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Photoreactions in clay media: singlet oxygen oxidation of electron-rich substrates mediated by clay-bound dyes

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Abstract

Photooxidation of electron-rich substrates such as quinol, 1-naphthol and anthracene to the corresponding 1,4-quinones with clay-bound methylene blue/rose bengal is studied in acetonitrile medium under oxygen atmosphere. A [4 + 2] cycloaddition between singlet oxygen and the substrate, followed by its subsequent cleavage is the predominant reaction with clay-supported sensitisers. With anthracene, while [4 + 2] cycloaddition is the favoured pathway, a minor reaction involving electron-transfer is also likely.

Keywords: Photooxidation; Clay microenvironment; Dye sensitisers; Electron-rich phenols; Anthracene

1. Introduction

Singlet oxygen is an effective electrophilic oxidant for a variety of electron-rich substrates [1–5]. Among them, phenols and naphthols are compounds of environmental interest as they are often released into the natural aquatic media from industrial wastes, petroleum spills [6,7] and also from natural products [8]. As these substances are rapidly oxidised by singlet oxygen, the natural photochemical oxidation, particularly the singlet oxygen mediated process in the presence of sunlight has been considered as an attractive and potential decontamination route since the process involves the simultaneous presence of dissolved oxygen and light-absorbing species in the medium.

Survey of literature shows instances of photochemical degradation of phenols and naphthols. The singlet oxygen oxidation of electron-rich phenols has been studied by Foote et al. [9,10]. Photooxidation of phenol and monochlorophenols in oxygen saturated aqueous medium in the presence of various sensitisers has been studied by Gerdes et al. [11]. The photocatalytic degradation of 4-chlorophenol by titanium dioxide has been reported [12,13]. The dye-sensitised singlet oxygen mediated oxidation of monosubstituted phenols has been studied by Soltermann et al. [14]. Supported sensitisers have also been successfully employed for oxidation of sulphides and alkenes [15,16]. Our interest [17] in utilising clays as media for photochemical investigations has prompted us to prepare clay-bound sensitisers and to utilise them in the present study as a simple, reusable heterogeneous catalyst for generating singlet oxygen.

2. Experimental

2.1. Materials

Methylene blue from E. Merck and rose bengal from Sigma were used as such. Bentonite and 2,6-di(*t*-butyl)phenol obtained from Aldrich were used as such. All the phenols used in the present study were supplied by E. Merck and were distilled before use and their purity was checked by gas chromatography. Naphthols, quinol and anthracene were also from E. Merck. Acetonitrile received from E. Merck was of AR grade. It was further purified by distillation after drying with activated silica gel [18]. The anionic hydrotalcite clay was prepared as per the reported procedure [19].

2.2. Photooxidation

Bentonite-bound methylene blue sensitiser was prepared by stirring 6 g of Na^+-exchanged bentonite clay with 150 ml of a 100 ppm dye solution for 3 days. It was filtered, washed well with distilled water and dried at 140 °C for 6 h and about 90% of the dye was found to be adsorbed. It was characterised by UV-diffuse reflectance (Fig. 2) and FT-IR spectra. Methylene blue intercalated bentonite showed absorption at 3113 and 2925 cm^{-1} (absent in Na^+-bentonite). In addition O–H stretching frequencies at

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3635 and 3445 cm^{-1} were shifted to 3628 and 3450 cm^{-1}, respectively. The hydrotalcite-bound rose bengal was also prepared by a similar procedure.

In a typical oxidation, 200 mg of the dye exchanged clay and 5 ml of 0.01 M solution of phenol in acetonitrile was irradiated as slurry under oxygen atmosphere under a 1000 W tungsten–halogen lamp through a 12 M sodium nitrite filter solution for the required time. After filtration of the solvent from the reaction mixture, the clay sample was extracted again with acetonitrile and the combined extracts after removal of solvent, was analysed by GC.

2.3. *Analysis*

The reaction mixture was analysed by capillary GC (Shimadzu 17A model SE-30 (10%) column, FID detector, high purity nitrogen as carrier gas). The products were identified by comparison with authentic samples. In the case of anthracene oxidation, the products were identified by GC–MS (Shimadzu QP 5050) and also by coinjection with the authentic samples. In all the GC analyses, retention times of starting materials were taken as the internal reference. The cyclic voltammetric measurements were recorded in BAS (Bio Analytical System) CV50W instrument at glassy carbon electrode in acetonitrile vs. silver/silver chloride electrode with tetrabutylammonium perchlorate as supporting electrolyte and platinum as counter electrode.

3. Results and discussion

Previous studies [20] have shown that in dye-sensitised photooxygenation of phenols, hydroperoxides are obtained. While simple phenol does not undergo oxidation as singlet oxygen is quenched efficiently by it, more electron-rich derivatives react chemically with singlet oxygen. A $[\pi^4 s + \pi^2 s]$ cycloaddition of the singlet oxygen to phenol and subsequent ring opening of the endoperoxide to its hydroperoxide or electron-transfer (ET) between singlet oxygen and phenol to afford the hydroperoxide by way of superoxide ion and phenol radical cation is proposed.

In the present study, electron-rich phenols like quinol and 1-naphthol are oxidised efficiently by clay-bound methylene blue/rose bengal in oxygen saturated acetonitrile medium and the corresponding quinones are formed as the sole products. Photooxygenation is also attempted on a wide range of phenols such as 1- and 2-naphthols, substituted phenols and cresols including benzyl alcohol. While only quinol and 1-naphthol are found to be oxidised efficiently with bentonite-bound methylene blue as the sensitiser and 2,6-di(*t*-butyl)phenol is oxidised very slowly, there is no oxidation of simple phenols, cresols, *para*-chlorophenol, *para*-methoxyphenol, resorcinol, 4-(*t*-butyl)phenol and 2-naphthol. The percentage conversion of quinol and 1-naphthol increases with an increase in irradiation time (Fig. 1). A closer look at Fig. 1 shows that at longer irradiation times, the percentage conversion slows down in the cases of quinol and anthracene. This may be attributed to a decrease in substrate concentration and also to light absorption by the photoproducts. Photooxidation is also studied at different substrate concentrations and the results are summarised in Table 1. Control experiments show that there is no oxidation in the absence of either methylene blue or oxygen. The significant observations from the present study, namely absence of any coupled products and also no reaction with 2-naphthol (while 1-naphthol undergoes oxidation) rules out the presence of radical intermediates and hence an ET route in the present study. This has prompted us to propose a [4 + 2] cycloaddition with singlet oxygen in this system as the predominant pathway.

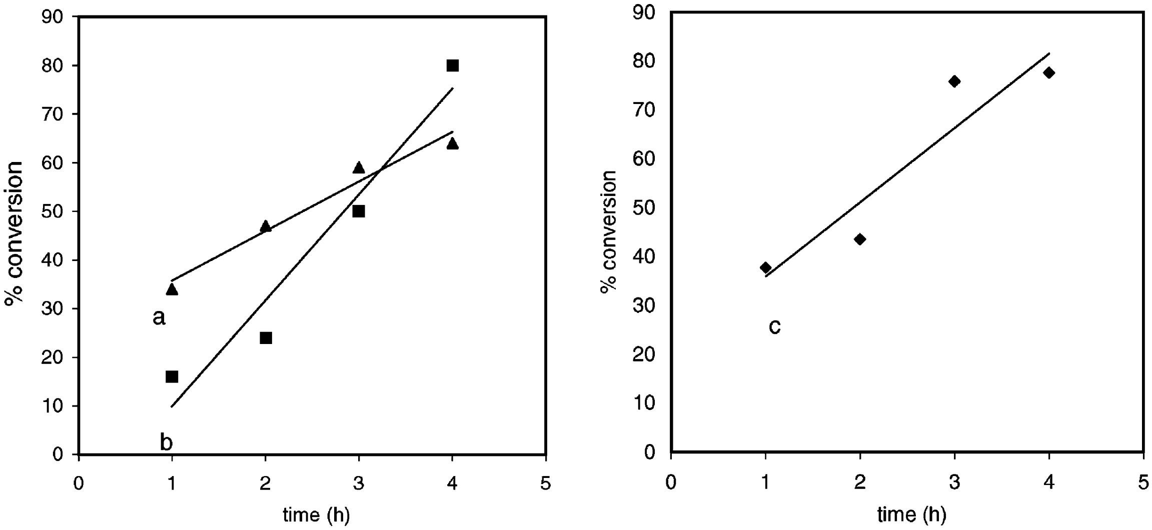


Fig. 1. Plot of percentage conversion as a function of time in singlet oxygen mediated oxidation of: (a) quinol; (b) 1-naphthol; (c) anthracene using clay–dye composite.

Table 1
Singlet oxygen oxidation of electron-rich substrates[a] mediated by dye–clay composite

Substrate	[Substrate] (M)	Irradiation time (h)	Product (%)[b]
Methylene blue–bentonite			
Quinol	0.02	2	37
	0.01	2	47
	0.005	2	100
	0.002	2	100
	0.01	1	34
	0.01	3	59
	0.01	4	64
1-Naphthol	0.01	2	17
	0.005	2	24
	0.0025	2	31
	0.0010	2	41
	0.005	1	16
	0.005	3	50
	0.005	4	80
2,6-Di(*t*-butyl)phenol	0.01	4	<5
Rose bengal–hydrotalcite			
Quinol	0.01	4	100
1-Naphthol	0.005	4	14
2,6-Di(*t*-butyl)phenol	0.01	4	15

[a] Irradiated in acetonitrile medium.
[b] Corresponds to GC yield; error limit ±2%.

Rose bengal bound to basic hydrotalcite clay (5:1) is also found to be an efficient generator of singlet oxygen (Tables 1 and 2). As phenolic compounds are major source of organic pollutants in oxygenated water, photocatalytic degradation is gaining importance as an advanced oxidation process for clean up of contaminated water. Efforts at improving the efficiency of this anionic clay–dye (rose bengal) composite for oxidation of simple phenols and hence extending the oxidation to other phenols such as cresols do not yield the desired results. An increase in the dye concentration by using a 3:1 Al–Mg-HTlc causes actually dye aggregation, thus decreasing the conversion. Increase in the pH to facilitate ET from the ionic form of the phenol; by addition of KOH or 1,4-diaminobutane is not successful as the dye is now displaced from the clay layer which now becomes colourless.

The studies are also extended to oxidation of anthracene by singlet oxygen. As evident from Fig. 1, an increase in irradiation time increases the yield of photoproducts. 9,10-Anthraquinone (I) is identified as the major product along with a small amount of monooxygenated derivative (identified by GC–MS) which may be either 9-hydroxy or 9-ketoanthracene (II). The I/II ratios are fairly high, indicating the predominance of energy-transfer route over the ET pathway. The ratio does not vary appreciably upon an increase in concentration and irradiation time, indicating that these variables do not alter the photooxygenation mechanism. These observations have prompted us to prepare the following mechanisms for the clay-bound dye-sensitised oxidation of the above electron-rich substrates (Schemes 1 and 2). A [4 + 2] cycloaddition between singlet oxygen and the substrate, followed by its subsequent cleavage is the predominant reaction with clay-supported sensitisers. With anthracene, while [4 + 2] cycloaddition is the favoured pathway a minor reaction involving ET is also likely.

The fact that only quinol and 1-naphthol undergoes facile oxidation, while other phenols are unaffected, has prompted a look at the oxidation potentials of the various phenols employed in the present study. It is interesting to note that the observed reactivities are in accordance with the oxidation potentials of the various phenols (measured by cyclic voltammetry in acetonitrile medium and are presented in Table 3). Quinol, 1-naphthol and 2,6-di(*t*-butyl)phenol have low values compared to other substrates and hence the presence of high electron density in these substrates compared to

Table 2
Percentage conversion and relative yields[a] of products in anthracene oxidation by singlet oxygen generated from bentonite-bound methylene blue

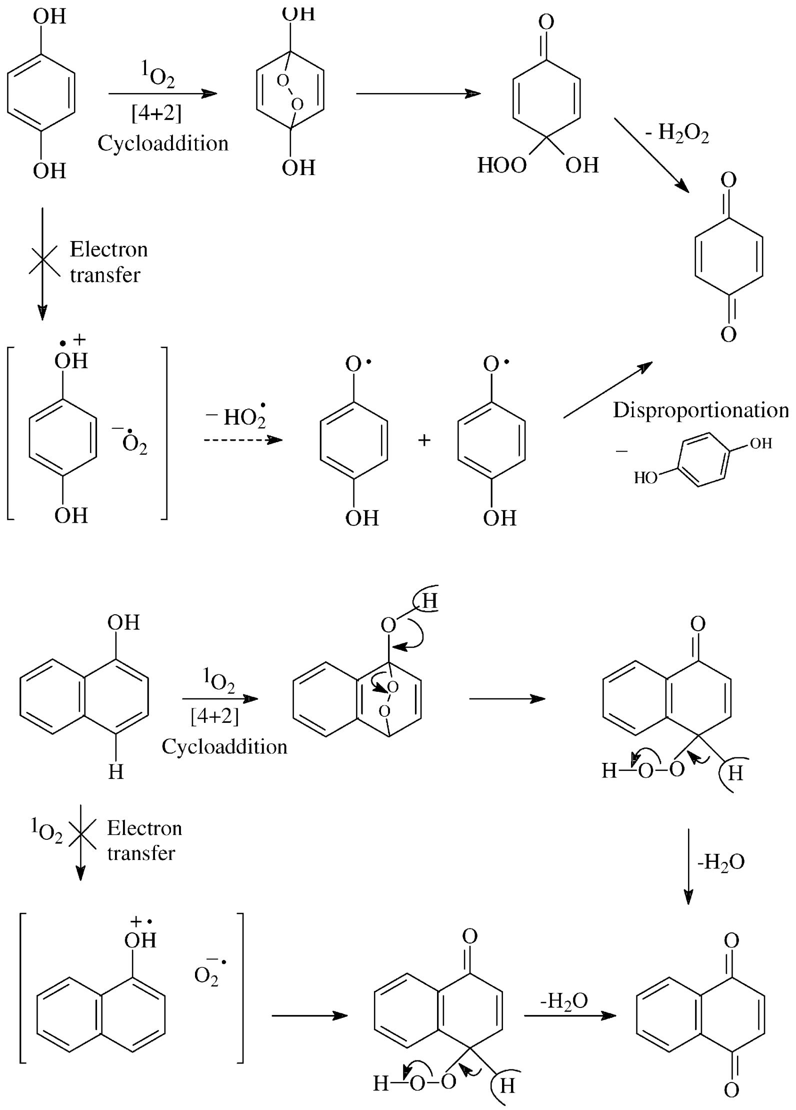
[Anthracene] (M)	Irradiation time (h)	Conversion (%)[b]	Yield of		I/II ratio
			I	II	
0.010	2	21.4	19.7	1.7	11.6
0.005	2	26.9	25.1	1.8	14.0
0.0025	2	43.8	40.7	3.1	13.0
0.0010	2	43.5	41.3	2.2	18.7
0.0025	1	37.7	34.9	2.8	12.5
0.0025	3	75.8	71.6	3.8	17.0
0.0025	4	77.6	73.5	4.1	17.9
0.0025[c]	4	15.2	15.2	–	–

[a] For structure of products I and II, refer Scheme 2.
[b] Corresponds to GC yield; error limit ±2%.
[c] Hydrotalcite-bound rose bengal sensitised reaction.

Table 3
Oxidation potential of phenols in acetonitrile medium

Phenol	Oxidation potential (V vs. Ag/AgCl)[a]
Phenol	+0.93 (0.561)[b] (0.812)[c]
ortho-Cresol	+0.92
para-Cresol	+0.89 (0.448)[b]
para-Chlorophenol	+0.83 (0.589)[b]
para-Methoxyphenol	+0.79
4-(*t*-Butyl)phenol	+0.78 (0.443)[b]
2-Naphthol	+0.90
Benzyl alcohol	+0.84
Quinol	+0.745
1-Naphthol	+0.746
2,6-Di(*t*-butyl)phenol	+0.720
Anthracene	+0.75 (0.73)[d]

[a] Measured in acetonitrile at room temperature in the range 0 to +1.5 V. Working electrode: glassy carbon; reference electrode: silver/silver chloride; supporting electrolyte: tetrabutylammonium perchlorate (0.01 M); counter electrode: platinum.
[b] Literature data (in volts vs. Ag/AgCl at pH 12 in water at room temperature [24]).
[c] Literature data (in volts vs. Ag/AgCl at pH 6.95 in water at room temperature [24]).
[d] Literature data (in CH_2Cl_2 at −70 °C [25]).



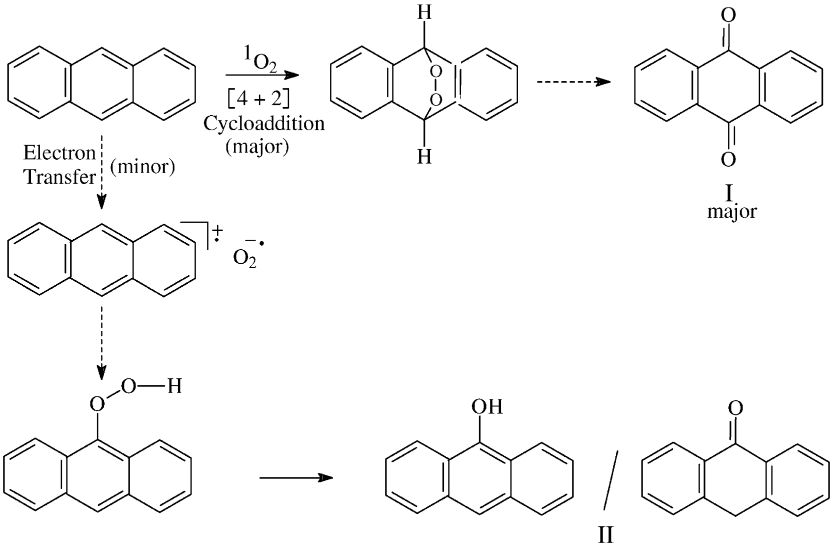
Scheme 1. Photooxidation of quinol and 1-naphthol by singlet oxygen using clay-bound methylene blue/rose bengal.

other phenols, facilitates their facile reaction with the electrophilic singlet oxygen. In the case of 2,6-di(*t*-butyl)phenol, however, the conversion is comparatively lower, and this may be attributed to steric constraints which are expected to be more significant in the constrained two-dimensional microenvironment present inside the clay interlayers. In the case of anthracene also, the oxidation potential is lower, indicating its vulnerability towards ready oxidation by singlet oxygen.

It is relevant to note here that a systematic time-dependent spectrophotometric study of interaction of methylene blue with montmorillonite clay gives valuable information about the nature of the dye species. The four bands of methylene blue at 575, 610, 670 and 760 nm are ascribed to dimer and higher aggregates (first two peaks), monomer and J band of the dimer, respectively (Scheme 3) [21,22]. Upon addition, the dyes are adsorbed on the external surface of the clays as induced aggregates or as monomers. A slower desorption followed by deaggregation tends to carry the methylene blue into the clay interlayer and the following sequence of steps is proposed.

Diffuse reflectance spectra of methylene blue–bentonite aggregate (Fig. 2) shows peak at 674 nm, indicating that the deaggregation has indeed occurred in the present study also and this suppression of aggregate formation of methylene blue in clays facilitates efficient oxidation. It is also established by another independent study that most methylene blue molecules can exist as monomers on the clay in suspensions of low loadings [23].

Thus, the present study highlights several salient features of this novel clay–dye composite. In addition to suppression of formation of H aggregates, the clay-bound sensitisers also offer other advantages, viz.: (a) the dye can be recycled, (for example the clay-bound sensitiser is used for three



Scheme 2. Photooxidation of anthracene using clay-bound methylene blue.

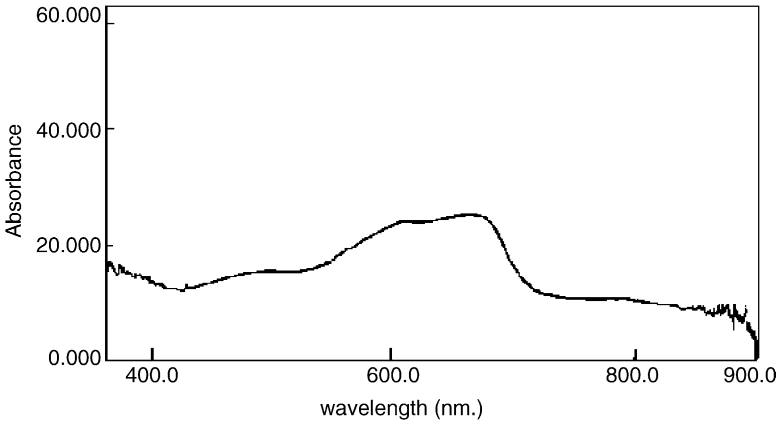


Fig. 2. Diffuse reflectance spectrum of bentonite-bound methylene blue.

times in the photooxidation with only a small decrease in its efficiency), (b) the sensitiser can be easily added and removed from the medium with little loss of efficiency. It is also more stable towards bleaching in the bound state and thus an environmentally-friendly sensitiser, (c) simplicity in work-up as removal of the dye from the reaction mixture is now unwarranted, (d) inexpensive and (e) the dye can be used as sensitiser in both polar as well as non-polar media.

$$\begin{tikzcd}
\begin{matrix}MB^+(soln)\\665\text{ nm}\end{matrix} \arrow[r, "fast"] \arrow[dr, "fast"'] & \begin{matrix}MB^+(ext)\\670\text{ nm}\end{matrix} \arrow[r, "slow"] & \begin{matrix}MB^+(int)\\670\text{ nm}\end{matrix} \arrow[d, leftrightarrow, "fast"] \\
 & (MB^+)_n(ext)\ 570\text{-}600\text{ nm} \arrow[u, leftrightharpoons, "slow"'] & MBH^{2+}(int)\ 765\text{ nm}
\end{tikzcd}$$

Scheme 3.

Acknowledgements

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