Sulfonation of phenalenone revisited: preparation and characterisation of sodium 1H-phenalene-1-one-5-sulfonate

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Treatment of 1H-phenalen-1-one in 95% H_2SO_4 at 180 °C for 2 days yields a highly water soluble red dye. Although a previous literature report, under similar conditions, described this reaction as producing the 2-substituted sulfonato adduct, the ^{1}H NMR spectrum we obtained for the product was inconsistent with the proposed structure. A detailed ^{1}H NMR spectroscopic study, however, using ^{1}H–^{1}H spin-decoupling and steady-state NOE-difference experiments revealed the product to be 1H-phenalen-1-one-5-sulfonate. Despite the extended planar aromatic π-system typical linear Beer-Lambert behaviour, up to a concentration of *ca* 2mM, is observed for a solution of the dye in phosphate-buffered water.

Keywords: phenalenone, sulfonation, isomer assignment, NOE experiments, electrochemistry

The need to develop new ways in which to eradicate organic pollutants from effluent water supplies is growing, particularly in a climate where clean technology is becoming ever more important.[1] Singlet oxygen ($O_2\Delta g$) as such a reagent[2] is very appealing, especially as the active species comes from a plentiful source, is readily renewed, and known to be highly reactive towards many compounds including amines,[3] phenols,[4] nitroxides,[5] and thiols.[6] There are a number of reported procedures for singlet oxygen generation, including direct laser excitation,[7] chemical methods[8] and decomposition of phosphite ozonides.[9] A widely used method is by way of triplet–triplet energy transfer to ground-state molecular oxygen using external photosensitisers such a methylene blue,[10] cyanine dyes[11] or porphyrins.[12]

In order for a photosensitiser to operate highly effectively, especially in aqueous media, a dye's physical and chemical properties are critical and several criteria can be envisaged to be of prime importance. For instance, a proficient photosensitiser would be expected to demonstrate: (i) minimal self-aggregation; (ii) generate singlet oxygen in near unity quantum yield; and (iii) suffer only minor degradation by photo-generated active oxygen species (*i.e.*, hydroxyl radicals). Clearly, deficiency in any of these factors leads to significant reduction in sensitiser performance, and rules it out as an effective agent for singlet oxygen production and hence water treatment. Indeed, it is interesting to note that in a review the use of singlet oxygen for water treatment was almost completely dismissed; the lack of interest however arising from reports that tested agents suffer from many of the outlined problems.[13] Note that within the average lifetime of $^1O_2$ the diffusion distance is short which limits its collisional encounters with near-by pollutants.

As well as the photophysical and chemical requirements of a dye, it may also be beneficial to have the reactive sensitiser covalently tethered to a heterogeneous support in order to aid its simple removal. A particular facile way in which to achieve such a goal is by the introduction of functional group directly into a dye. This unit can act as an anchor point for attachment to, for example, a polymeric bead. With the above mentioned design criteria in mind our goal was to locate a dye that met, as far as possible, within the laid down constraints.

The reported high quantum yields of singlet oxygen generation ($\phi_{so} \sim 1$) by the planar aromatic molecule, 1H-phenalen-1-one,[14] in a wide range of organic solvents led us to believe that a water soluble version would indeed fulfil both the photophysical, chemical and structural requirements of a potential water decontaminant. A relatively cheap and easily carried out method of solubilising organics is by the introduction of an ionic group, such as a carboxylate, sulfonate or quaternary amine, into an aromatic ring. Indeed, already in the literature[15] was reported a water soluble version of 1H-phenalen-1-one in which a sulfonato group was introduced adjacent to the carbonyl function. Despite following carefully the literature preparation, we constantly obtained a product that was confirmed to be the sodium salt of 1H-phenalen-1-one-5-sulfonic acid **1**. This short paper discusses the NMR identification of **1** as well as its basic electrochemistry and photochemistry.

Results and discussion

Despite repeated attempts, and following the literature procedure closely, to sulfonate 1H-phenalen-1-one the product obtained did not analyse to the expected, 1H-phenalen-1-one-2-sulfonic acid. Indeed, the lack of loss of the doublet at $\delta = 6.80$ ppm (unambiguously assigned to the proton adjacent to the carbonyl function) in the ^{1}H NMR spectrum of the purified sample confirmed production of an entirely different product. Furthermore, the appearance of a new singlet ($\delta = 8.35$ ppm), doublet ($\delta = 8.21$ ppm) and removal of the triplet resonance ($\delta = 7.70$ ppm) unequivocally indicated mono-sulfonation had occurred exclusively in one of the aromatic rings. As two regioisomers could theoretically account for the observed ^{1}H NMR data (Fig. 2), absolute confirmation of substitution position was confirmed by a combination of ^{1}H–^{1}H spin-decoupling (not shown) and steady-state nuclear Overhauser Effect (NOE) experiments.

The steady-state NOE difference spectra recorded for **1** in d_6-DMSO (DMSO = dimethylsulfoxide) are shown in Fig. 3, along with complete assignment of the proton resonances. A detailed breakdown of how this assignment was made is as follows: Irradiation of the resonance at $\delta = 6.80$ ppm (confirmed to be H_2 from its characteristic chemical shift) led to a positive NOE with the doublet at $\delta = 8.21$, which in view of their similar coupling constants ($J = 9.8$ Hz) confirmed this resonance to be H_3. A similar irradiation of the triplet

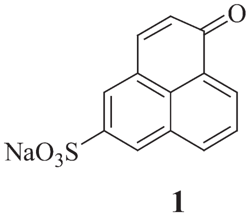

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Fig. 1 The sulfonated phenalenone molecule discussed in the text.

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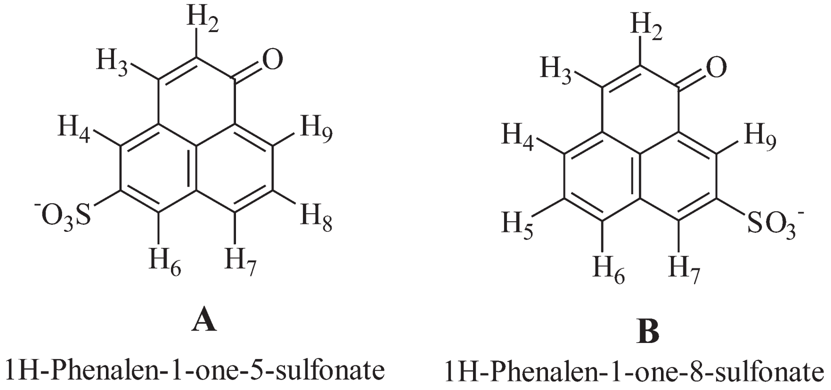

A

1H-Phenalen-1-one-5-sulfonate

B

1H-Phenalen-1-one-8-sulfonate

Fig. 2 Two possible regioisomers from sulfonation of phenalenone.

resonance at $\delta = 8.02$ ppm resulted in NOEs to the two doublet patterns at $\delta = 8.56$ and 8.63 ppm, respectively. Because of the interdependency of these three resonances it can be concluded that these peaks are either H_4–H_6 of structure **B** or H_7–H_9 in structure **A**. However, only in structure **A** is the NOE expected between H_3 and H_4 to result in a singlet since in structure **B** the pattern would have to be a doublet. This hypothesis is backed up further since irradiation of the signal assigned to H_4 only leads to an NOE to one signal (a doublet) which must be H_3. Therefore, the NOE results unequivocally confirms the regioisomer to that of structure **A**. From considerations of both the observed resonance patterns and electronic factors no other structures are possible in which the sulfonate is situated in any of the aromatic rings.

It is not entirely clear why two apparently very similar reaction conditions produce the two isomers, since previously published data[15] were fully consistent with the proposed 1H-phenalen-1-one-2-sulfonic acid structure. One possibility is the sulfonation reaction is highly critical on temperature. In passing it is noted that the product distribution from direct nitration of phenalenone is decidedly dependent on the conditions used; the strength of the H_2SO_4 and temperature being extremely important.[16]

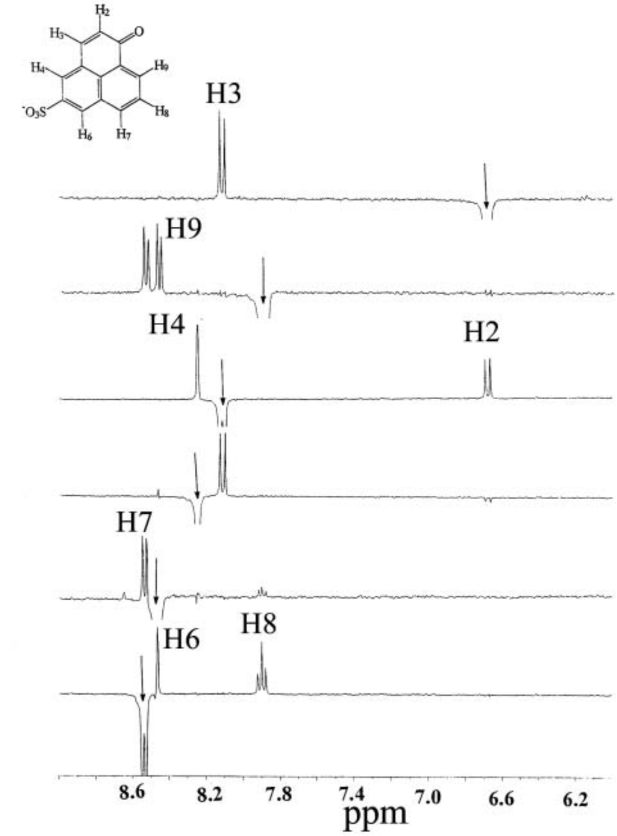

Fig. 3 NOE difference spectra recorded in d_6-DMSO for the sulfonation product of phenalenone.

Electrochemistry of **1** *in H_2O*

The electrochemical behaviour of **1** was studied at a glassy carbon working electrode using cyclic voltammetry in N_2-purged H_2O containing $NaNO_3$ and buffered to various pHs. In general, at high pH = 9.2 a one-electron wave is observed at $E_{red} = -0.61$V (vs SCE) which even at relatively fast scan rates displays no sign of its reverse re-oxidation peak. At pH = 4.1, however, the electrochemical behaviour is somewhat different and the counterpart wave is clearly observable at all scan rates; the peak separation being relatively large at high scan rates (ΔE = 170 mV, 100 mV s^{-1}) and diminishing at slower scan rates (ΔE = 90 mV, 5 mV s^{-1}). In view of the structure it seems reasonable that the observed electrochemistry can be explained in terms of carbonyl reduction at the α,β-unsaturated ketone portion of the dye. The observed pH dependency is consistent with protonation of a ketyl radical (Fig. 4).[17]

Absorption spectrum of **1** *in H_2O*

The absorption profile of **1** in buffered water is depicted in Fig. 5, the absorption maximum λ_{ABS} = 519 nm being significantly more red-shifted when compared to 1H-phenalen-1-one. However, as previously reported for 1H-phenalen-1-one-2-sulfonic acid,[15] the dye at room temperature is non-fluorescent presumably because of efficient singlet-to-triplet intersystem crossing that is characteristic of such compounds. Despite the highly planar nature of the molecule, the lack of deviation from regular Beer-Lambert behaviour in phosphate buffered water suggests that no significant dye self-aggregation occurs, at least up to a concentration of *ca* 2mM. This behaviour is very similar to that observed for the 2-substituted isomer.[18]

Conclusion

The identity of the sulfonation product from reaction of 1H-phenalen-1-one with concentrated sulfuric acid appears to be very much dependent on the reaction conditions. Whereas a previously published report[15] identified the product with the sulfonate at the 2-position in our hands the group is substituted into the 5-position. It is not entirely clear why this difference is observed but it may be a result of reaction temperature or even the quality of the sulfuric acid used. Current studies are involved in elucidating the singlet oxygen generation properties of **1** both in water and tethered to inert supports. Full details of these studies will be published at a later date.

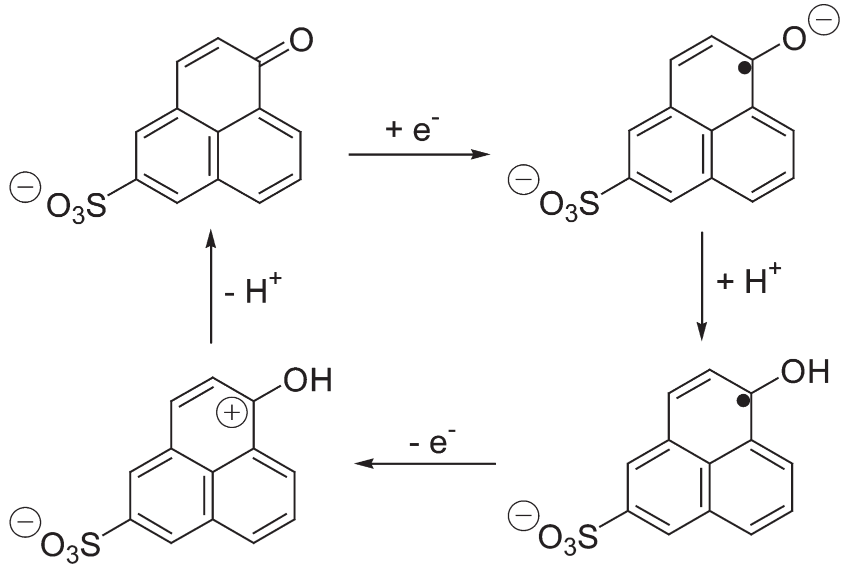

Fig. 4 Proposed proton dependent electrochemistry for compound **1** in water.

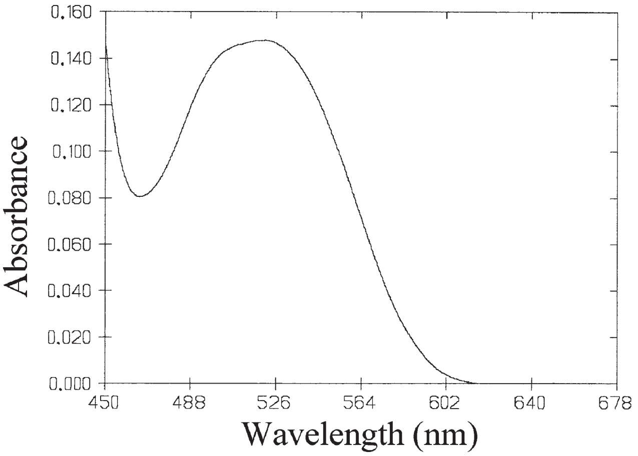

Fig. 5 Absorption profile recorded for **1** in phosphate buffered H_2O (pH 7.2) at 25 °C .

Experimental

Chemicals unless stated otherwise were purchased from Aldrich Chemical Co. and used as received. Sulfuric acid (Rectapur 95%) was purchased from Prolabo. ^{1}H NMR spectra were obtained using a Bruker AM 360 spectrometer using the solvent as the internal reference. ^{1}H–^{1}H spin-decoupling and Nuclear Overhauser Effect (NOE) experiments were performed using standard Bruker software. Water was doubly-distilled and deionised using a Millipore purification system. Methanol and acetone were used as received. Absorption spectra were recorded with a Shimadzu UV-3101PC Spectrophotometer. Electrochemical measurements on **1** were carried out at 22 °C in nitrogen purged H_2O (0.2 M $NaNO_3$ background electrolyte) containing either 0.01M $Na_2B_4O_7$, or 0.05M potassium hydrogen phthalate as buffers, and a standard three electrode set-up of a glassy carbon working electrode, platinum gauze counter electrode and Saturated Calomel Electrode (S.C.E.) reference electrode in conjunction with a Princeton Potentiostat and X–Y chart recorder.

Preparation of **1:** 1H-Phenalen-1-one (0.56 g, 3.1mmol) dissolved in 95% H_2SO_4 (3 mL) with vigorous stirring was heated to 170–180 °C for 48h. After allowing the mixture to cool to room temperature it was poured into ice/water (20 mL) and extracted with CH_2Cl_2 (5 × 25 mL) to remove unreacted starting material. Neutralisation of the acidic solution to pH~10 with Na_2CO_3, followed by removal of the solution under vacuo, gave a deep red/brown solid. Extraction of the solid with MeOH followed by filtration to remove inorganic salts afforded crude **1** after solvent removal. Recrystallisation of this solid from MeOH/acetone gave pure title compound as a deep red solid. Yield 0.38 g, 47%. The purity of the compound, and more importantly the unequivocal substitution pattern in the aromatic rings (see ESI available through stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data), was confirmed by ^{1}H NMR spectroscopy. ^{1}H NMR ($(CD_3)_2SO$, 360 MHz): 6.78 (d, 1H, *J* = 9.8 Hz); 8.01 (t, 1H, *J* = 7.5 Hz); 8.21 (d, 1H, *J* = 9.8 Hz); 8.35 (s, 1H,); 8.57 (dd, 1H, *J* = 7.3 Hz, *J'* = 2.5 Hz); 8.57 (s, 1H); 8.63 (d, 1H, *J* = 7 Hz). ^{13}C NMR ($(CD_3)_2SO$, 90 MHz): 130.57; 131.11; 131.82; 132.03; 132.53; 132.82; 133.96; 134.03; 135.43; 140.13; 146.34; 150.76; 188.52. IR (KBr disc): 3448 cm^{-1} (OH), 3053 cm^{-1} (C-H); 1642 cm-1 (CO); 1581 cm^{-1}; 1449 cm^{-1} ; 1197 cm^{-1}; 1050 cm^{-1} (SO). FAB-MS *m/z* = 177 $[M-SO_3Na]^+$. Elemental anlaysis Calcd (Found) for $C_{13}H_7NaO_4S.2H_2O$: C, 51.65 (52.00); H, 3.67 (3.23)%.

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