indigo is 0.0023 for the keto form, but 0.348 for the leuco form in DMF.³⁷ The structures of the keto and leuco forms of indigo are shown below. The low fluorescence of indigo dyes in their keto form was explained by the small energy gap between S_0 and S_1 . According to the golden rule for radiationless transitions, a small value in the S_1 – S_0 energy gap favors a nonradiative decay pathway by increasing the vibrational overlap (Franck–Condon integrals) of the wave functions for the nonradiative modes of these two states.^{22,23}



The formation of 1O_2 is predominantly a triplet quenching process. The 1O_2 quantum yields (Φ_Δ) were determined using Eq. 1.³⁸ Eq. 1 represents a theoretical understanding of quantum yields of 1O_2 generation.

$$\Phi_\Delta = \Phi_T P_{T,^3O_2} f_{T,\Delta} \quad (1)$$

Here Φ_T is the quantum yield of triplet formation for the photosensitizer, $P_{T,^3O_2}$ the proportion of triplet quenched by ground state oxygen and $f_{T,\Delta}$ the fraction of triplet state quenched by ground state oxygen that leads to the formation of 1O_2 .

There is limited solubility of **1** in DMSO (~ 0.7 mM) and in $CHCl_3$, CH_2Cl_2 , CH_3CN , and CH_3OH (< 0.1 mM). However, because of its pair of sulfonate groups, indigo carmine **2** dissolves in water (~ 0.02 M) and MeOH (~ 0.8 M) to a higher extent. A number of reports discussing photochemistry in ionic liquids have appeared in the past several years.^{39–43} The ability of ionic liquids to retain other ionic compounds suggested the idea of using a photosensitizer bearing a charge, thereby making it preferentially soluble in the ionic liquid. Imidazole-tagged aryl ketones have been developed that can efficiently sensitize photochemical reactions in ionic liquids and are isolated simply by extraction of the ionic liquid solution with an appropriate organic solvent after use.⁴⁴ The [2+4] reaction between 1O_2 and 1,4-dimethylnaphthalene has been investigated in several 1-methyl-3-butylimidazolium cation ($BmIm^+$) ionic liquids along with the following counter anions: PF_6^- , SbF_6^- , and BF_4^- .⁴⁵

Information regarding the quantum efficiency of 1O_2 generation in ionic liquids is unavailable.

We report that absorption of visible light by **1** and **2** in the presence of O_2 leads to the production of 1O_2 . Singlet oxygen generation was measured for **1** in DMSO, and **2** in CH_3OH , D_2O , and $BmIm-BF_4$ using a time-resolved method. Oxidizing intermediates produced during the reaction led to the decomposition of **1** and **2**.

2. Experimental

2.1. General aspects

Indigo **1**, indigo carmine **2**, isatin **4**, rose bengal, methylene blue, and di-*n*-butyl sulfide were purchased commercially and used without further purification. The solvents used (DMSO, D_2O , CH_3OH , and $BmIm-BF_4$) were of spectroscopic or equivalent grade and were used as received. Light at 532 nm was obtained from a time-resolved Nd:YAG laser set-up with pulse width 3–4 ns and maxima energy 50 mJ at 532 nm (Polaris II-20, New Wave Research Merchantek Products). A liquid N_2 cooled germanium photodetector (Applied Detector Corporation) was used for the determination of quantum yields and luminescence quenching rates of 1O_2 . A Rayonet 250 W tungsten lamp equipped with a 1 cm 1.5 M $NaNO_3$ solution cutoff filter was used for steady-state generation of 1O_2 . UV–visible spectra were recorded on a Varian 300 Bio (Cary) spectrophotometer. Mass spectrometry data was collected on an Agilent 1100 LC/MSD instrument using either electrospray ionization or atmospheric pressure photoionization methods. All experiments were carried out at room temperature and with air or O_2 -saturated solutions. Shaking, stirring, and/or sonication were conducted to dissolve **2** and methylene blue in $BmIm-BF_4$.

2.2. 1O_2 Quantum yield measurements

Absorbances of **1** and **2** ranged from 0.03 to 0.6 at the excitation wavelength 532 nm. The absorbance of **1** and **2**, and rose bengal (known to possess a quantum yield of 1O_2 generation 0.76 in DMSO, methanol, and heavy water)^{46,47} all matched to within 80%. The quantum yield values may change according to the reference used. The initial 1O_2 intensity is extrapolated to $t=0$. The data points of the initial 3–4 ns are not used due to electronic interference signals from the detector. The intensity of the pulses at 532 nm were controlled between 40 and 50 mJ. The quantum yield for production of 1O_2 is calculated according to Eq. 2. Unlike Eq. 1, Eq. 2 is practical to use along with the time-resolved method.

$$\frac{\Phi_{\Delta\text{sample}}}{\Phi_{\Delta\text{reference}}} = \frac{S_{\text{sample}}}{S_{\text{reference}}} \quad (2)$$

Here $\Phi_{\Delta\text{sample}}$ and $\Phi_{\Delta\text{reference}}$ are the quantum yields for samples and the reference. Rose bengal was used as a reference sensitizer. S_{sample} and $S_{\text{reference}}$ represent the slopes obtained from the plot of initial intensity of 1O_2 via the absorbance at excitation wavelength 532 nm for the sample and the reference, respectively.

2.3. Quenching rate constants of $^1\text{O}_2$

The phosphorescence of $^1\text{O}_2$ at 1270 nm was measured as previously described.⁴⁸ The $^1\text{O}_2$ quenching rates were measured by monitoring the deactivation of $^1\text{O}_2$ by **1** and **2**. Stern–Volmer analyses were conducted with rose bengal as the sensitizer in DMSO, methanol, and D_2O .

3. Results and discussion

3.1. Spectral properties of **1** and **2**

Normalized UV–visible spectra for **1** and **2** are shown in Figure 1. The λ_{max} and absorptivity at maxima of **1** and **2** and their 532 nm excitation wavelengths are collected in Table 1. The absorption of **1** and **2** consists of a band in the visible region between 500 and 700 nm with a small inflection or shoulder at shorter wavelengths (Fig. 1). The high absorptivity indicates that **1** and **2** can be excited upon the absorption of light in this range.

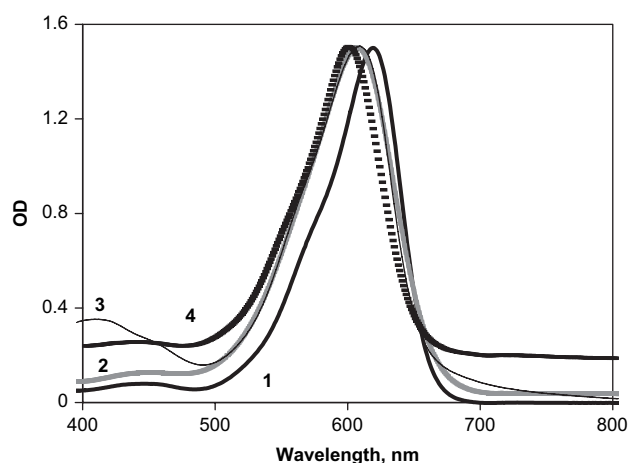


Figure 1. Normalized absorption spectra of **1** and **2**. (1) DMSO solution of **1**. (2) D_2O solution of **2**. (3) BmIm– BF_4 solution of **2**. (4) CH_3OH solution of **2**.

Table 1. Absorption maxima and extinction coefficients of solutions containing **1**, **2**, and methylene blue

Sensitizer	Solvent	λ_{max} , nm	ϵ_{max} , $\text{M}^{-1}\text{cm}^{-1}$	$\epsilon_{532\text{nm}}$, $\text{M}^{-1}\text{cm}^{-1}$
1	DMSO	620	2.26×10^3	3.26×10^2
2	CH_3OH	598	4.76×10^3	1.59×10^3
2	D_2O	607	7.92×10^3	2.02×10^3
2	BmIm– BF_4	609	—	—
Methylene blue	BmIm– BF_4	661	—	—

3.2. Possible $^1\text{O}_2$ quantum yields and quenching rates

The quantum yields for $^1\text{O}_2$ generation were determined by time-resolved laser measurements of its near-infrared luminescence (1270 nm) upon excitation at 532 nm with rose bengal $\Phi_{\Delta}=0.76$ as the reference in DMSO,⁴⁶ CH_3OH , and D_2O (Fig. 2).⁴⁷ Ideally, the straight lines should go

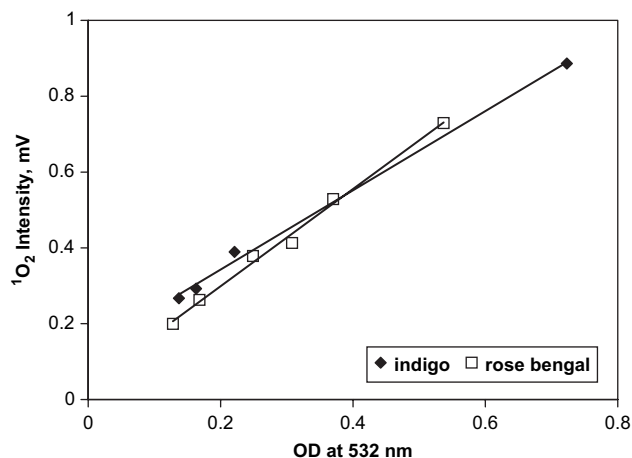


Figure 2. $^1\text{O}_2$ Emission intensity as a function of absorbance in DMSO with the excitation wavelength of 532 nm.

through zero in Figure 2, and we attribute the deviation to systematic errors. Thus, the quantum yields were determined from the slopes of the plots. Triplet–triplet annihilation appears to be negligible at absorbances ranging from 0.03 to 0.60 from excitation at 532 nm, as indicated by the $^1\text{O}_2$ intensity showing a linear correlation with the absorption of the complexes. We estimate that the Φ_{Δ} for **1** is 0.6, and for **2** is 0.3–0.6, where these Φ_{Δ} 's were obtained in the common solvents noted above. No reference photosensitizer is available for ionic liquids. Thus, the relative Φ_{Δ} for **2** in BmIm– BF_4 was calculated assuming $\Phi_{\Delta}=1.0$ for methylene blue. Our results show that Φ_{Δ} for **2** is about half that of methylene blue (Table 2).

The total $^1\text{O}_2$ quenching rate constants (k_T) of **2** with $^1\text{O}_2$ were determined in D_2O and CH_3OH by Stern–Volmer analyses, since a large quenching rate would severely limit their potential as photosensitizers. The quenching rate constants range from 5×10^7 to $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for **2** in CH_3OH and D_2O . This is similar to other photosensitizers, e.g., rose bengal ($2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in CH_3OH ⁴⁹) and methylene blue ($2.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in CH_3OH ⁵⁰ and $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in D_2O ⁵¹). The quenching rates of $^1\text{O}_2$ by **1** in DMSO and **2** in BmIm– BF_4 cannot be observed because of their limited solubility. The self-decay rate constants (k_d , s^{-1}) measured in the present work are comparable to published values of $7.1 \times 10^4 \text{ s}^{-1}$ in DMSO,⁵² $8.9 \times 10^4 \text{ s}^{-1}$ in CH_3OH ,⁵³ $1.8 \times 10^4 \text{ s}^{-1}$ in D_2O ,⁵⁴ and $6.3 \times 10^4 \text{ s}^{-1}$ in BmIm– BF_4 .⁴⁵

Indigo **1** and indigo carmine **2** exhibit absorption bands in the range of 500–700 nm, and can be activated to higher energy levels by absorbing excitation light in this region. Photosensitization processes have been reviewed in detail by Wilkinson and Brummer.²⁷ A brief summary is given below (Eqs. 3–10). A Type II mechanism involves the generation of $^1\text{O}_2$ via energy transfer between T_1 of a photosensitizer and ground state $^3\text{O}_2$ (Eq. 7). A Type I mechanism involves hydrogen-atom abstraction or electron-transfer between the excited photosensitizer and a substrate, and the subsequent generation of oxygen radicals. One example of the Type I reaction is an electron-transfer from an excited sensitizer to $^3\text{O}_2$, to form superoxide (Eq. 8).

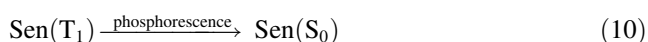
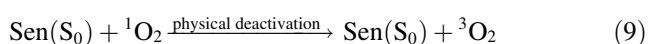
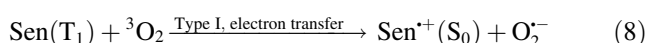
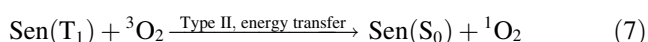
Table 2. Summary of $^1\text{O}_2$ quantum yields (Φ_Δ), total quenching rate constants (k_T , $\text{M}^{-1} \text{s}^{-1}$) and self-decay rate constants in various solvents (k_d , s^{-1})^a

Photosensitizer	Solvent	$\Phi_\Delta \pm \text{S.D.}$	Reference	k_T , $\text{M}^{-1} \text{s}^{-1}$	k_d , s^{-1}
1	DMSO	0.61±0.09	Rose bengal 0.76	—	$(9.1 \pm 2.0) \times 10^4$
1	DMSO/0.5% H_2SO_4	0.62±0.05	Rose bengal 0.76	—	$(6.0 \pm 1.0) \times 10^4$
2	CH_3OH	0.53±0.07	Rose bengal 0.76	$(5.6 \pm 0.1) \times 10^7$	$(8.1 \pm 0.5) \times 10^4$
2	D_2O	0.31±0.03	Rose bengal 0.76	$(3.2 \pm 0.7) \times 10^8$	$(1.9 \pm 0.3) \times 10^4$
2	BmIm-BF ₄ ^b	0.53±0.11	Methylene blue ^c	—	$(6.1 \pm 0.9) \times 10^4$

^a All experiments were measured at room temperature in air-saturated solutions with an excitation wavelength of 532 nm.

^b There is no reference $^1\text{O}_2$ photosensitizer available for BmIm-BF₄.

^c The $^1\text{O}_2$ quantum yield for indigo carmine **2** in BmIm-BF₄ was calculated assuming $\Phi_\Delta=1.0$ for methylene blue.



The apparent production of $^1\text{O}_2$ by the photolysis of **1** and **2** suggests that a triplet energy transfer process takes place. The proposal of energy transfer from excited **1** or **2** to $^3\text{O}_2$ is consistent with measured E_T 27–32 kcal/mol for thioindigo compounds since the triplet ground and first excited singlet state of O_2 is 22.5 kcal/mol.^{16,17} Indigo dyes in their excited triplet states may react with $^3\text{O}_2$ and generate $^1\text{O}_2$ via Eq. 7. Alternatively, the redox potential of O_2/O_2^- and O_2/HO_2^- are -0.60 V and 0.12 V versus NHE in DMF,⁵⁵ respectively, also suggests that electron-transfer is thermodynamically favored, in particular by increasing the acidity of the solution. The excited state redox potentials E ($\text{Sen}^{+*/s}$) for **1** and **2** are unknown. Our results do not appear to support the Type I mechanism (Eq. 8) due to the fact that constant and unvarying high quantum yields (Φ_Δ) for $^1\text{O}_2$ generation are observed in both of DMSO and DMSO/0.5% H_2SO_4 for **1**. The quantum yields for $^1\text{O}_2$ generation suggest intersystem crossing and the formation of triplet states of **1** and **2** under these conditions. However, the quantum efficiency of singlet oxygen can potentially vary with the excitation wavelength, light intensity, solvent, solute, etc. Our results support the notion of low fluorescence efficiency and the formation of excited triplet state of **1** and **2** in their keto form.^{16,17,37,56}

The Φ_Δ for $^1\text{O}_2$ generation from indigo carmine **2** in D_2O (0.31) is lower compared to that in CH_3OH (0.53). This may be explained by a larger acidic dissociation of indigo carmine in water than methanol. We conclude that the k_T

values measured for **1** and **2** are mainly the result of physical quenching since photooxidation products are only observed after extended irradiation periods (several hours) under visible light and oxygen. Physical quenching of $^1\text{O}_2$ may be related to trans–cis isomerization or the presence of the imide nitrogens. The k_T value for **2** is $5.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in CH_3OH , and $3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in D_2O .

Due to the lack of reference photosensitizers in ionic liquids, the relative Φ_Δ values were determined by assuming $\Phi_{\Delta(\text{methylene blue})}=1.0$ in BmIm-BF₄, yielding $\Phi_{\Delta(\text{methylene blue})}/\Phi_{\Delta(\text{indigo carmine } 2)}=2:1$. In contrast, the Φ_Δ ratio of methylene blue to indigo carmine **2** is 1:1 in CH_3OH . Furthermore, the Φ_Δ is 0.5 for methylene blue in CH_3OH has been reported previously.⁴⁷ The change in relative $^1\text{O}_2$ quantum yields may result from a competition reaction for the triplet state. The enhancement of the lifetimes of triplet state and radical ions is observed for xanthone in 1-butyl-3-methylimidazolium hexafluorophosphate (BmIm-PF₄).⁴³ This statement is speculative since influence of ionic liquids on the deactivation of triplet states is not established. Thus, it is difficult to assess whether the quantum yields for $^1\text{O}_2$ generation from rose bengal and indigo carmine **2** are significantly increased or decreased in different solvents.

3.3. Possible $^1\text{O}_2$ sensitization

Singlet oxygen may be formed under the conditions we have used in our experiments. Figure 3 contains the data of a representative 1270 nm signal decay produced by irradiation of **2** in CH_3OH . We attribute the 1270 nm signal to $^1\text{O}_2$, which is quenched by addition of NaN_3 (0.20 mM) to the solution. The self-decay rate constants k_d measured in various solvents are consistent with the literature values,^{45,52–54} where the k_d ranges from 10^4 to 10^5 s^{-1} , which correspond to $^1\text{O}_2$ lifetimes between 10 and 100 μs (vide supra, Section 3.2). The 1270 nm signal also decreases with a decreasing concentration of oxygen in the solution. The generation of $^1\text{O}_2$ can be very sensitive to reaction conditions. The amount of $^1\text{O}_2$ produced by **1** and **2** is likely influenced by the concentrations of the sensitizer and oxygen, temperature, and irradiation time. Although the quenching rate constant of $^1\text{O}_2$ by **2** measured in this paper ($5.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in methanol) is similar to that of rose bengal ($2.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in methanol), higher concentrations of **2** will be required to obtain the same absorbance at the excitation wavelength because of a lower absorptivity [compare ϵ (**2** at 532 nm) = $1600 \text{ M}^{-1} \text{ cm}^{-1}$ with ϵ (rose bengal at 532 nm) = $30,000 \text{ M}^{-1} \text{ cm}^{-1}$]. Therefore, low concentration, high excitation intensity, and long irradiation times should be employed when using **1** or **2** as $^1\text{O}_2$ photosensitizers.

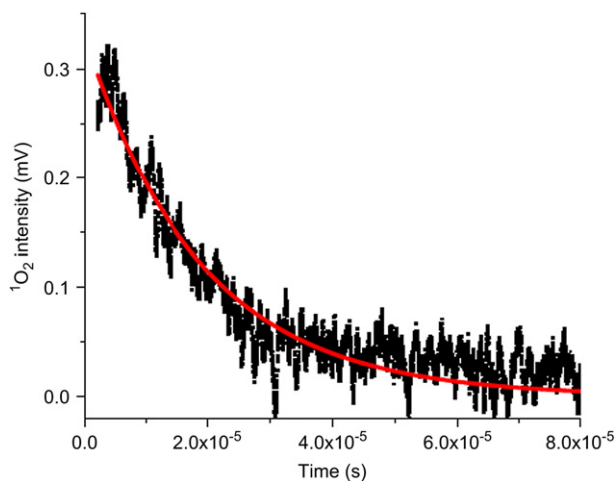
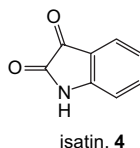


Figure 3. Decay kinetics of $^1\text{O}_2$ for **2** (OD=0.4 at 532 nm; 40 mJ) in CH_3OH . The phosphorescence emission of $^1\text{O}_2$ was monitored at 1270 nm. The dots are experimental data, and the solid line is calculated from a 1st order kinetic fitting.

3.4. Indigo and indigo carmine sensitized photooxidations

In 1979, Kuramoto and Kitao attributed the photofading of indigo **1** in solution to a self-sensitized photooxidation involving singlet oxygen.²⁵ We observed a cleavage of **1** into isatin (**4**) after 8 h of visible light irradiation in an O_2 -saturated solution of $\text{DMSO}-d_6$, or in an O_2 -saturated solution of CDCl_3 in the presence of methylene blue. The LC–MS data is indicative of isatin **4** since we find a molecular ion peak m/z 148 ($\text{M}+\text{H}$)⁺, and under various ionization conditions find m/z 146 ($\text{M}-\text{H}$)⁻, m/z 165 ($\text{M}+\text{NH}_4$)⁺, m/z 180 ($\text{M}+\text{CH}_3\text{OH}_2$)⁺, m/z 183 ($\text{M}+\text{Cl}$)⁻ representing the addition of solvent molecules or ions. Isatin **4** was also identified by ^1H NMR spectroscopy and the comparison to a commercial sample of isatin **4**. Singlet oxygen may contribute to the oxidative degradation of **1** by a reaction with the central $\text{C}=\text{C}$ double bond of **1**. Alternatively, oxidation of **1** may take place via a Type I photooxidation pathway, similar to the reaction of **2** with superoxide reported recently.⁵⁷ The mechanism by which active oxygen species initiates a process leading to the oxidative cleavage of the double bond of **1** and **2** will require further investigation. Greater yields of **4** are observed when a co-sensitizer, such as methylene blue is present.²⁵



A sulfide trapping experiment was conducted to study the indigo carmine **2**–sensitized photochemical reaction. We detect dibutyl sulfoxide (51%) by GC–MS in a reaction of **2** (6×10^{-4} M) with dibutyl sulfide (0.15 M) in O_2 -saturated CD_3OD after 48 h of visible light irradiation with a Rayonet lamp. An experiment with rose bengal (6×10^{-4} M) and butyl sulfide (0.15 M) in O_2 -saturated CD_3OD led to 88% conversion to dibutyl sulfoxide after 1 h of visible light

irradiation. These preliminary results may point to the intermediacy of $^1\text{O}_2$, which then oxidizes dibutyl sulfide. However, we have not explored this reaction in sufficient detail to confirm whether $^1\text{O}_2$ is trapped and responsible for the oxidation of dibutyl sulfide.

4. Conclusion

Quantum yields for the possible generation of $^1\text{O}_2$ by indigo **1** and indigo carmine **2** have been measured, which suggest that ISC competes with fluorescence and internal conversion for S_1 . We believe that **1** and **2** may serve as $^1\text{O}_2$ photosensitizers in conventional polar solvents and an ionic liquid. However, low molar absorptivities and physical quenching of **1** and **2** limits their utility as $^1\text{O}_2$ photosensitizers. High intensity of excitation light, longer irradiation times, and low concentrations of **1** or **2** would be needed when attempting to use them as $^1\text{O}_2$ photosensitizers. A better understanding of the photooxidation mechanism of **1** and **2** under the conditions will require further study.

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