

Photooxidation of a Conjugated Diene by an Exciplex Mechanism: Amplification via Radical Chain Reactions in the Perylene Diimide-Photosensitized Oxidation of α -Terpinene

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Irradiation of the perylene diimide (**1**) or 9,10-dicyanoanthracene (DCA) in the presence of α -terpinene (**2-HH**) in the presence of molecular oxygen leads to moderately efficient oxidation of **2-HH** to *p*-cymene (**2**). Although **1** might be expected to photosensitize oxidations by the conventional "singlet oxygen" pathways, spectroscopic studies indicate that while oxygen can quench the fluorescent singlet of **1**, no singlet oxygen is produced. **2-HH** is also an efficient quencher of the fluorescent singlets of **1** and DCA and, for nonpolar solvents such as methylene chloride, in each case the quenching results in formation of an exciplex or contact radical ion pair. Under conditions where quenching by **2-HH** to form the exciplex is complete, maximum quantum yields of **2** are obtained, thus indicating that the exciplex is the precursor to its formation. Nonproductive decay of the exciplex to starting materials is its major fate, thus the moderately high quantum efficiencies for formation of **2** require a mechanism involving amplification. Spin-trapping experiments suggest the role of hydroperoxy radicals and amplification by a radical chain mechanism involving these radicals and the intermediate **2-H•** is proposed. Possible paths for reaching these radicals from the exciplex are considered; either oxygen quenching of the exciplex or proton transfer within the exciplex followed by oxygen interception of the semireduced perylene diimide appear viable. For the reaction of DCA with **2-HH** and oxygen, it is found that the much longer-lived exciplex undergoes quenching by oxygen.

Introduction

Photooxidations proceeding by dye sensitization of singlet oxygen are regarded as almost ubiquitous for aerated organic solutions containing dyes and electron-rich substrates such as alkenes, dienes, and amines.^{1–4} We have recently found that irradiation of aerated acetonitrile or methylene chloride solutions of perylene diimides, such as **1** with the conjugated dienes abietic acid and α -terpinene (**2-HH**), results in formation of product distributions, for the former, similar to those obtained when the same substrate is irradiated in the presence of well-known singlet oxygen sensitizers such as methylene blue or eosin.⁵ While it was anticipated that the perylene diimides should be potential photosensitizers for singlet oxygen and a "conventional" singlet oxygen mechanism seemed most likely for these photooxidations, we were surprised to find that no evidence could be obtained for the sensitization of $^1\text{O}_2^*$ by **1** or related imides, despite the moderately high quantum efficiencies for the above reactions. In the present paper we report a detailed study of the sensitization of the photooxidation of

α -terpinene by **1**. The results of this study indicate a novel photooxidation that proceeds by an initial electron transfer quenching of the dye singlet by the diene, followed by a reaction of this exciplex (or products derived from it) with oxygen. The subsequent amplification through a radical chain sequence allows the overall reaction to occur with moderate efficiency despite what must be a highly inefficient reaction from the exciplex.

Experimental Section

Reagents were generally purchased from Aldrich Chemical Co. and were used as received unless noted otherwise. α -Terpinene was purified by three separate distillations prior to use. 9,10-Dicyanoanthracene (DCA), a gift from Dr. Samir Farid at Eastman Kodak, was used as received. The heterocyclic fulgide actinometer (Aberchrome 540) was purchased from Aberchromics Ltd. The synthesis of perylene bis(2,5-di-phenyl)imide was previously described.⁶

The degassed samples were prepared by six cycles of freeze–pump–thaw degassing and sealed under high vacuum (ca. 1×10^{-5} Torr). A Hewlett-Packard 8453 diode array spectrophotometer and a Spex 111A Fluorolog 2 spectrofluorimeter were used to record the UV–vis and fluorescence spectra, respectively. GC–MS experiments were carried out on a HP 5890

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series gas chromatograph equipped with a 30 m HP-5 high-performance capillary column (cross-linked 5% Ph Me Silicone) and an HP 5970 series mass-selective detector. A Bruker ESR spectrometer was used for the ESR spin-trapping experiments. The ESR spectrometer was operated at 100 kHz modulation, the microwave power was 20 mW, and the modulation amplitude was 0.5 G. 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was used as the spin-trapping reagent. Hyperfine coupling constants were obtained by simulating and optimizing the experimental spectra using a commercial ESR data program (Keithley Instrument, Inc.). High-performance liquid chromatography was used to follow the photooxidation reaction for α -terpinene with the perylene diimide. HPLC analysis was performed using a HP 1050 series liquid chromatograph system with a pump system, an autosampler, and a diode-array detector. A Waters Nova-Pak C18 column was used with acetonitrile as the mobile phase.

Steady-state quantum yield measurements for the formation of *p*-cymene were carried out by HPLC analysis. Typically, a solution of 1×10^{-5} M perylene and 0.31 M α -terpinene in acetonitrile (in which case, 95% of the fluorescence from perylene diimide was quenched by α -terpinene) was irradiated at room temperature using a 200 W high-pressure mercury lamp with a Corning 3-71 cutoff filter ($\lambda > 460$ nm) and a 509 nm interference filter. The progress of the reaction was followed by monitoring the *p*-cymene peak with HPLC. A correlation plot for the peak area of pure *p*-cymene as a function of concentration was made so that the formation of product could be monitored quantitatively. Irradiation time was controlled by periodically performing HPLC analysis to achieve ca. 1–5% conversion of the starting material. Heterocyclic fulgide 540 actinometry was used to determine the excitation light intensities.

Singlet oxygen phosphorescence was probed by laser flash photolysis.⁷ The emission from singlet oxygen phosphorescence was monitored at 1270 nm with the detector perpendicular to the laser excitation using a Ge diode detector. The output was digitized with a Tektronix TDS 620 digitizing oscilloscope and then analyzed by computer. The transient absorption spectra were obtained by picosecond time-resolved laser flash photolysis. The instrumental setup has been described in the literature⁸ and the fast kinetic decay analysis was treated by home-built user software (SIMPLEX, Version 3) in which a first-order exponential fit was applied to the data in conjunction with the deconvolution of the instrument response.

Results and Discussion

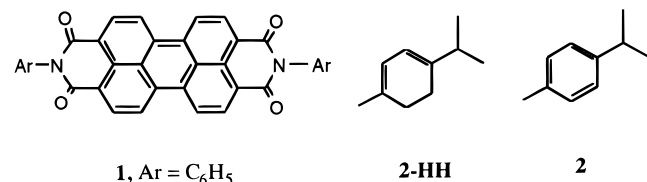
The perylene diimides such as **1** show strong absorption in the visible and fluorescence quantum yields near unity; the high fluorescence efficiency correlates with a relatively large S_1-T_1 gap (27 kcal/mol) which should be sufficient to promote the spin conversion, 3O_2 to $^1O_2^*$, which requires 22 kcal/mol.⁹ Although oxygen quenches the fluorescence of **1** at a near

tions using phenalenone¹⁰ as a sensitizer quite clearly demonstrated the presence of $^1O_2^*$ from its phosphorescence. In addition, laser flash interrogation of nondegassed methylene chloride solutions of **1** showed no evidence for the triplet-triplet absorption of **1** at 500 nm which should have arisen if the singlet sensitization of oxygen had occurred.

As indicated above, irradiation of **1** in the presence of oxygen and the above-mentioned dienes does lead to the formation of typical photooxidation products. In the case of α -terpinene, the chief oxidation product detected under irradiation of **1** at 509 nm is the corresponding aromatic hydrocarbon, *p*-cymene (**2**).¹¹ HPLC product studies and steady-state quantum yield measurements showed that the overall transformation to **2** occurs only in the presence of oxygen and with no consumption of **1**. In degassed solution no products corresponding to **2** were observed. Clearly oxygen serves to oxidize **2-HH** to **2** in a fairly efficient net two-electron process that is driven by formation of the aromatic product. Interestingly, **2-HH** and related dienes have been found to form mostly endoperoxide adducts under sensitizing conditions with other dyes known to produce singlet oxygen,^{12,13} whereas our results indicate a clean, relatively high yield of the aromatic product **2** with a quantum yield of 30–40%. Since it had been shown several years ago that conjugated dienes such as **2-HH** quench the fluorescence of aromatic hydrocarbons by an “exciplex” mechanism,^{14–16} it appeared possible that the initial step in the sensitized reaction might be a fluorescence quenching of **1** by **2-HH**. The quenching constant for the fluorescence of **1** by **2-HH** in methylene chloride was found to be $1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. Since **2-HH** is a liquid and infinitely soluble in methylene chloride, it was easy to conduct experiments in which all of the excited **1** is quenched by **2-HH** to the exclusion of all other potential excited-state pathways for the photooxidation. Under these conditions, with oxygen-saturated solutions, a limiting high quantum yield for the formation of **2**, 0.4, was obtained. Since the fluorescence quenching should produce a contact radical ion-pair or exciplex ($[1^{\bullet-}, 2\text{-HH}^{\bullet+}]$, $\Delta G \sim -0.1 \text{ V}$), it was logical to interrogate the system with laser flash photolysis.

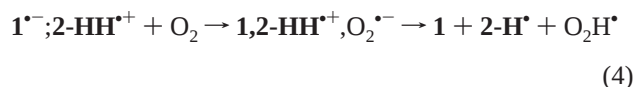
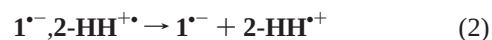
Picosecond transient absorption spectra of both degassed and nondegassed methylene chloride solutions of **1** and **2-HH** display the same moderately strong signal centered at 705 nm corresponding to absorption of the radical anion of **1** (decay constant $1.5 \times 10^{10} \text{ s}^{-1}$). The singlet-singlet absorption of **1** is also in the same region, but excess **2-HH** (4.2 M) quenches the lifetime of **1** to essentially within the instrumental response function (<40 ps).

From the above results it is possible to outline possible mechanistic paths for the overall reaction. The involvement of $^1O_2^*$ can be completely eliminated from the lack of phosphorescence and the conditions (high concentration of **2-HH**, rendering all quenching of 1^* via the exciplex). Thus, exciplex (or contact radical ion pair) formation by electron-transfer quenching (eq 1) and subsequent reactions of the exciplex must



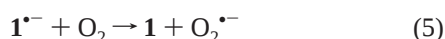
diffusion-controlled rate ($k_q = 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile), no singlet oxygen phosphorescence can be detected under these conditions, whereas control experiments under the same condi-

be responsible for the eventual formation of product **2** in moderately high efficiency. Some reasonable possibilities for



reaction of the exciplex, $[1^{\bullet-}, 2\text{-HH}^{\bullet+}]$, leading toward product include dissociation or cage escape, eq 2; proton transfer within the exciplex, eq 3; or reaction with oxygen, eq 4. However, each or all of these reactions must proceed with very low efficiency since no intermediates other than the exciplex are detectable by laser flash photolysis and the rapid decay of the exciplex ($\tau = 67$ ps), even in the presence of oxygen, results mostly in regeneration of the ground states of **1** and **2-HH**.

Due to the relatively high efficiencies of formation of **2** (0.3–0.4), there must be some kind of amplification mechanism which can be initiated by one or more of the above steps. In fact, the subsequent reaction of intermediates generated in eqs 2–4 can lead to the observed products in moderate efficiencies since for each of these reactions there exist paths to radicals which may participate in chain reactions providing such an amplification mechanism. Thus cage escape (eq 2), followed by oxygen interception of the perylene anion radical $1^{\bullet-}$, can lead to superoxide (eq 5), which, together with the radical cation



2-HH $^{\bullet+}$, could lead to the formation of chain-carrying radicals **2-H** $^{\bullet}$ and **OOH** $^{\bullet}$. The same radicals may be generated directly, if oxygen reacts with a semireduced perylene radical formed from proton transfer within the exciplex (eqs 3 and 6) or from



decay of the exciplex-oxygen quenching complex (eq 4).

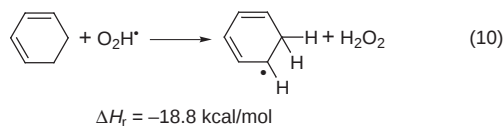
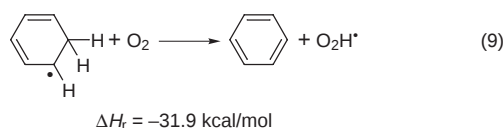
That **OOH** $^{\bullet}$ and **2-H** $^{\bullet}$ are involved in the reaction seems clear from the following. ESR studies were carried out with **1**, **2-HH**, and excess DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) as a spin trap. Very strong ESR signals were recorded which could be attributed to either the superoxide–DMPO adduct or the protonated superoxide–DMPO adduct (g -value = 2.0085, $a^N = 14.5$, $a_H^B = 11.6$, $a_H^Y = 1.2$ and $a^N/a_H^Y = 1.25$).^{17–19} No signals were observed for corresponding degassed solutions. Whether the species trapped by DMPO is superoxide or the hydroperoxyl radical formed via eqs 3 and 4 (or direct scavenging of a radical by atom transfer) cannot be distinguished; however, the trapping to produce only the single species corresponding to an oxygen adduct provides support for a mechanism such as that shown (eqs 7 and 8). Hydrogen peroxide, the other final product



besides **2**, according to the sequence proposed, was also detected by the iodide–thiosulfate procedure.^{20,21}

The proposed chain carrying steps which could provide the amplification necessary to reach the moderately high observed quantum yield are shown in eqs 7 and 8. Approximate heats of reaction for these reactions can be obtained by reference to eqs 9 and 10, which estimate heats of reaction for propagation steps, based on the transformation of 1,3-cyclohexadiene to benzene.^{22–25} These heats of reactions are sufficiently exothermic to lend support for the sequence proposed. The chain propagation steps may be primarily limited by the rate and efficiency of eq 9 which proceeds at a rate of 8×10^5 s^{–1} for the cyclohexadiene–benzene case.^{26,27}

From a mechanistic perspective, it thus seems reasonable that an initial exciplex formation can be followed by generation of the chain-carrying radicals **2-H** $^{\bullet}$ and **OOH** $^{\bullet}$ and that their reaction through propagation steps 7 and 8 provides the



amplification that allows the reaction to proceed with moderate efficiency. The major mechanistic question is which of the paths from the exciplex to the pair of radicals is most probable. The rate constant for cage escape for oppositely charged ions from a solvent-separated radical ion pair in methylene chloride is estimated to be 3×10^8 s^{–1}.^{28–30} Considering the measured rate for exciplex decay, this decay path should provide for at most 1–2%. However, since the mechanism involving cage escape and subsequent capture of $1^{\bullet-}$ by oxygen³¹ involves additional steps, most likely involving bimolecular reaction between intermediates present in very low concentrations (e.g., $O_2^{\bullet-}$ and **2-HH** $^{\bullet+}$) to reach the chain carrying radicals, we think it unlikely to be a major reaction path.

The second possible path between the exciplex and the chain-carrying radicals involves proton transfer within the exciplex (eq 3) and subsequent interception of **1-H** $^{\bullet}$ by oxygen. This path appears reasonable, since the cation radical **2-HH** $^{\bullet+}$ and anion radical $1^{\bullet-}$ should be anticipated to be strong acids and bases, respectively.^{32,33} However, we have no estimate for the rate of eq 3 and hence its importance as a decay path for the exciplex. The fact that the perylene functions as a catalyst and no products from its degradation are produced indicates that if **1-H** $^{\bullet}$ is generated, its capture by oxygen must be very efficient.

The third possible path between the exciplex and the radicals involved in eqs 7 and 8 involves direct oxygen quenching of the exciplex. However, as the laser flash photolysis results indicate, the very short exciplex lifetime is the same, within experimental error, for aerated and degassed solutions. It is not surprising that oxygen does not ostensibly affect the decay rate of the exciplex/ion-pair (lifetime ~67 ps) since if it assumed to quench the ion-pair according to eq 4 at an upper limit diffusional quenching rate (ca 1×10^{10} M^{–1} s^{–1}), the effective quenching is limited to no more than 0.6%, well within experimental error.³⁴

Based on the evidence available both the second and third mechanisms described above are reasonable and for the present system there is no basis for determining whether either or both are predominant. However for a related system, it is possible to obtain evidence supporting a potential role of the third mechanism. Since it is known that irradiation of **DCA**/diphenylethylene in aerated solutions gives rise to superoxide, presumably by oxygen quenching of the exciplex,³⁵ we investigated the possibility that a similar reaction to that sensitized by **1** might occur with enhanced quantum efficiencies when solutions containing **DCA** and **2-HH** are irradiated. Indeed, laser flash excitation of **DCA** in the presence of **2-HH** under complete quenching conditions in methylene chloride led to detection of a transient assigned to the **DCA**,**2-HH** exciplex which has a lifetime of 500 ps in degassed solutions. In air-saturated solution the same transient was observed but with a reduced lifetime (300 ps), which is consistent with a Stern–Volmer quenching constant of 70, assuming diffusion controlled kinetics with oxygen. **2** is the only photoproduct detected under these conditions, and its quantum yield, measured upon steady-

state irradiation of the air-saturated solutions, is 0.9, a value 3 times higher than that observed for the system **1**–**2-HH**. Here again, the relatively high quantum yield under conditions where only a moderate fraction of the initially excited molecules can be intercepted by oxygen points to amplification by a chain process.

The results reported here suggest that related mechanisms involving coupling of radical chain amplification with inefficient generation of superoxide or hydroperoxy radicals may be important in a number of other reactions involving dye fading or other photoredox reactions where production of singlet oxygen is unlikely or impossible.

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