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Photosensitive dyes and self-detoxifying textiles: Degradation products and dye durability

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ABSTRACT

The photochemical destruction of 2-(phenylthio)ethanol, a benign model for the toxic chemical, sulphur mustard, was investigated in both aqueous solution, and on a textile substrate. In both cases the first formed product was the sulphoxide, 2-(phenylsulphinyl)ethanol. Increasing the concentration of sensitiser did not necessarily lead to an increase in the rate of destruction of sulphide; which is attributed to the self-quenching of the reaction in the presence of higher concentrations of Rose Bengal. The oxidation of sulphide was more efficient on nylon fabric that had been dyed with Rose Bengal, than in aqueous solution; however, a significant quantity of sulphone was also formed on the fabric. The dyed fabric could be used repeatedly to destroy the model sulphide, although the Rose Bengal itself was gradually destroyed, but at a much slower rate than the model sulphide. The ability for the fabric dyed with Rose Bengal to destroy a biological organism was also demonstrated.

1. Introduction

The availability of methods for the destruction of chemical and biological (CB) agents is an essential prerequisite for any effective protocol for the decontamination of military equipment. Although powerful chemical reagents exist which are capable of destroying many CB warfare agents [1] they are invariably extremely strong oxidising agents, and their widespread use in itself can be hazardous. Several specific formulations, such as combinations of nucleophilic and oxidizing agents [2], hydrophobic silica in the presence of ammonium peroxosulphate [3] and tetraperoxymolybdates and peroxy anions [4] have been reported. Other related methods require the use of specialist apparatus such as plasma decontamination chambers [5] or apparatus for containing mixtures of singlet oxygen and hydroxyl radicals [6]. These approaches are unsuitable for the decontamination of military apparel whilst being worn. Moreover they represent protocols that are adopted only when contamination has been either confirmed or is suspected. Technologies that possess an inherent self-decontaminating property would be particularly useful since they would not be reliant on the detection of a contamination event.

It has long been known that singlet oxygen is an extremely reactive chemical intermediate which reacts indiscriminately with a wide variety of organic species [7]. It can be generated *in situ*, as and when required. Additionally, because of its very high chemical reactivity, its half life is short under typical ambient conditions. Two broad approaches are used for its production; it can be prepared either chemically or photochemically. Photochemically, a sensitiser, such as TiO_2 [8–14] or a dye such as Rose Bengal [15,16], absorbs light energy and then, in an excited state, reacts with molecular oxygen to form singlet oxygen. In practice this can be readily achieved simply by irradiating a sensitiser with a suitable light source.

A number of studies have been reported on the ability of nano-particulate TiO_2 to destroy various micro-organisms [8–14] and also mineralise various organics [17–20].

Photo-degradation of sulphur mustard and related simulants has been reported [21–24]. One of these studies specifically investigated the photo-degradation of sulphur mustard and utilised a titania–silica photocatalyst that was doped with various metals so as to overcome the limited efficiency of TiO_2 under visible irradiation [21]. When used on textiles, additional issues arise that are associated with the conditions normally used to obtain the preferred anatase crystalline phase of TiO_2 [25,26]. The preparation conditions generally used to form the anatase phase require relatively high temperatures that are not usually compatible with textiles substrates [27]. Whilst it has recently been demonstrated that the anatase phase can be coated onto cotton,

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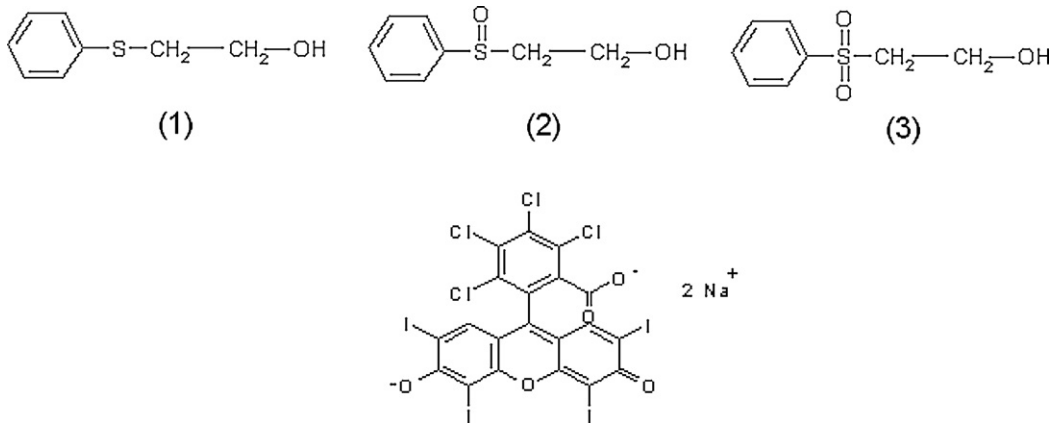

Fig. 1. 2-(Phenylthio)ethanol (1) 2-(phenylsulphinyl)ethanol (2), 2-(phenylsulphonyl)ethanol (3) and Rose Bengal.

and that the modified fabrics do possess favourable photocatalytic behaviour; the acidic conditions used result in a 50% reduction in the tearing strength of the cotton [27]. In our study we wish to report the use of Rose Bengal (Fig. 1) as a photosensitiser. As a dye, standard dyeing techniques can be used to incorporate this chemical into a suitable textile substrate. The ability of this known photosensitiser [15,16] to decontaminate chemical and biological agents is considered. 2-(Phenylthio)ethanol (Fig. 1) was used as a model for the toxic chemical sulphur mustard (*bis* 2-chloroethyl sulphide). The micro-organism used was *Escherichia coli*. The study identifies the products formed when the photosensitiser was used in an aqueous solution and when the photosensitiser was immobilised on a textile. An assessment of the efficacy of both artificial light and daylight is reported.

2. Experimental

Rose Bengal, 2-(phenylthio)ethanol and 2-(phenylsulphonyl)ethanol were obtained form Aldrich. A Hewlett Packard 1100 high performance liquid chromatography instrument, equipped with a diode array detector was used; column size was 125 mm × 4 mm packed with Purospher 18E of particle size 5 μm. The mobile phase was 30% acetonitrile, h.p.l.c. grade, and 70% water containing dicyclohexyl ammonium phosphate, 0.25%. Flow rate was 2 ml/min and the temperature was 40 °C. Mass spectra were recorded by Hall Analytical Laboratories Ltd. of Manchester, using a Micromass Instruments LCT orthogonal time of mass spectrometer fitted with time Z-spray Electrospray ion source, operating in negative mode, at 3 kV needle potential. A Multilight cabinet, from Datacolor International, housing the light source, TL84, was used for this study. This was chosen since it emits light (two fluorescent Philips tubes, MCFE 20w/84 P15; Philips, Holland) with a wavelength that corresponds to the adsorption spectrum of Rose Bengal (λ_{max} 500 nm).

2.1. Synthesis of 2-(phenylsulphinyl)ethanol

An authentic sample of 2-(phenylsulphinyl)ethanol was required with which to calibrate the h.p.l.c. and determine the concentration of sulphoxide formed upon irradiation. This sulphoxide was synthesized according to the following method. A 50 ml flask, fitted with a small magnetic stirrer and thermometer, was heated to 36 °C. 2-(Phenylthio)ethanol (7 ml, 51.88 mmol) and water 20 ml were added, followed by the drop-wise addition of hydrogen peroxide (100 vol., 6.2 g). The mixture was stirred at 36 °C for 18 h and monitored by tlc. After 18 h, excess hydrogen peroxide was destroyed by the addition of a small amount of sodium sulphite. Sodium chloride was added and the aqueous mixture extracted with ethyl acetate (3× 20 ml). The combined organic extracts were washed with saturated aqueous sodium sulphite (20 ml), dried over sodium sulphate and concentrated under reduce pressure to leave a colourless oil which was one component as judged by h.p.l.c. Mass spectrometry indicated that this was the required product, M+H, *m*/*z* 171 as predicted.

2.2. Destruction of a stimulant for mustard gas on a solid substrate (glass)

A solution of 2-(phenylthio)ethanol, 1.132 mg., and Rose Bengal 0.75 mg in acetonitrile, 3 ml., was placed on a Petri-dish and allowed to evaporate. Two controls were prepared, the first contained the same quantity of 2-(phenylthio)ethanol and the second control sample contained both 2-(phenylthio)ethanol and Rose Bengal. The second control containing both chemicals was wrapped in several layers of aluminium foil immediately so as to exclude light. The first control and the sample that contained both the Rose Bengal and the sulphide were irradiated for 3 h under the TL 84 light source. After irradiation the solutions were diluted to 25 ml with distilled water and analysed by h.p.l.c.

2.3. Dyeing of nylon with Rose Bengal

Nylon was dyed at two depths of shade (0.5% and 1.0% of mass of fabric) with the sodium salt of Rose Bengal at pH 5.5 and with a liquor ratio of 20:1. A Mathis Labomat Becatron Datex System was used for all dyeings. The temperature was initially increased to, and held at, 40 °C for 10 min. The temperature of the dye bath was then increased to 95 °C (4 °C/min). After 30 min the dye bath was cooled at 5 °C/min to 60 °C. The dyed fabrics were finally rinsed in cold water and allowed to dry at room temperature. The extent of dye exhaustion (%*E*) onto the fabric was ascertained by means of UV–vis spectrophotometry using a Phillips M350 Double Beam Spectrophotometer. The optical density of the dye bath, before and after dyeing was used to determine the level of dye exhaustion. For the dyeing at 1.0% depth of shade the percent exhaustion (%*E*) was 40%. For the dyeing at 0.5% depth of shade there were no discernible colour in the exhausted dye bath; hence exhaustion was essentially 100%. The visual depth of shade on the dyed fabrics were assessed spectrophotometrically using a Spectraflash 600 spectrophotometer to determine the percentage reflectance and K/S values across the spectrum from 400 to 700 nm.

2.4. Oxidation of 2-(phenylthio)ethanol on Rose Bengal dyed nylon

Samples of Rose Bengal dyed nylon fabrics were placed at a distance of 12 cm from the light source and irradiated for 3 h, after