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Vesicle controlled selectivity in photosensitized oxidation of olefins

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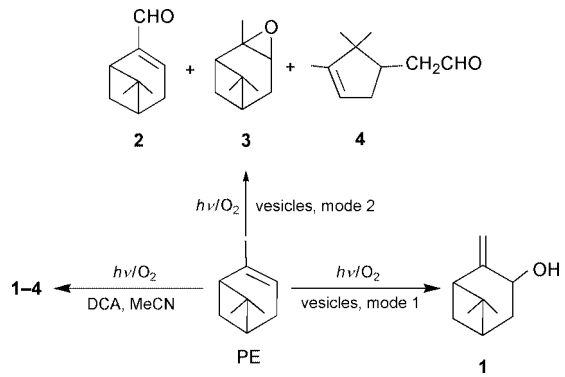
The photooxidation of α-pinene (α-PE) and *trans,trans*-1,4-diphenyl-1,3-butadiene (DPB) sensitized by 9,10-dicyanoanthracene (DCA) in mixed surfactant vesicles was selectively directed toward either the singlet oxygen mediated or the superoxide radical anion mediated products by controlling the status and location of the substrate and sensitizer molecules in the reaction media.

Dye-sensitized photooxidation of alkenes has been extensively investigated.[1] There are two well established types of dye-sensitized photooxidation: an energy-transfer pathway and electron-transfer pathway.[2] The energy-transfer pathway involves energy transfer from the triplet sensitizer to ground-state oxygen to generate singlet oxygen ($^1O_2$) which then reacts with the substrate. In the electron-transfer photosensitized oxidation, electron-deficient sensitizers are generally used. Electron transfer from the alkene to the sensitizer in its excited states results in formation of the alkene radical cation and the sensitizer radical anion, which subsequently reduces O_2 to give the superoxide radical anion ($O_2^{\bullet-}$). The generated superoxide radical anion then reacts with the alkene radical cation to yield the oxidation products. Unfortunately, in many cases the two types of photooxidation occur simultaneously, and the selectivity of the oxidation reactions is poor. Of the various approaches to increase selectivity, use of organized and constrained media has shown considerable promise.[3] Here, we report the photooxidation of α-pinene (α-PE) and *trans,trans*-1,4-diphenyl-1,3-butadiene (DPB) sensitized by 9,10-dicyanoanthracene (DCA) in mixed surfactant vesicles. We found that the oxidation could be directed selectively toward the products derived either from the energy transfer pathway or the electron transfer pathway by controlling the status and location of the substrate and sensitizer molecules in the reaction media.

The vesicles used in the present study were prepared by sonicating an equimolar mixture of a cationic surfactant (octyltrimethylammonium bromide, 8.2×10^{-2} M) and an anionic surfactant (sodium laurate, 8.2×10^{-2} M) in buffered solution (pH = 9.2) for 30 min at 50 °C.[4] These vesicles were found to be stable at room temperature and the dispersion solution was optically clear. The photosensitized oxidation was performed in two modes. In the first (mode 1), the sensitizer DCA was incorporated in the bilayer membrane of one set of vesicles and the substrate solubilized in another set of vesicles. Equal volumes of the two sets of vesicle dispersions were then mixed to prepare the samples for photolysis. Although sonication was performed during preparation of the component solutions, the final mixture was not sonicated. In this way intermixing of the solubilizates was prevented. In the second mode (mode 2) both the sensitizer and the substrate were incorporated in the bilayers of the same set of vesicles. Generally, the concentration of the olefins was *ca.* 1.0×10^{-3} M corresponding to thousands of substrate molecules in each vesicle, while the concentration of the sensitizer was generally *ca.* 1.0×10^{-4} M. The samples were irradiated under oxygen by using light with wavelength $\lambda > 400$ nm, ensuring the absence of direct excitation of the alkene substrate. After irradiation, the products were extracted with CH_2Cl_2 and analysed by gas chromatography. The material balance for all the reactions was generally > 95%.

Photooxidation of α-PE sensitized by DCA in homogeneous solution followed by reduction of the reaction mixture with sodium sulfite solution gave the ene product pinocarveol **1** and the non-ene products myrtenal **2**, epoxide **3** and aldehyde **4**, as shown in Scheme 1. The ene and the non-ene products have been proposed to be derived from the energy- and electron-transfer pathways, respectively.[5] The product distributions in acetonitrile and dichloromethane are given in Table 1. The product distribution of the photosensitized oxidation of α-PE in vesicles is dramatically altered compared with that in homogeneous solutions, and is remarkably dependent on the experimental mode. Photooxidation in mode 1 exclusively produced the ene product **1** (Table 1). In contrast, photooxidation in mode 2 only gave the non-ene products **2**–**4** (Table 1). These observations can be easily understood by consideration of the status and location of the substrate and sensitizer molecules in the reaction media. It has been established that DCA can act both as an energy-transfer sensitizer and an electron-transfer sensitizer.[6] In mode 1, the isolation of α-PE in one set of vesicles from DCA in another set of vesicles prevents them from undergoing electron transfer. Thus, no non-ene products were detected. On the other hand, $^1O_2$ can be generated in the DCA-incorporating vesicles by energy transfer from the triplet excited state of DCA to the ground state of oxygen. The species $^1O_2$ is small and uncharged and has a relatively long lifetime and properties which allow it to diffuse freely from one set of vesicles to another set of vesicles where reaction with the



Scheme 1

Table 1 Product distribution in the DCA-sensitized photooxidation of α-PE and DPB in solutions and in vesicles

	PE				DPB					
Media	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
MeCH	52	32	13	3	80	80	2	13	0	5
CH_2Cl_2	85	10	5	0	75	75	12	3	5	5
Vesicles (mode 1)	100	0	0	0	100	100	0	0	0	0
Vesicles (mode 2)	0	55	4	41	53	53	23	0	24	0

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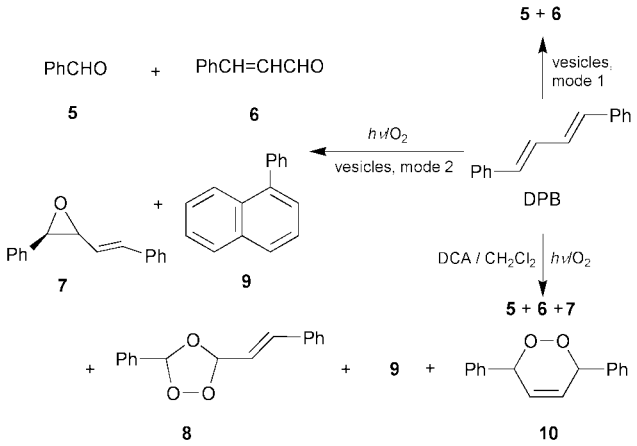

Scheme 2

olefins produces the ene product **1**. In mode 2, the DCA molecule is surrounded by a number of α-PE molecules. The high "local concentration" of α-PE and the close contact between DCA and α-PE molecules in the confined bilayer of vesicles leads to efficient quenching of the singlet excited state of DCA by α-PE *via* an electron-transfer process, generating DCA radical anions and α-PE radical cations. As a result, intersystem crossing from the singlet excited state to the triplet state of DCA can not compete with the quenching process by α-PE. Thus, subsequent triplet energy transfer to O_2 can not occur, and no singlet oxygen mediated product is produced. On the other hand, the generated DCA radical anions will efficiently undergo electron transfer to oxygen to produce superoxide radical anions, which subsequently react with α-PE radical cations located in the same vesicle to yield the non-ene products **2**–**4**.

Photosensitized oxidation of DPB in homogeneous solution has been extensively investigated.[5,7] Irradiation of an oxygen-saturated DPB solution in CH_2Cl_2 containing DCA with visible light gave benzaldehyde **5**, cinnamaldehyde **6**, epoxide **7**, ozonide **8**, 1-phenylnaphthalene **9** and endoperoxide **10** (Scheme 2) and the product distribution is shown in Table 1. **10** is a product of 1,4-cycloaddition of singlet oxygen ($^1O_2$) to DPB. Products **7**–**9** are derived from the electron-transfer pathway. Products **5** and **6** could be produced either *via* an energy- or electron-transfer pathway.[6] The photosensitized oxidation of DPB in vesicles in mode 1 gave **5** and **6** as the unique products (Table 1 and Scheme 2). We believe that these products are derived from the singlet oxygen pathway. In contrast, the photosensitized oxidation of DPB in vesicles in mode 2 only produced the electron-transfer mediated products **5**–**7** and **9** (Table 1) and no singlet oxygen products were detected. These observations demonstrate once again that the selectivity in photosensitized oxidation of alkenes can be directed by incorporation of the sensitizer and substrate in different or the same set of vesicles.

It is of note that the products in the reaction of DPB with singlet oxygen in vesicles are remarkably different from those in homogeneous solutions. The reaction in homogeneous solution yielded endoperoxide **10**, a 1,4-cycloaddition product of the diene to $^1O_2$, as the unique product (Scheme 2). In sharp contrast, the photosensitized oxidation in vesicles produced benzaldehyde **5** and cinnamaldehyde **6** in quantitative yield. Evidently, these products were derived from an intermediate dioxetane, a 1,2-cycloaddition product. It has been established that DPB in solution exists mainly in its transoid conformer,[7] and the cisoid form amounts to *ca.* 1%. The 1,4-cycloaddition of singlet oxygen to the 1,3-diene to form the endoperoxide is concerted and requires a six-membered ring transition state; only the cisoid conformer can satisfy such a requirement. Obviously, the organized semirigid environment in vesicles prevents DPB from undergoing transoid to cisoid conformational change and thus only the 1,2-cycloaddition products were obtained.

In conclusion, vesicles can be used to direct the photosensitized oxidation of olefins either toward the singlet oxygen mediated or the superoxide radical anion mediated products by controlling the status and location of the olefin and sensitizer molecules in the reaction media.

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