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Perylene dye photodegradation due to ketones and singlet oxygen

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ABSTRACT

The photodegradation rate of a perylene dye (*Lumogen F Yellow 083*) in methyl isobutyrate was found to increase with ketone concentration for two different ketones. Of the ketones employed, methyl pyruvate, an impurity in methyl methacrylate, was found to be particularly deleterious to dye stability. In agreement with other published studies, the addition of the anti-oxidant DABCO (1,4-diazabicyclo-[2.2.2] octane) to the dye matrix was found to increase dye stability; however when ketones were present, DABCO lead to increased photodegradation. These results highlight the importance of removing ketone impurities from dye matrices during production of Luminescent Solar Concentrators (LSCs).

1. Introduction

Luminescent Solar Concentrators (LSCs) provide a useful, low-cost method of passively collecting and concentrating solar energy. LSCs consist of a clear host material (such as sol-gel glass [1,2] or poly(methyl methacrylate) (PMMA) [3–7]) containing a fluorescent species (such as a fluorescent dye [4,5,7,8] or quantum dots [9]). The fluorescent species may either be homogeneously doped within the host material or restricted to a thin film layer on top of the substrate [3,10,11]. Direct and diffuse sunlight are absorbed by the fluorescent species, resulting in fluorescent emission and a subsequent concentration of light towards the edges of the sheet due to total internal reflection. LSCs are predominantly used for photovoltaic electricity generation [3,11–15], although they have also been used for heat generation [16] and lighting [17]. The light transmitted through the LSC can also be used in greenhouses to enhance plant growth [10].

One of the major technical obstacles preventing the widespread usage of LSCs in solar energy applications is the limited stability of the fluorescent species [5,7,14]. Quantum dots have recently been shown to hold promise for good stability in LSCs, although their low quantum efficiency and high cost are inhibitive at present [9]. Some recent studies have demonstrated that good stability can be achieved if the LSCs are produced carefully [12,15]. High stability has been achieved recently with a coumarin red fluorescent dye by doping the matrix with SiO_2 nanoparticles [12].

Various degradation mechanisms may be responsible for the poor stability of fluorescent dyes. UV radiation causes significant degradation, although this can be avoided by the use of a UV blocking cover or additive [8]. Degradation can also occur from the photo excitation of the dyes by light in the visible wavelength range [8]. This visible-light induced photodegradation is particularly sensitive to trace levels of impurities in the matrix, such as residual monomer, initiator, stabiliser or other additives [8,15]. Some of these impurities can be removed by distillation of the monomer before casting leading to improved photostability [15].

In recent attempts by the authors to prepare LSCs consisting of a perylene dye (*Lumogen F Yellow 083*; BASF) in PMMA, degradation of the dye was observed to occur at rates much faster than we have previously observed for similar systems. Subsequent analysis by GC/MS of the methyl methacrylate (MMA) used to prepare the LSCs revealed the presence of small amounts ($\sim 0.3\%$) of methyl pyruvate (see Fig. 1) in the MMA. This prompted an investigation of both the influence of ketones on the degradation of perylene dyes in LSCs as well as the use of DABCO (1,4-diazabicyclo-[2.2.2] octane), which has previously been shown [18] to improve dye stability in

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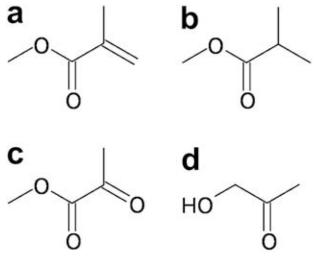

Fig. 1. Chemical structures of various compounds used in this study:(a) Methyl methacrylate (MMA); (b) Methyl isobutyrate; (c) Methyl pyruvate; (d) Acetol.

PMMA matrices through the quenching of photo-generated singlet oxygen.

2. Experimental

2.1. Materials and instruments

Methyl pyruvate was prepared following a literature procedure [19]. The crude product obtained was used without further purification. The following were purchased commercially and used as received; *Lumogen F Yellow 083* (BASF), methyl methacylate (Mitsubishi), acetol (Aldrich), methyl isobutyrate (Aldrich), DABCO (Aldrich).

UV–visible spectra were recorded using an Agilent 8453 UV–Visible spectrophotometer. Samples were irradiated with a 150W metal halide lamp using an 18 mm diameter polymer optic fibre (Lumenyte). The intensity of the light was measured to be 5100 klux, using a T-10M lux meter (Minolta) and a heat-resistant 1.0% transmission filter (Oriel).

2.2. Photodegradation measurements

Six solutions of *Lumogen F Yellow 083* in methyl isobutyrate were prepared. The dye concentration was 0.21 mM, which is equal to dye concentrations commonly used in LSCs. Ultrasonic agitation of the samples for 5 min was used to ensure complete dissolution of the dye. The dye solutions were then doped with Acetol, methyl pyruvate, DABCO, or combinations thereof, in various concentrations as outlined in Table 1. DABCO was added in an equimolar concentration (0.21 mM) to the *Lumogen* F 083 dye.

The dye solutions were then transferred into tightly sealed quartz cuvettes. After measurement of the initial dye absorption, the cuvettes containing the dye solution were exposed with the optic fibre illuminator. After each period of exposure, the dye absorption was re-measured. Photodegradation was followed by monitoring the decrease in the dye absorption band at 472 nm.

Table 1
Photodegradation rates of F083 in methyl isobutyrate with various additives.

Solution	[F083] (mM)	[Acetol] (v/v)	[Methyl pyruvate] (v/v)	[DABCO] (mM)	photodegradation rate (h^{-1})
1	0.21	0	0	0	0.037
2	0.21	0.5	0	0	0.040
3	0.21	5	0	0	0.329
4	0.21	0	0	0.21	0.014
5	0.21	0.5	0	0.21	0.085
6	0.21	0	0.5	0	1.16

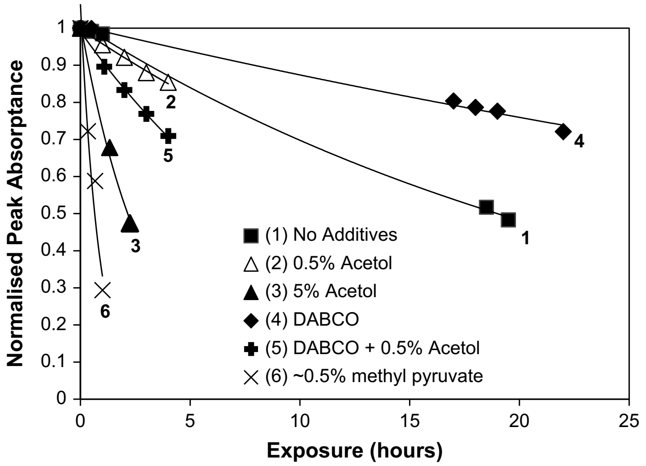

Fig. 2. Peak absorbance photodegradation curves for 0.21 mM *Lumogen* F083 dye dissolved in methyl isobutyrate with various additives.

3. Results and discussion

The results for the photodegradation experiments are shown in Fig. 2, and summarised in Table 1. The amount of dye that had degraded was determined by comparison of the intensity of the perylene absorption band at 472 nm to the intensity recorded prior to exposure.

In this study a liquid matrix, rather than a solid PMMA matrix, was used in order to achieve more rapid degradation, which has been shown previously to occur due to increased diffusion processes [18]. Methyl isobutyrate was selected due to its structural similarity to PMMA (see Fig. 1). In previous dye photostability studies involving solid PMMA matrices, fluorescence has been observed to decay with a double exponential relationship [10,20]. In our solution based study, single exponential equations fit the data with R^2 values $>$ 99%, with the exception of solution 6 (methyl pyruvate), which gave a fit of $R^2 = 0.93$. Thus single exponential coefficients were used to compare the photodegradation rates for each solution.

It is clear from the degradation data that the presence of ketones in the dye matrix had a substantial effect on the rate of dye degradation. Photodegradation rates in Solutions 2 and 3 were accelerated compared to the control (Solution 1). From Solutions 2 and 3 it is also evident that the rate of degradation increases with the concentration of acetol in the dye matrix. The solution containing methyl pyruvate (Solution 6) shows the most rapid degradation of all solutions tested, with an exponential loss coefficient of 1.16 h^{-1}, 31 times greater than the control solution (0.037 h^{-1}).

The rate of photodegradation observed in Solution 4 containing DABCO was approximately one third of the rate for the control Solution 1. This marked decrease may be attributed to quenching of singlet oxygen, generated from dissolved dioxygen. Similar improvements in perylene dye stabilities have been observed [18,21]. Interestingly, when DABCO was added to a 0.5% acetol doped solution (Solution 5), the observed photodegradation rate was greater than that recorded for the solution containing only 0.5% acetol (Solution 2). We are currently unable to explain the increased photodegradation rate of the acetol/dye solution in the presence of DABCO. Further testing is required to identify the specific mechanism responsible for this result. Nonetheless, this result suggests that the addition of DABCO to a dye matrix (such as PMMA), may infact have an adverse effect on dye stability if the matrix is contaminated with ketone impurities.

It has previously been reported that the presence of impurities in PMMA-based LSCs leads to an increase in photodegradation of dye species [8,15], and that distillation of MMA prior to LSC fabrication has a beneficial effect on dye stability [15]. The beneficial effect may be party attributed to the removal of ketone impurities from the MMA. However, due to the possibility of low boiling point ketone impurities we recommend that MMA be distilled over a ketone reagent such as 2,4-DNP to ensure the removal of ketones. Ketones and other carbonyl compounds can be fairly easily removed from MMA by treatment with amines followed by distillation [22]. Thus dye stability in LSCs may be readily improved by purification of the monomer prior to casting.

4. Conclusions

This work reveals the hitherto unreported finding that ketones are capable of increasing the photodegradation of perylene dyes in solution. The rate of photodegradation was found to increase with increasing ketone concentration. Of the ketones tested, methyl pyruvate, which we have found as an impurity in MMA, was found to be particularly deleterious to dye stability. The addition of DABCO to the dye matrix was found to increase dye stability, however where ketones were present, DABCO lead to an increase in photodegradation. These results highlight the importance of removing ketone impurities from dye matrices during the fabrication of LSCs.

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