Sensors and Actuators B 136 (2009) 458–463

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Hydrogen peroxide vapour indicator

Andrew Mills*, Pauline Grosshans, Eilidh Snadden

WestCHEM, University of Strathclyde, Department of Pure and Applied Chemistry, Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL, UK

ARTICLE INFO

Article history:
Received 2 August 2008
Received in revised form
29 November 2008
Accepted 12 December 2008
Available online 25 December 2008

Keywords:
Indicator
Hydrogen peroxide
Lissamine green
Triarylmethane
Vapour
TATP

ABSTRACT

A hydrogen peroxide vapour indicator is described comprising a triarylmethane dye, lissamine green (LG), dissolved in a polymer, polyvinyl alcohol (PVA). The indicator is green/blue in the absence of hydrogen peroxide vapour but is rapidly bleached in the presence of hydrogen peroxide vapour. The kinetics of LG bleaching appear approximately first order with respect [LG] and the concentration of H_2O_2, which, in turn, is proportional to the partial pressure of H_2O_2. However, the kinetics also appear to depend directly upon the reciprocal of the film thickness, implying some dependence upon the diffusion of the H_2O_2 vapour through the indicator film. Like most other H_2O_2 indicator films (such as starch-iodide paper), the LG/PVA indicator is not particularly selective and responds to most other volatile strong oxidising agents, such as ozone and chlorine. However, it is rapid in response (<5 min) and easy to use and has potential as a simple indicator of strong oxidising agents; in particular it may be used to screen the headspace above liquids for H_2O_2, which can be used for making *in situ* explosives, such as triacetone triperoxide (TATP).

1. Introduction

Hydrogen peroxide, H_2O_2, is a pale blue liquid, slightly more viscous than water. It is a weak acid with strong oxidising properties and is inexpensive and readily available for use as a common bleaching agent and disinfectant [1]. Its widespread use is in part due to its environmentally friendly nature, given that it decomposes to produce water and oxygen. Popular uses include as a disinfectant for medical equipment and surfaces [2] and for sterilising surgical instruments [3,4]. Hydrogen peroxide has been used in the standard method for cleaning and storing many types of soft contact lenses since 1990 [5]. Further applications include the chemical treatment of water systems to control diseases such as Legionnaires' disease in hospitals [6], a slurry disinfectant [7], and as a bleach for paper production in the wood pulp industry [8].

A more recent use of hydrogen peroxide is in the production of “kitchen sink” explosives by terrorists. As the name suggests these improvised explosive devices are usually made with common household ingredients. One such example is triacetone triperoxide (TATP), the structure of which is shown in Fig. 1. TATP has been used in several, well-publicised terrorist attacks in recent years, including the July 2005 London bombings and the attempted bombing by Richard Reid, the ‘shoe bomber’, of a trans-Atlantic flight in December 2001 [9]. TATP itself is a white crystalline material with a low chemical stability that is highly sensitive to mechanical stress and open flames [10]. It is very volatile, losing 68% of its weight within 14 days at room temperature [11], and has an explosive power comparable with that of TNT [10].

TATP can be easily synthesised by mixing acetone, hydrogen peroxide and a strong acid catalyst using ingredients that are readily available for purchase in the public domain. For example, H_2O_2 can be purchased from a chemist as a disinfectant at 6 wt% in water and concentrated down to *ca.* 30 wt% for TATP synthesis [9,10], acetone is available over the counter in nail polish remover, and many household drain cleaners contain sulphuric acid. Not only are the ingredients cheap and readily accessible but TATP is sufficiently easy to make that there are concerns it could be prepared *in situ* at the target site from otherwise apparently innocuous materials.

Of all the key ingredients, hydrogen peroxide is the most difficult to detect. It is very soluble in water and has a high boiling point (150 °C), thus there is very little present, *ca.* 360 ppm, above the headspace of even a highly concentrated (50 wt%) aqueous solution [12]. Such solutions are effectively odourless and cannot be easily sensed, even by sniffer dogs.

With the increased threat of terrorist attacks at airports and on aircraft, there is a real need for a simple and easy-to-use hydrogen peroxide vapour indicator that will alert security officials to its presence in any liquids that are carried on board. Ideally the indicator should be cheap to produce, straightforward to use and understand, non-invasive (i.e. responds rapidly when held over suspect liquid), and undergoes a clear response, such as a striking colour change, when exposed to hydrogen peroxide vapour. Obviously, other possible applications of such an indicator include the detection of H_2O_2

---

* Corresponding author. Tel.: +44 141 548 24 58; fax: +44 141 548 48 22.
E-mail address: a.mills@strath.ac.uk (A. Mills).

0925-4005/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2008.12.032

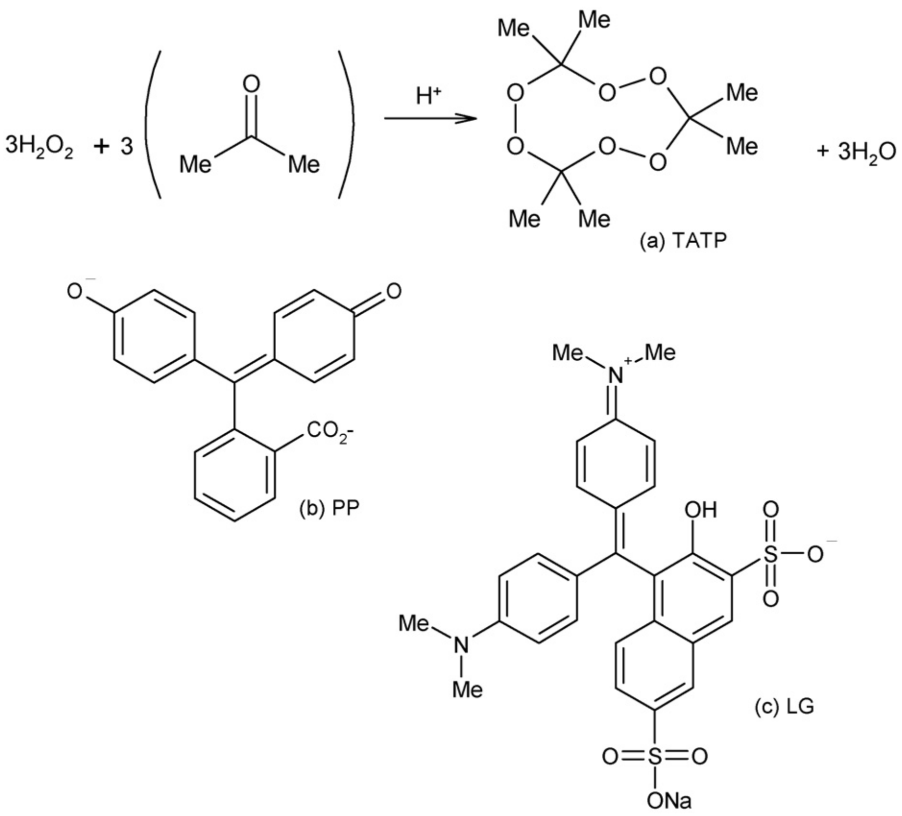

Fig. 1. The chemical structure of the cited compounds (a) triacetone triperoxide (TATP), (b) phenolphthalein (PP) and (c) lissamine green (LG).

vapour in sterilisers and water disinfectant units in hospitals, or, indeed, wherever H_2O_2 is produced or used.

Hydrogen peroxide is a common oxidising agent capable of generating highly reactive hydroxyl radicals, which are able to oxidise many complex organic compounds, including dyes [13–17]. Previous studies have shown that alkaline, aqueous solutions of triarylmethane dyes such as phenolphthalein (PP) and lissamine green (LG) (see Fig. 1) undergo rapid oxidative degradation, accompanied by bleaching, upon the addition of H_2O_2; although under neutral or acidic conditions this reaction is usually very slow [18–22].

Intriguingly, initial work showed that the triarylmethane dye, lissamine green (see Fig. 1), is particularly vulnerable to oxidative bleaching by H_2O_2 vapour when encapsulated in a largely neutral, polymeric environment. Thus, this paper details the characterisation of a simple colorimetric H_2O_2 vapour indicator, comprising the triarylmethane dye, LG, in the polymer, polyvinyl alcohol (PVA).

2. Experimental

2.1. Materials

All chemicals were purchased from Aldrich Chemicals and used as received unless specified. The water used to produce the casting inks was double distilled and deionised, and the polymer used to produce the films was average Mol. Wt 124 000–186 000, 98–99% hydrolysed polyvinyl alcohol. The hydrogen peroxide solutions were prepared from a 50 wt% aqueous hydrogen peroxide stock solution.

2.2. Preparation of LG ink and films

A typical LG/PVA ink solution was prepared as follows: 10 g of PVA were dissolved in 90 ml of water at 90 °C, cooled to room temperature and stirred overnight. 40 mg of LG dye were then dissolved in 4 g of the PVA solution at room temperature with stirring to generate an ink with LG present at 10 parts per hundred resin (phr) (≡0.21 M). The ink (pH 5.7) was dark green/blue in appearance. Films of the ink were then cast onto 25 mm diameter borosilicate glass discs, using a spin coater. Thus, a few drops of casting ink were deposited on to the surface of the disc and then spun at 2400 rpm for 25 s. The product was dried for 2 min in an oven at 70 °C and allowed to cool to room temperature before use. The final product was a green/blue film, typically *ca.* 1.1 μm thick (as measured by SEM) on a glass disc and is referred to henceforth as a typical LG film. The LG/PVA films when stored in a cool dark place, under otherwise ambient conditions, appear unchanged and active for over 1 year.

2.3. UV–visible spectrometry

In a H_2O_2-containing solution well equilibrated with its headspace, the vapour pressure due to the H_2O_2, $p_{H_2O_2}$, is directly proportional to the concentration of H_2O_2 in the solution, i.e. $[H_2O_2]$ [12]. Thus, gas streams containing different levels of hydrogen peroxide vapour were generated by passing air (flow rate = $2\,\mathrm{l\,min^{-1}}$) through 150 ml of aqueous solutions of H_2O_2 of different concentrations contained in a Drechsel bottle, fitted with a glass sintered tip to ensure the effective dispersion of the carrier gas as bubbles and their saturation with H_2O_2 vapour.

UV–visible spectra for sample films were recorded using a Cary Model 50 UV-Visible Spectrophotometer. Typically, upon exposure of a LG film to H_2O_2 vapour, the absorbance spectrum of the film was recorded every 30 s until the film was fully bleached. In order to carry out this work, any film under test was housed in a gas cell through which was flowed the gas stream containing the H_2O_2 vapour under test; typically derived from a 1 wt% H_2O_2 solution ($p_{H_2O_2}$ = *ca.* 7 ppm) for most work.