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Controllable Selectivity of Photosensitized Oxidation of Olefins Included in Vesicles

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Abstract—9,10-Dicyanoanthracene (DCA) sensitized photooxidation of α-pinene, *trans*-stilbene and *trans*,*trans*-1,4-diphenyl-1,3-butadiene in mixed surfactant vesicles was investigated. While the oxidation in homogeneous solution yields the products derived from both the energy transfer and the electron transfer pathways, that within vesicles selectively yields either the singlet oxygen mediated or the superoxide radical anion mediated products depending on the status and location of the substrate and sensitizer molecules in the reaction medium. Upon incorporating the alkene in the bilayer membranes of one set of vesicles and DCA in another set of vesicles, the isolation of the substrate from the sensitizer prevents them from undergoing electron transfer. The singlet oxygen produced in the DCA-containing vesicles diffuses into the alkene-containing vesicles and reacts with the alkene. Thus, only the singlet oxygen oxidation products are obtained, and no product derived from the superoxide radical anion is detected. In contrast, incorporating both the sensitizer and the substrate within the same set of vesicles results in the two dissimilar molecules close to one another in the restricted space of the bilayer membranes of the vesicles. Thus, electron transfer from the alkenes to $^1DCA^*$ is enhanced, and the efficiency of the intersystem crossing from $^1DCA^*$ to $^3DCA^*$ is reduced. The photosensitized oxidation in this case only gives the products derived from the electron transfer pathway. Moreover, the reaction of singlet oxygen with DPB in vesicles results exclusively in the 1,2-cycloaddition products rather than the 1,4-cycloaddition product. This result indicates that the organized semirigid environment in vesicles prevents the olefin molecules from conformational change. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Selective oxidation of alkenes by molecular oxygen is one of the current challenges in the manufacture of organic building blocks and industrial intermediates,[1] and photosensitized oxidation holds special promise for yielding product specificity.[2] There are two well-established types of dye-sensitized photooxidation: the energy-transfer pathway and the electron-transfer pathway.[3] The energy-transfer pathway involves energy transfer from the triplet sensitizer to the ground-state oxygen to generate singlet oxygen ($^1O_2$), then the generated singlet oxygen reacts with the substrate.[4] In the electron-transfer photosensitized oxidation, electron deficient sensitizers are generally used.[5] Electron transfer from the alkene to the sensitizer in its excited states results in the alkene radical cation and the sensitizer radical anion, which subsequently reduces O_2 to give a superoxide radical anion ($O_2^{-\cdot}$). The generated superoxide radical anion 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 very low. To gain selectivity in this reaction, various efforts have been made in the past decades, and remarkable control of the reaction pathway has been obtained by the use of organized and constrained media.[6] In our previous works, we reported the photosensitized oxidation of alkenes included within ZSM-5 zeolite[7] or in water-swollen Nafion membranes.[8] We trapped the alkenes in the channels of ZSM-5 zeolites or within Nafion clusters and isolated the photosensitizers in the surrounding solution. The isolation of the substrate within the zeolite or the water-swollen Nafion membranes from the sensitizer in the external solution inhibits the electron transfer. On the other hand, singlet oxygen can still be generated in the solution, and is able to diffuse into the ZSM-5 channel or the Nafion cluster to react with the alkene. Moreover, we also trapped both the sensitizer and the alkene into the Nafion cluster. The close contact between the sensitizer and alkene molecules in the confined Nafion cluster leads to efficient quenching of the singlet excited state of the sensitizer by the alkene via an electron-transfer process. As a result, the intersystem crossing from the singlet excited state to the triplet state of the sensitizer cannot compete with the quenching process by the alkene. Therefore, the subsequent triplet energy transfer to O_2 cannot occur, and no singlet oxygen mediated product was produced. Thus, we could successfully direct the oxidation selectively toward either the singlet oxygen mediated or the superoxide radical

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Keywords: selective oxidation; olefins; vesicles.

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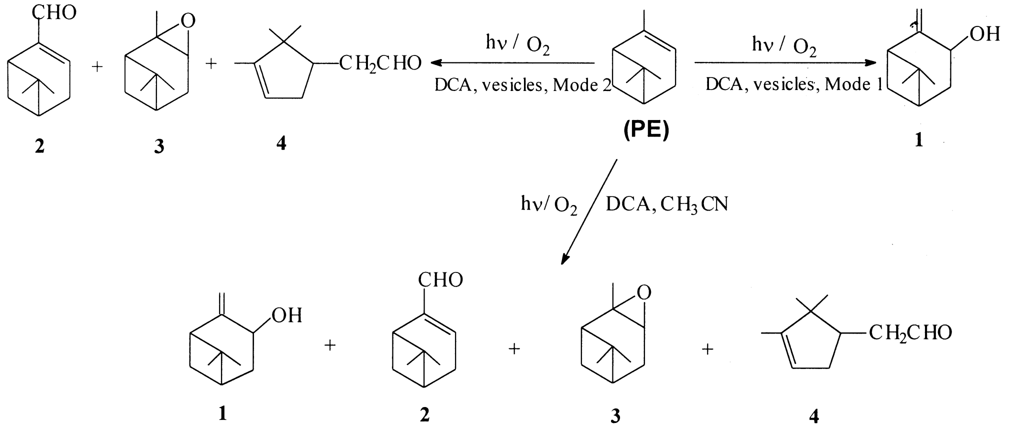


Scheme 1.

anion mediated products by controlling the status and location of the substrate and sensitizer molecules in the reaction media, which has not been observed in the solution photooxygenation. In the present work, we extend the study to a mixed surfactant vesicle medium to establish the scope of this approach.

Vesicles are widely used as simplified models of cell membranes.[9] Generally, vesicles are prepared from double-tailed surfactants. Simple single-tailed surfactants cannot form vesicles due to their relatively large hydrophilic head effect. However, it was recently established that stable vesicles could be simply produced by mixing commercially available single-tailed cationic and anionic surfactants.[10] This phenomenon arises from the strong electrostatic interaction between the oppositely charged head-groups of the components.[11] As a result, the mean effective head-group area decreases considerably, while the hydrophobic volume of the tails remains the same. Thus, this dynamic ion pairing yields a pseudo-double-tailed zwitterionic surfactant, which has the preferred geometry of a vesicle-forming surfactant. In the present work we use such easily prepared and inexpensive vesicles as the reaction medium to conduct the oxidation of α-pinene (PE), *trans*-stilbene (TS) and *trans,trans*-1,4-diphenyl-1,3-butadiene (DPB) photosensitized by 9,10-dicyanoanthracene (DCA). With the isolation of the substrate within one set of vesicles from the sensitizer in another set of vesicles, we only obtained the products derived from the singlet oxygen. On the other hand, by incorporation of both the substrate and sensitizer molecules in the same set of vesicles, we only observed the products derived from superoxide radical anion.

Results and Discussion

The vesicles used as the reaction medium 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. Vesicle formation was demonstrated by transmission electron microscopy with negative technique (stained with uranyl acetate). The unilamellar layer of the vesicle was clearly shown in the electron microscope and its thickness was measured to be ~4–5 nm. These vesicles were polydisperse with radii ranging from 80 to 150 nm, and the average vesicle radius was ~100 nm. The vesicles were stable at room temperature, and the dispersion solution was optically clear. The substrates PE, TS and DPB and the sensitizer DCA can all be easily incorporated into the bilayer membranes of the vesicles by sonication, since they are hydrophobic.[12]

The photosensitized oxidation was performed in two modes. In the first mode (Mode 1), we incorporated the sensitizer DCA in the bilayer membranes of one set of vesicles, and solubilized the substrate in another set of vesicles. Equal volumes of the two sets of vesicle dispersions were then mixed to prepare the samples for irradiation. Although sonication was carried out during preparation of the component solutions, the final mixture was not sonicated. In this way intermixing of solubilizates was prevented. We have carried out a control experiment: the mixed solution prepared from DCA-containing vesicles and substrate-containing vesicles was stored in the dark at room temperature for one day, and then was irradiated. The products and the efficiency of the product formation for the photosensitized oxidation were found to be identical within experimental error limit to those of the sample that was immediately irradiated after the preparation. This observation suggests that the intervesicular exchange both of the substrate and the sensitizer indeed did not occur, and the photosensitized oxidation process in this mode involved the generation of $^1O_2$ in one vesicle and reaction with alkene molecules in other vesicles. In the second mode (Mode 2) both the sensitizer and the substrate were incorporated in the bilayer of the same set of vesicles. Generally, the concentration of the olefins was $\sim1.0\times10^{-3}$ M corresponding to thousands of substrate molecules in each vesicle (see below), while the concentration of the sensitizer was generally $\sim1.0\times10^{-4}$ M. The samples were irradiated under bubbling oxygen by using a 450 W Hanovia high pressure Hg lamp as the light source, and a glass filter to cut off the 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 or ether and analyzed by gas chromatography. Material balance for all the reactions was generally greater than 95%, suggesting that any unidentified products must be minor.

Table 1. Product distribution in the DCA-sensitized photooxidation of PE in solutions and in vesicles (error range is ~2%)

Media	**1**	**2**	**3**	**4**
CH_3CN	52	32	13	3
CH_2Cl_2	85	10	5	0
Vesicles, mode 1	100	0	0	0
Vesicles, mode 2	0	55	4	41

Oxidation of PE

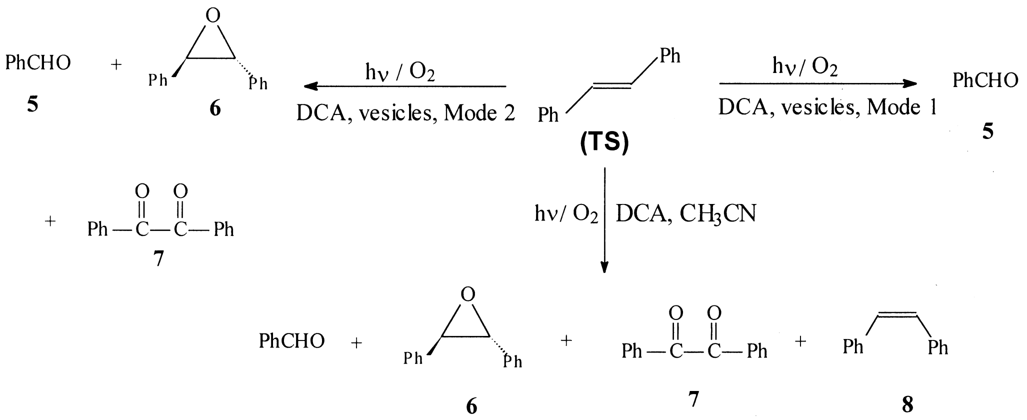
It has been established that DCA can act both as an energy-transfer sensitizer and an electron-transfer sensitizer.[5] The photooxidation of PE sensitized by DCA in homogeneous solution followed by reduction of the reaction mixture with sodium sulfite solution gave the ene product pinocarveol **1** and the non-ene products myrtenal **2**, epoxide **3** and aldehyde **4**, as shown in Scheme 1. The ene product and the non-ene products have been proposed to be derived from the energy-transfer and electron-transfer pathways respectively.[13] The product distributions in acetonitrile and dichloromethane are given in Table 1, which show significant dependence on the solvents.

The product distribution of the photosensitized oxidation of PE in vesicles is dramatically altered compared with those in the above homogeneous solutions, and remarkably dependent on the experimental mode. The photosensitized oxidation in Mode 1 followed by mixing the sample with a sodium sulfite aqueous solution to reduce the reaction mixture exclusively produced the ene product **1**. No trace of the non-ene products **2**–**4** was detected. Evidently, the isolation of PE in the bilayer membranes of one set of vesicles from DCA in another set of vesicles prevents them from undergoing electron transfer. Thus, no photooxidation products derived from the electron-transfer pathway were detected. On the other hand, singlet oxygen can be generated in the DCA-containing vesicles by the energy-transfer from the triplet excited state of DCA to the ground state of the oxygen. The vesicles used in this study have an aggregation number (number of surfactant molecules per vesicle) in the region of 10^5–10^6, and the average aggregation number is ~7.2×10^5, as estimated from the vesicle size and the volume of the surfactant molecule.[14] Thus, at surfactant concentration of 8.2×10^{-2} M the vesicle population is equivalent to a molarity of ~1.0×10^{-7} M, which in turn gives the inter-vesicular distance on average to be ~134 nm.[15] On the other hand, the species $^1O_2$ is small and uncharged and has a relatively long lifetime and properties that allow it to diffuse a long distance in non-viscosity media. The average diffusion length of $^1O_2$ molecule in aqueous solution is estimated to be ~780 nm.[16] This diffusion length is much larger than the intervesicular distance estimated above. Thus, the $^1O_2$ generated in DCA-containing vesicles is indeed capable of diffusing into the PE-containing vesicles to react with the alkene molecules to produce the ene product **1**. In a previous work,[14] we demonstrated that in the experimental condition identical to that described above ~20% of the generated singlet oxygen in the sensitizer-containing vesicles could diffuse to other vesicles to react with the substrate.

In contrast, the photooxidation in Mode 2 followed by mixing the sample with a sodium sulfite aqueous solution to reduce the reaction mixture exclusively gave the non-ene products **2**–**4** (Scheme 1). No product derived from the energy-transfer pathway was detected. The loading levels used in the present study were hundreds of DCA and thousands of PE molecules per vesicle. Thus, each DCA molecule is surrounded by a number of PE molecules. The high 'local concentration' of PE and the close contact between DCA and PE molecules in the confined bilayer of vesicles lead to efficient quenching of the singlet excited state of DCA by PE via an electron-transfer process, generating DCA radical anion and PE radical cation. As a result, the intersystem crossing from the singlet excited state to the triplet state of DCA can not compete with the quenching process by PE. Therefore, the subsequent triplet energy transfer to O_2 can not occur, and no singlet oxygen mediated product is produced. On the other hand, the DCA radical anion generated above will efficiently undergo electron transfer to oxygen to produce superoxide radical anion, which subsequently reacts with PE radical cation located in the same vesicle to yield the non-ene products **2**–**4**.

Oxidation of TS

As observed in the case of PE, the product distribution of the DCA-photosensitized oxidation of TS incorporated in vesicles significantly differs from that in homogeneous solution, and is dependent on the experimental mode. The DCA-photosensitized oxidation of TS in homogeneous



Scheme 2.

Table 2. Product distribution in the DCA-sensitized photooxidation of TS in solutions and in vesicles (error range is ~2%)

Media	5	6	7	8
CH_3CN	53	20	23	4
CH_2Cl_2	40	32	18	10
Vesicles, mode 1	100	0	0	0
Vesicles, mode 2	21	73	6	0

Table 3. Product distribution in the DCA-sensitized photooxidation of DPB in solutions and in vesicles (error range is ~2%)

Media	5	9	10	11	12	13
CH_3CN	80	80	2	13	0	5
CH_2Cl_2	5	5	12	3	5	75
Vesicles, mode 1	100	100	0	0	0	0
Vesicles, mode 2	53	53	23	0	24	0

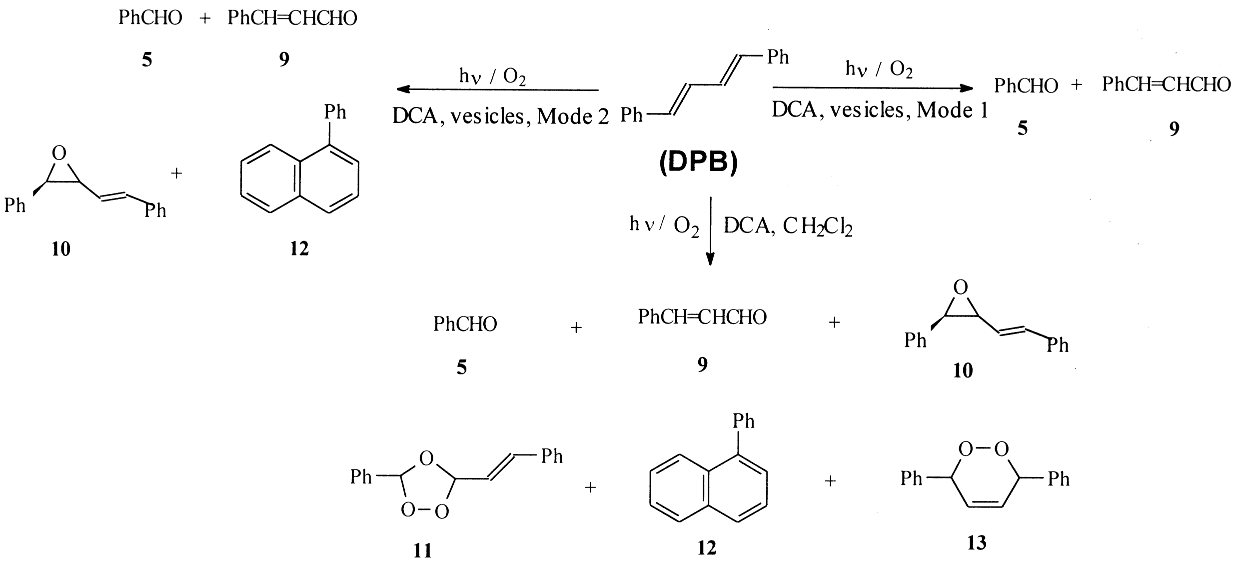
solution produced benzaldehyde **5**, *trans*-2,3-diphenyloxirane **6**, benzil **7** and *cis*-stilbene **8** (Scheme 2).[5c] Table 2 shows the product distributions in acetonitrile and dichloromethane. It has been well established that products **6**, **7** and **8** are produced via the electron-transfer pathway, while product **5** can be generated either via the energy-transfer or the electron-transfer pathway.

The DCA-photosensitized oxidation of TS in vesicles in Mode 1 yielded benzaldehyde **5** as the unique product. The mass balance of this reaction was greater than 95%. Evidently, this product was produced via the energy-transfer pathway. As in the case of PE, the isolation of TS in the bilayer membranes of one set of vesicles from DCA in another set of vesicles inhibits the electron-transfer between the substrate and the sensitizer. Hence, no superoxide anion product was expected to be produced. The singlet oxygen generated in the DCA-containing vesicles via the energy transfer from the triplet state of DCA to the ground state oxygen diffuses into the TS-containing vesicles and reacts with TS to form **5**. In contrast, the photosensitized oxidation of TS in vesicles in Mode 2 only produced the electron-transfer mediated products **5**, **6** and **7** (Scheme 2). The product distribution is shown in Table 2. Again, confining the sensitizer and substrate molecules within the restricted space of the bilayer membranes of vesicles enhances the electron-transfer process and reduces the efficiency of the intersystem crossing from the excited singlet state of the sensitizer to its triplet state. Thus, only the products derived from the electron-transfer pathway can be produced.

Oxidation of DPB

The photo sensitized oxidation of DPB in homogeneous solution has been extensively investigated.[17] Irradiation of oxygen-saturated DPB solution in CH_2Cl_2 containing DCA with visible light gave benzaldehyde **5**, cinnamaldehyde **9**, epoxide **10**, ozonide **11**, and endoperoxide **13** (Scheme 3). In addition, a small amount of 1-phenylnaphthalene **12** was detected. The product distributions in CH_3CN and CH_2Cl_2 are shown in Table 3. Compound **13** is a product of 1,4-cycloaddition of singlet oxygen ($^1O_2$) to DPB. Products **10**–**12** are derived from the electron-transfer pathway. Products **5** and **9** could be produced either via the energy-transfer or the electron-transfer pathway.[7] The photosensitized oxidation of DPB in vesicles in Mode 1 gave **5** and **9** as the unique products (Table 3 and Scheme 3). 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**, **9**, **10** and **12** (Table 3). No singlet oxygen products were detected. These observations demonstrate once again that one can control the selectivity in photosensitized oxidation of alkenes by incorporation of the sensitizer and substrate either in different or the same sets of vesicles.

It is worth noting 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 **13**, a



Scheme 3.

1,4-cycloaddition product of the diene to $^1O_2$ as the unique product (Scheme 3). In sharp contrast, the photosensitized oxidation in vesicles in Mode 1 produced benzaldehyde **5** and cinnamaldehyde **9** in quantitative yield as described above. Evidently, these products were derived from an intermediate dioxetane, a 1,2-cycloaddition product. The preferential formation of the product of 1,2-cycloaddition over that of 1,4-cycloaddition in vesicles is probably best explained in terms of the greater difficulty of achieving the necessary geometry for 1,4-cycloaddition in this organized medium. It has been established that DPB in solution exists in two conformational isomers: cisoid and transoid.[18] At equilibrium the main conformer is the transoid (~99%), and the cisoid is presented only in ~1%. The 1,4-cycloaddition of singlet oxygen to 1,3-diene to form endoperoxide is concerted and analogous to the Diels–Alder reaction. This reaction requires a six-membered ring transition state. Only the cisoid conformer can satisfy such a requirement, and in order to undergo 1,4-cycloaddition with singlet oxygen the transoid conformer first has to be isomerized to the cisoid one. Due to the kinetic equilibrium between the two conformers in solution, the cycloaddition can proceed until all the diene is converted to the products. Obviously, in vesicles the organized semirigid environment prevents DPB molecules from the conformational change. Thus, only the 1,2-cycloaddition products were obtained.

Conclusion

The product distributions of DCA-photosensitized oxidation of PE, TS and DPB in mixed surfactant vesicles are significantly different from those in homogeneous solutions, and remarkably dependent on reaction mode. By incorporating the alkenes within the bilayer membranes of one set of vesicles and DCA in another set of vesicles, the isolation of the substrate from the sensitizer prevents them from undergoing electron transfer. The singlet oxygen generated in the sensitizer-containing vesicles can diffuse into the substrate-containing vesicles to react with the substrate. Thus, only the products derived from the energy-transfer pathway are produced. In contrast, by incorporating both the sensitizer and the substrate in the same set of vesicles, the close contact between the substrate and sensitizer molecules in the restricted space of the vesicle bilayer membranes enhances the electron transfer from the substrate to the singlet excited state of DCA, thus reduces the efficiency of the intersystem crossing from the singlet excited state to the triplet state of the sensitizer and the subsequent formation of singlet oxygen. Therefore, the photosensitized oxidation of the three alkenes exclusively yields the products derived from the electron-transfer pathway, and no singlet oxygen mediated product is detected. Moreover, in the photosensitized oxidation of DPB, the organized semirigid environment in vesicles prevents the diene from the conformational change to adapt the necessary geometry for 1,4-cycloaddition with singlet oxygen. Thus, only the 1,2-cycloaddition products were obtained, which was contrast with that in homogeneous solution where the 1,4-cycloaddition product was the unique product.

Experimental

General

Surfactants octyltrimethylammonium bromide and sodium laurate were Aldrich products, and were recrystallized twice from ethanol–ether before use. Doubly distilled water was used throughout this work. TS, DPB and DCA were purchased from Fluka and used as received. PE was Aldrich product, and was distilled under reduced pressure under nitrogen and stored in the dark before use. Gas chromatography was performed on a Shimadzu GC-7A with a 3% OV-17 column. Mass spectra were run on a VGZAB GC-MS spectrometer. Electron microscopy was examined on a Hitachi H-600 electron microscope.

Preparation of samples

To the equimolar mixture of octyltrimethylammonium bromide and sodium laurate was added H_2O buffered solution (pH=9.2, $Na_2B_2O_7$) to form a suspension solution with the concentration of $\sim 8.2\times10^{-2}$ M for each surfactant. A known amount of substrate was added to the above suspension. The concentration of the substrate in the suspension was $\sim 1.0\times10^{-3}$ M. The suspension was sonicated for 30 min at 50°C. The solution became clear, and the substrate-containing vesicles were produced. By using the same procedure the DCA-containing vesicle dispersions were prepared. The concentration of the sensitizer was $\sim 1.0\times10^{-4}$ M. Mixing of equal volumes of the above substrate- and sensitizer-containing vesicle dispersions gave the Mode 1 irradiation samples.

To prepare the Mode 2 samples both the substrate (1.0×10^{-3} M) and the sensitizer (1.0×10^{-4} M) were added to the surfactant suspension. Subsequently, the suspension was sonicated as described above.

Negative staining electron microscopy

The vesicle samples were negatively stained with a 2% (w/w) uranyl acetate solution and examined on a Hitachi H-600 electron microscope.

Photooxidation of olefins and product analysis

The sample in a Pyrex reactor was bubbled with oxygen during irradiation. A 450-W medium pressure Hanovia Hg lamp was employed as the light source, and a glass filter was used to cut off light with a wavelength below 400 nm. The filter thus ensured the absence of direct excitation of the olefin substrates. After irradiation, the products were extracted with CH_2Cl_2 or ether, analyzed by GC, and identified by their spectral properties and by comparing with authentic samples.[8,13e] In the photosensitized oxidation of PE, after irradiation the sample was mixed with a sodium sulfite aqueous solution to reduce the reaction mixture, and then the products were worked up as described above.

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