Remarkable Product Selectivity in Photosensitized Oxidation of Alkenes within Nafion Membranes

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Abstract: 9,10-Dicyanoanthracene (DCA)-sensitized photooxidation of *trans*,*trans*-1,4-diphenyl-1,3-butadiene (DPB), *trans*-stilbene (TS), and α-pinene (PE) incorporated in Nafion membranes has been investigated. While the oxidation in homogeneous solution yields the products derived from both the energy transfer and the electron transfer pathways, that within Nafion membranes selectively gives 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 media. Upon incorporating the alkene within the water-swollen Nafion membranes and dissolving DCA in the surrounding CH_2Cl_2 solution, the sensitizer is isolated from the substrate during the irradiation time and the electron transfer between them is prevented. The singlet oxygen produced in the surrounding solution diffuses into the Nafion clusters and reacts with the alkenes. Thus, only the singlet oxygen oxidation products are obtained and no product derived from superoxide radical anion is detected. In contrast, incorporating both the substrate and the sensitizer within the water-swollen Nafion membranes leads to the possibility of situating the two dissimilar molecules near one another within the restricted space of the Nafion cluster. Thus, the electron transfer from the alkenes to the singlet excited state of DCA is enhanced, and the efficiency of the intersystem crossing from ^{1}DCA* to ^{3}DCA* is reduced. The photosensitized oxidation in this case only gives products derived from the electron-transfer pathway, and no singlet oxygen mediated product is observed.

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] The key problem in such reactions is the product specificity, and here photosensitized oxidations hold special promise.[2] There are two well-established types of dye-sensitized photooxidation: energy-transfer pathway and electron-transfer pathway.[3] The energy-transfer pathway involves the 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] For example, Diels−Alder reaction of conjugated dienes, "ene" reaction of olefins with allylic hydrogen, and dioxetane reaction of olefins that do not feature an allylic hydrogen belong to this type. In the electron-transfer photosensitized oxidation electron-deficient sensitizers are generally used.[5] Electron transfer from alkene to the sensitizer in its excited states results in alkene radical cation and sensitizer radical anion, which subsequently reduces O_2 to give superoxide radical anion ($O_2^{-\bullet}$). 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 poor.

To gain the selectivity in photosensitized oxidation of alkenes, various efforts have been made in the past decades, and remarkable control of the reaction pathway has been obtained by use of organized and constrained media.[6−14] Whitten and co-workers[6] reported that the oxidation of protoporphyrin IX

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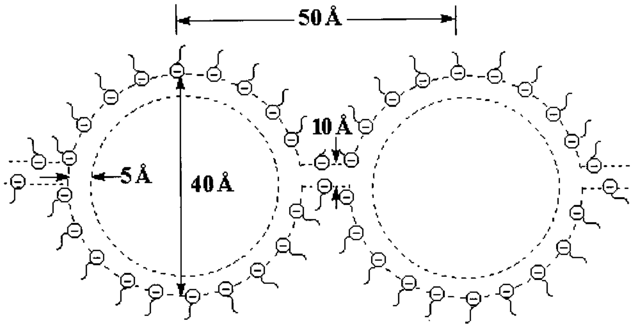
in micelles, monolayer films, and organized monolayer assemblies predominately results in the product of 1,2-addition of $^1O_2$ to the protoporphyrin vinyl groups, while the oxidation in solution mainly gives the product of 1,4-addition of $^1O_2$ to a diene unit in the protopophyrin consisting of one endocyclic double bond and the vinyl group. Kagiya et al.[7] studied the photosensitized oxidation of methyl 9-*cis*,12-*cis*-octadecadienoate in aqueous emulsion and found that the product distribution is comparable to that in homogeneous solution. Maldotti and co-workers investigated the oxidation of hydrocarbons photocatalyzed by iron porphyrins which are confined inside cross-linked polystyrene,[8] bound on semiconducting transition metal oxides such as TiO_2,[9] or included within Nafion clusters[10] and revealed that the heterogeneous media or organized systems affect the chemoselectivity of the oxidation process and increase the photochemical efficiency. Recently, many works have been reported on the photosensitized oxidation of alkenes included within zeolites.[11−14] Fox and co-workers[11] used $Ru(bpy)_3^{2+}$ exchanged into zeolite Y as the sensitizer to oxidize tetramethylethylene and 1-methylcylohexene. The photolysis was performed in $Ru(bpy)_3^{2+}$-exchanged zeolite slurry in methanol containing the alkenes. They found that the photogenerated singlet oxygen within zeolite cages freely diffuses to solution where it reacts with the alkene with normal selectivity. Frei and co-workers[12] could stabilize olefin·O_2 charge transfer (CT) complex by enclosure of the reactants in the cages of zeolite NaY. Irradiation of the complex at its long wavelength absorption band results in oxidation of the alkene. Ramamurthy and co-workers[13a] studied the oxidation of *trans*-stilbene and *trans*-4,4′-dimethoxystilbene included in X and Y zeolites. The zeolite having adsorbed both the alkene and the sensitizer was photolyzed in hexane slurry under oxygen atmosphere. They found that the oxidation is initiated via an electron-transfer pathway, which is contrasted with that in homogeneous solution (the energy transfer pathway). On the other hand, in the studies of oxidation of a series of olefins included within dye-exchanged X and Y zeolites, they could generate singlet oxygen within the zeolite by irradiating the dye and direct the reactive oxygen toward a particular face of the olefin, thus obtaining a high selectivity in the products of the oxidation.[13b−e] Furthermore, they assembled a supermolecular structure of an olefin, a thiazine dye, and oxygen within the NaY zeolite framework.[13f] In the presence of a chiral inductor (ephedrine hydrochloride) irradiation of the system results in a high regioselecitivity and a modest enantioselectivity. In a previous paper,[14] we reported the photosensitized oxidation of alkenes included within ZSM-5 zeolite. We trapped the alkenes in the channels of ZSM-5 zeolites and isolated the photosensitizers in the surrounding solution. The isolation of the substrate within the zeolite from the sensitizer in the solution outside inhibits the electron transfer. On the other hand, singlet oxygen still can be generated in the solution, and is able to diffuse into the ZSM-5 channel to react with the alkene. Thus, we successfully conducted photosensitized oxidation with a high degree of selectivity, which is not observed in the solution photooxygenation. In the present work, we extend the study to Nafion medium to establish the scope of this approach.

Scheme 1. Schematic Representation of the Two-Phase Cluster Network Model for Nafion Membranes



Nafion represents a novel and unique family of polymers which consist of a perfluorinated backbone and short pendant chains terminated by sulfonic groups. When swollen in water, the structure of Nafion resembles that of an inverse micelle (Scheme 1).[15−17] The hydrated SO_3^- headgroups are clustered together in a water-containing pocket of ca. 40 Å in diameter which are interconnected by short channels (ca. 10 Å in diameter) within the perfluorocarbon matrix. It has been established[18−20] that water-swollen Nafion can incorporate high concentrations of aromatic hydrocarbons and organic dyes. These optically transparent membrane systems are readily amenable to spectroscopic and photochemical investigations. Because of these attractive properties, this polymer has been utilized as a medium for photophysical and photochemical studies in recent years.[21−24] However, the use of Nafion for directing the selectivity of photosensitized oxygenation has never been reported. Here, we use Nafion membranes as the reaction medium to conduct the oxidation of *trans*,*trans*-1,4-diphenyl-1,3-butadiene (DPB), *trans*-stilbene (TS), and α-pinene (PE) photosensitized by 9,10-dicyanoanthracene (DCA). With the isolation of the substrate within Nafion clusters from the sensitizer in the surrounding solution, we only observed the products derived from the singlet oxygen pathway. On the other hand, using the double loading technique whereby first one guest (either substrate or sensitizer) molecule and then a second one are introduced into a Nafion cluster, we only detected the products derived from superoxide radical anion. Thus, we are able to direct the oxidation selectively 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.

Results and Discussion

Incorporation of the Substrate and Sensitizer into Nafion Membranes. The Nafion membranes used in the present study were in the sodium form (Nafion-Na^+). High concentrations of water-insoluble substrates, DPB, TS, and PE, can be successfully incorporated into water-swollen Nafion by the method described below: The membrane was immersed in the substrate solution in methanol. After reaching equilibration, the membrane was removed and the methanol adsorbed in the membrane was eliminated by evaporation under vacuum. The membrane having adsorbed the substrate was soaked in water

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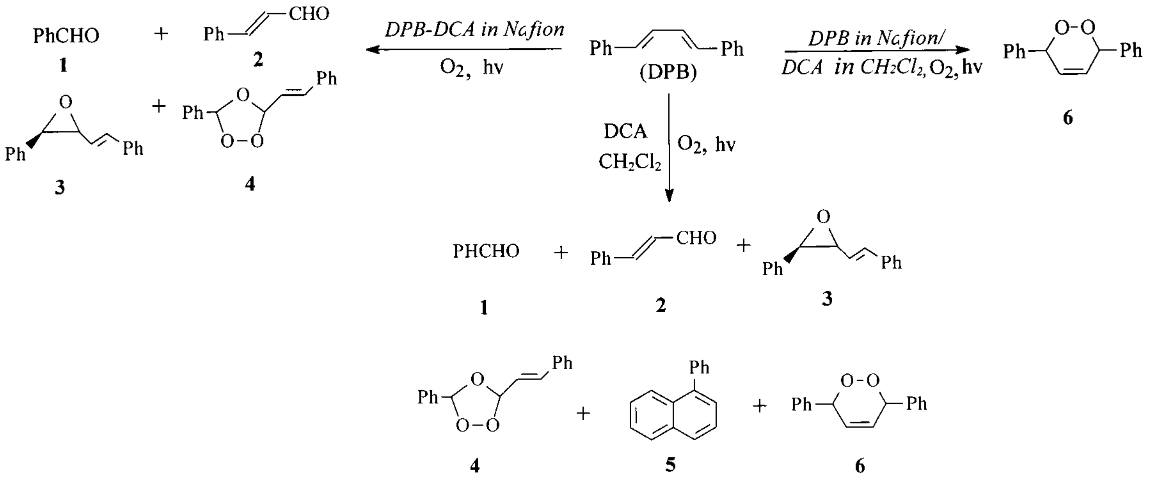
Scheme 2



to prepare the water-swollen sample. The solubilities of these substrates in water-swollen Nafion-Na^+ can be rather high (ca. 0.046, 0.022, and 0.040 M for DPB, TS, and PE, respectively). Using the parameters reported in the literatures,[17,25] we could calculate the average occupancy numbers (the number of the substrate molecules contained in each water cluster of Nafion) of the samples of DPB, TS, and PE to be 4.2, 2.7, and 3.6, respectively. The UV absorption spectra of DPB and TS in water-swollen Nafion exhibit blue shifts (4 and 18 nm for DPB and TS, respectively) compared with those in methanol. Since the absorption of DPB and TS is of $\pi-\pi^*$ transition character,[26] the blue shifts suggest that the environment around the molecules of the substrates in Nafion is less polar than that in methanol. The UV absorption of PE is in the shorter wavelength region compared with those of DPB and TS, and does not show significant change when incorporated into the Nafion membrane. Considering the hydrophobicity and insolubility of these substrates in water, it is proposed that in water-swollen Nafion these molecules are primarily solubilized in the hydrophobic perfluorocarbon backbone region. By analogy with the studies on nonpolar aromatic compounds in Nafion by Mau and coworkers,[27,28] the solubilization site may be close to the fluorocarbon/water interface.

The samples incorporating both the substrate and the sensitizer were prepared by the double loading technique. First, we prepared the samples incorporating the substrate by the method described above. These samples were then immersed in water containing a certain amount of solid DCA. To prepare the samples with a high concentration of DCA, the mixture has to be continuously stirred for a long time. The concentration of DCA in Nafion used in the present study is in the range of 3.7 $\times 10^{-5}$ to 5.2 $\times 10^{-5}$ M. Because of the insolubility of DCA in water, it is expected that its solubilization site in water-swollen Nafion also is in the perfluorocarbon backbone region and close to the perfluorocarbon/water interface.

The photosensitized oxidation was performed in two modes. The first involves irradiation of DCA in dichloromethane solution (5 $\times 10^{-5}$ M) in which the water-swollen Nafion sample incorporating the substrate is immersed (substrate in Nafion/DCA in CH_2Cl_2). Since dichloromethane cannot swell Nafion and is insoluble in water, the substrate and water within Nafion cannot be extracted into the solution, and CH_2Cl_2 and DCA in the solution cannot diffuse into the Nafion. Thus, the substrate and sensitizer are isolated from each other during irradiation. Control experiments revealed that no DCA was adsorbed into Nafion as determined by UV absorption after a water-swollen Nafion sample was immersed in a DCA solution in CH_2Cl_2 for 3 days, and no substrate was extracted into CH_2Cl_2 after the substrate-incorporated water-swollen Nafion was soaked in this solvent. The second mode involves irradiation of the water-swollen Nafion sample which has incorporated both the substrate and the sensitizer (substrate-DCA in Nafion). Generally, after 20 h of photolysis the conversion of the starting material in the first mode was ca. 40%. By using the same sensitizer concentration, similar conversion was obtained in CH_2Cl_2 solution in the absence of Nafion with about 4 h of irradiation. The photosensitized oxidation in the second mode proceeded relatively slowly. Under the condition of absorbing the same amount of light as above, to meet ca. 35% conversion, 30 h of irradiation was required. After irradiation, the products were extracted with methanol and analyzed by gas chromatography. Material balance in general was greater than 90%.

Table 1. Product Distribution in DCA-Sensitized Photooxygenation of DPB in CH_2Cl_2 Solution, DPB in Nafion/DCA in CH_2Cl_2, and DPB-DCA in Nafion

medium	**1(2)**	**3**	**4**	**6**	**5**
CH_2Cl_2	5	12	3	75	5
DPB in Nafion/DCA in CH_2Cl_2	0	0	0	100	0
DPB-DCA in Nafion	66	25	9	0	0

Oxidation of *trans,trans*-1,4-Diphenyl-1,3-butadiene (DPB). The photosensitized oxidation of DPB in homogeneous solution has been extensively investigated.[14,29] Irradiation of oxygen-saturated DPB solution in CH_2Cl_2 containing DCA with visible light gave benzaldehyde **1**, cinnamaladhyde **2**, epoxide **3**, ozonide **4**, and endoperoxide **6** (Scheme 2). In addition, a small amount of 1-phenylnaphthalene **5** was detected. All the products were isolated by column chromatography and identified by their spectral properties and by comparison with authentic samples. The product distribution is shown in Table 1. It has been established[5] that DCA can act both as a singlet oxygen sensitizer and an electron-transfer sensitizer. Obviously, **6** is a product

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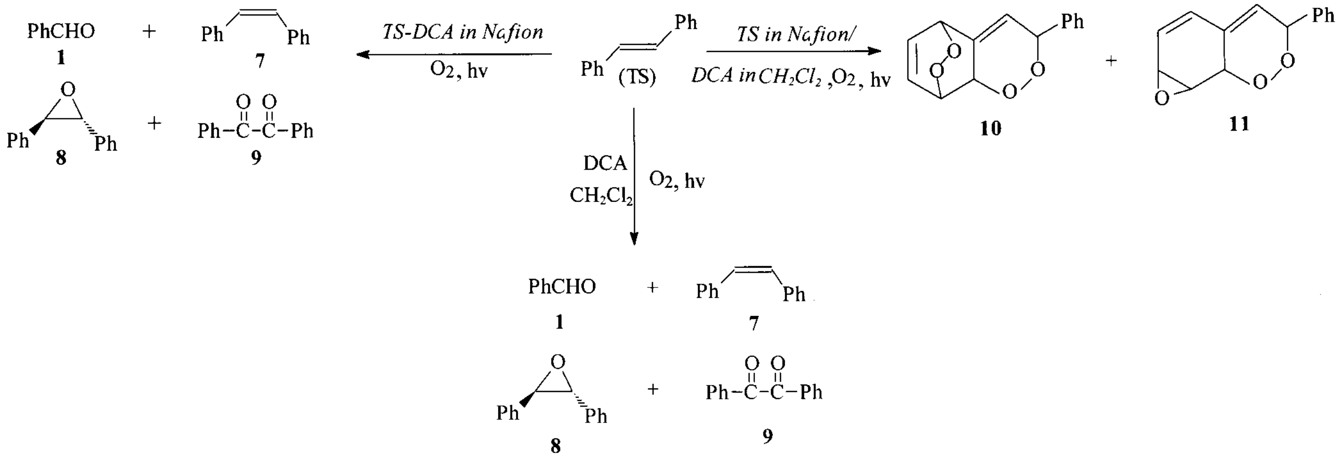
Scheme 3



of 1,4-cycloaddition of singlet oxygen ($^1O_2$) to DPB. The other products are presumably derived via the electron-transfer pathway.[29] As Foote suggested for the DCA-sensitized oxidation of stilbene,[5b] **1** and **2** are most likely derived from an intermediate dioxetane, a cycloaddition product of DPB$^+$, and superoxide anion (O_2^-), which would decompose under reaction conditions. **3** could be formed by the Bartlett reaction.[29,5b] **4** is possibly a secondary photooxygenation product[29] from **3**. Formation of **5** is probably due to cationic rearrangement of DPB.[14]

The product distribution of the photosensitized oxidation of DPB within Nafion membranes is dramatically altered compared with that in homogeneous solution, and it is remarkably dependent on the experiment mode. The sensitized photooxidation in the DPB in Nafion/DCA in CH_2Cl_2 mode gave **6** as the unique product (Table 1 and Scheme 2). The yield of this product was 100% based on the consumption of the starting material. Evidently, the isolation of DPB within the Nafion clusters from the sensitizer in the surrounding solution prevents them from undergoing electron transfer. Thus, no photooxidation products derived from the electron-transfer pathway were detected. On the other hand, $^1O_2$ can be formed in the solution by the energy transfer from the triplet-state sensitizer to the ground-state oxygen. The species $^1O_2$ is small and uncharged and has a relatively long lifetime and properties which allow it to diffuse freely from the surrounding solution to the Nafion clusters. 1,4-Cycloadditon of $^1O_2$ to DPB in the Nafion clusters results in endoperoxide **6**.

In contrast, irradiation of the water-swollen Nafion sample incorporating both DCA and DPB (DPB-DCA in Nafion mode) only resulted in the electron-transfer-mediated products **1**, **2**, **3**, and **4**. No singlet oxygen product, **6**, was detected (Scheme 2, Table 1). The material balance was near 100%. The loading levels used in the present study were one DCA molecule per ca. 200 water clusters and 4.2 DPB molecules per water cluster of Nafion. Thus, each DCA molecule is surrounded by a number of DPB molecules. The high "local concentration" of DPB and the close contact between DCA and DPB molecules in the confined cluster of Nafion lead to efficient quenching of the singlet excited state of DCA by DPB via an electron-transfer process, generating DCA radical anion and DPB radical cation. As a result, the intersystem crossing from the singlet excited state to the triplet state of DCA cannot compete with the quenching process by DPB. Thus, the subsequent triplet energy transfer to O_2 cannot occur, and no singlet oxygen mediated product was produced.[30] On the other hand, the concentration of oxygen inside Nafion is more than 10 times higher than that in organic solvents.[31] The DCA radical anion generated above would efficiently undergo electron transfer to oxygen to produce superoxide radical anion, which subsequently reacts with DPB radical cation to yield **1**, **2**, **3**, and **4**.

Table 2. Product Distribution in the DCA-Sensitized Photoxygenation of TS in CH_2Cl_2 Solution, TS in Nafion/DCA in CH_2Cl_2, and TS-DCA in Nafion

medium	1	7	8	9	10	11
CH_2Cl_2	40	10	32	18	0	0
TS in Nafion/DCA in CH_2Cl_2	0	0	0	0	96	4
TS-DCA in Nafion	35	47	7	10	0	0

Oxidation of *trans*-Stilbene (TS). As observed in the case of DPB, the product distribution of the DCA-photosensitized oxidation of TS incorporated in Nafion significantly differs from that in homogeneous solution, and is dependent on the experiment mode. It has been well established[5c] that photosensitized oxidation of TS in homogeneous solution via the electron-transfer pathway produces benzaldehyde **1**, *cis*-stilbene **7**, *trans*-2, 3-diphenyloxirane **8**, and benzil **9** (Scheme 3). On the other hand, the photosensitized oxidation via the energy-transfer pathway results in diendoperoxide **10**, **1**, and epoxy endoperoxide **11**.[32,33] We found that DCA-photosensitized oxidation of TS in CH_2Cl_2 only gave the electron-transfer mediated products **1**, **7**, **8**, and **9**. The product distribution is listed in Table 2. This result is analogous to the observation of Foote on the DCA-photosensitized oxidation in acetonitrile.[5c]

The photosensitized oxidation of TS in the TS in Nafion/DCA in CH_2Cl_2 mode yielded diendoperoxide **10** and epoxy endoperoxide **11** (Scheme 3). The main product was **10**, and the amount of **11** only was ca. 4% in the products (Table 2). The mass balance of this reaction was close to 100%. Evidently, these products were produced via the energy-transfer pathway.[32,33] The mechanism leading to **11** has been proposed by Foote to involve polar intermediates such as perepoxide or

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(30) To support this proposal, we carried out the photosensitized oxidation in CH_2Cl_2 solution with different DPB concentrations, and found that the ratio of the electron-transfer mediated products (**1**, **2**, **3**, and **4**) to the singlet oxygen product **6** indeed slightly increases with the increase of substrate concentration. Due to the limitation of the solubility of DPB in CH_2Cl_2, even for the sample with saturated DPB, the main product is **6**.

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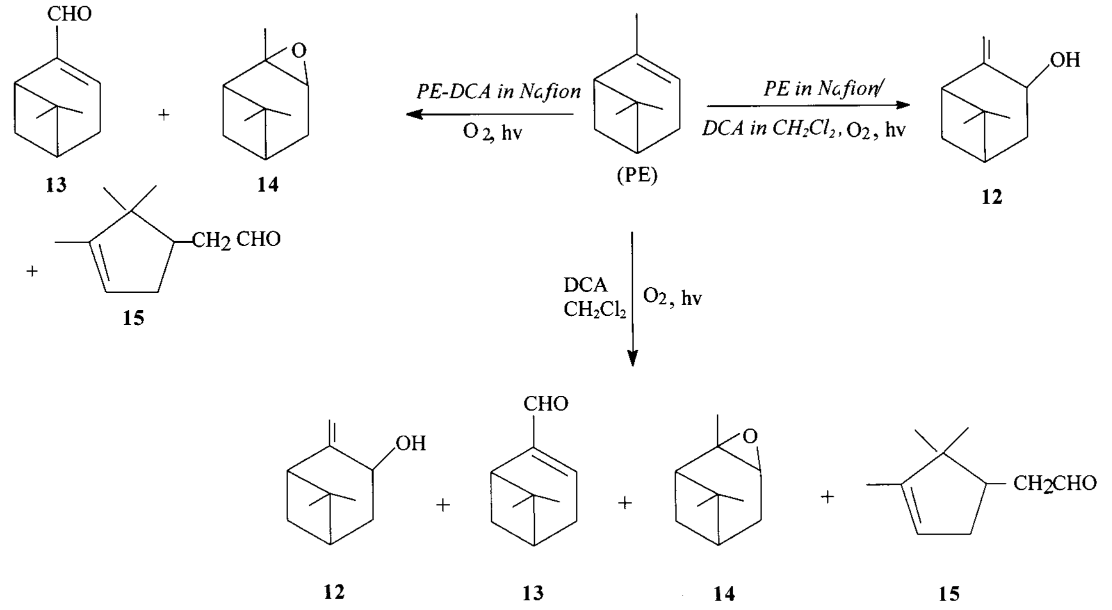
Scheme 4



zwitterion.[33b] As in the case of DPB, the isolation of TS within Nafion from DCA in the solution outside inhibits the electron transfer between the substrate and the sensitizer. Thus, no superoxide anion product is expected to be produced. The singlet oxygen generated in solution via the energy transfer from the triplet state DCA to the ground oxygen diffuses into the clusters of Nafion and reacts with TS to form **10** and **11**. This is the first example of formation of endoperoxides from the oxidation of TS photosensitized by DCA.

The photosensitized oxidation of TS in the TS-DCA in Nafion mode only produced the electron-transfer-mediated products **1**, **7**, **8**, and **9** (Scheme 3). The mass balance was close to 100%. The product distribution is slightly different from that in CH_2Cl_2 solution (Table 2). Again, confining the sensitizer and substrate molecules within the restricted space of Nafion cluster results in the preference of the electron-transfer over the energy-transfer pathway.

Oxidation of α-Pinene (PE). In 1964, it was established[34] that the photosensitized oxidation of PE to form ene product is a typical example of singlet oxygen oxidation reactions. Later on, Zhang and Cao reported[35] that irradiation of an oxygen saturated solution of PE with DCA in acetonitrile followed by reduction of the reaction mixture with sodium sulfite solution gave, in addition to the ene product pinocarveol **12**, the non-ene products myrtenal **13**, epoxide **14**, and aldehyde **15**, as shown in Scheme 4. The non-ene products **13**−**15** were proposed to be derived from the electron-transfer pathway. We conducted this oxidation reaction in CH_2Cl_2 and obtained both the ene and non-ene products. The product distribution is significantly dependent on the solvents and is shown in Table 3.

Table 3. Product Distribution in the DCA-Sensitized Photoxygenation of PE in CH_3CN and CH_2Cl_2 Solutions, PE in Nafion/DCA in CH_2Cl_2, and PE-DCA in Nafion

medium	12	13	14	15
CH_2CN	52	32	13	3
CH_2Cl_2	85	10	5	0
PE in Nafion/DCA in CH_2Cl_2	100	0	0	0
PE-DCA in Nafion	0	94	4	2

The photosensitized oxidation of PE in the PE in Nafion/DCA in CH_2Cl_2 mode followed by immersing the sample in a sodium sulfite aqueous solution to reduce the reaction mixture exclusively produced the ene product **12**. No trace of the non-ene products **13**−**15** was detected. The material balance was near 100%. The exclusive formation of **12** is attributed to the isolation of PE in Nafion clusters from DCA in the surrounding solution. While the electron transfer from PE to the excited state of DCA is inhibited because of the isolation, singlet oxygen can be generated in solution via the energy-transfer process, and can diffuse into the Nafion clusters to react with PE. In a study of cyanoaromatic sensitized photooxidation of α- and *β*-pinenes in solution,[35] it was proposed that the singlet oxygen comes from the back-electron transfer in the radical ion pair of the superoxide radical anion and the substrate radical cation. Obviously, this mechanism does not operate in the oxidation of PE in the substrate in Nafion/sensitizer in CH_2Cl_2 mode.

In contrast, irradiation of the water-swollen Nafion sample incorporating both DCA and PE followed by immersing the sample in a sodium sulfite aqueous solution to reduce the reaction mixture exclusively gave the non-ene products **13**−**15** (Table 3). No product derived from the energy-transfer pathway was detected. Material balance was excellent (close to 100%). This observation demonstrates once again that confining the sensitizer and the substrate molecules within Nafion clusters enhances the electron-transfer process and reduces the efficiency of the intersystem crossing from the excited singlet state to the triplet state of the sensitizer due to the high local concentration of the substrate. Thus, only the products derived from the electron-transfer pathway can be produced. The main product in the above reaction is myrtenal **13**. The yield of this product reached ca. 94% (Table 3). Gollnick and Schenek reported[34a] that the radical initiated oxygenation of PE yields a complex mixture of products, none of them in higher than 33% yield. Although myrtenal **13** is also found in the radical-initiated oxygenation, it is formed only in very low yield (<13%). In the DCA-sensitized photooxygenation of PE Zhang and Cao[35]

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(34) (a) Gollnick, K.; Schenck, G. O. *Pure Appl. Chem.* **1964**, *9*, 507. (b) Foote, C. S.; Wexler, S. S.; Ando, W. *Tetrahedron Lett.* **1965**, 4111. (c) Jefford, C. W.; Boschung, A. F.; Moriarty, R. M.; Rimbault, C. G.; Laffer, M. H. *Helv. Chim. Acta* **1973**, *56*, 2649. (d) Gollnick, K.; Kuhn, H. J. In *Siglet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 287.

(35) Zhang, B.-W.; Ming, Y.-F.; Cao, Y. *Photochem. Photobiol.* **1984**, *40*, 581.

could isolate **13** in 62% yield by carrying out the reaction in the presence of a singlet oxygen quencher. Compared with those results, the yield of **13** in the photosensitized oxidation of PE in the PE-DCA in Nafion mode is rather high. We suggest that this reaction may be applied to the synthesis of myrtenal, an important raw material in the perfume industry.

Conclusions

The DCA-sensitized photooxidation of DPB, TS, and PE differed significantly when incorporated within water-swollen Nafion membranes compared to that in homogeneous solution. By incorporating the alkenes within Nafion clusters and dissolving DCA in the surrounding CH_2Cl_2 solution, the isolation of the substrate from the sensitizer inhibits the electron-transfer reaction. The singlet oxygen generated in the solution can diffuse into the water-swollen Nafion cluster and reacts with the substrates. Thus, only the products derived from the energy-transfer pathway were produced. The photosensitized oxidation of DPB, TS, and PE gave endoperoxide **6**, diendoperoxide **10** and epoxy endoperoxide **11**, and the ene product **12**, respectively, as the unique products. In contrast, when both the substrate and the sensitizer are incorporated in the Nafion clusters, the photosensitized oxidation of these three alkenes exclusively gave the products derived from the electron-transfer pathway, and no singlet oxygen mediated products were detected. This observation is attributed to the confining of the substrate and sensitizer molecules within the restricted space of Nafion cluster. The high local concentration of the substrate enhances the electron transfer from the substrate to the singlet excited state of DCA, and 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. This work demonstrates that with the proper choice of medium and by controlling the status and location of the substrate and sensitizer molecules in the medium one can achieve very high selectivity in photosensitized oxidation reactions.

Experimental Section

Materials and Instrumentation. Nafion membrane 117 in acid form (Nafion-H^+) with an equivalent weight of 1100 and thickness of 0.0175 cm was a product of Du Pont and was kindly donated by Drs. A. W.−H. Mau and L. M. Dai of CSIRO, Division of Molecule Science, Australia. Prior to use, the membrane was cleaned by boiling in concentrated nitric acid for 4 h, and then thoroughly washed with distilled water and finally immersed in water for 24 h. The membrane in sodium form (Nafion-Na^+) was obtained by immersing the pretreated Nafion-H^+ membrane in 1 N NaOH aqueous solution. Excess base was then removed by stirring the samples in water. Doubly distilled water was used throughout this work. All the solvents were of spectral grade. TS, DPB, and PE were purchased from Fluka and used as received. Gas chromtography was performed on a Shimadzu GC-7A with a 3% OV-17 column. Mass spectra were run on a Finnigan 4021C GC-MS spectrometer. ^{1}H NMR spectra were recorded at 400 Hz with a Varian VXR-400 spectrometer. UV absorption spectra were recorded on a HP 8451A spectrometer.

Preparation of Nafion Samples. The weighed Nafion membrane samples were immersed in a solution of the substrate in methanol, and the solution was continuously stirred. To prepare the Nafion samples with the substrates in high concentration, in the methanol solution a certain amount of the substrate solid was presented. To reach equilibration, the samples were kept in the solution for at least 1 day. The amount of uptake of the substrate by the membranes was determined by the UV absorbance. After reaching equilibration, the membrane samples were taken off and the methanol was evaporated under vacuum. The dry samples having incorporated the substrate were immersed in water to prepare water-swollen samples.

To prepare the samples incorporating both the substrate and the sensitizer, the membrane having absorbed the substrate prepared above was soaked in water containing a certain amount of DCA solid. The mixture was continuously stirred for 1 day. The amount of uptake of DCA by the membrane was determined by the UV absorption.

Photooxidation and Product Analysis. The photooxidation was carried out in two modes. In the substrate in Nafion/DCA in CH_2Cl_2 mode, the water-swollen Nafion sample incorporating the substrate was immersed in DCA solution in CH_2Cl_2 in a Pyrex photolysis cell. Oxygen was bubbled through the solution during irradiation. In the substrate-DCA in Nafion mode, the water-swollen Nafion samples incorporating both the substrate and the sensitizer were placed in a Pyrex photolysis cell. The cell was connected to a oxygen source. A 450-W medium press 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 alkene substrates. After irradiation, the samples were extracted with methanol. The products were analyzed by GC, and the mass balance was measured by using an internal standard. For preparative samples, the products were isolated by column chromatography and identified by their spectral properties.

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