

## Micoreactor-controlled selectivity in organic photochemical reactions\*

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**Abstract:** Molecular-sieve zeolites, Nafion membranes, low-density polyethylene films, and mixed surfactant vesicles have been used as micoreactors to carry out organic photochemical reactions. The photo-cycloadditions of diaryl compounds with long flexible chains included in NaY zeolite or low-density polyethylene films yield intramolecular photocyclomers to the exclusion of intermolecular products. The photosensitized oxidation of alkenes included in pentasil zeolites or Nafion membranes or vesicles can be directed 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. The photo-Fries rearrangement of phenyl phenylacetates included within NaY and pentasil zeolites or Nafion membranes gives either *ortho*-hydroxyphenones or decarbonylation products depending on the size/shape of the micoreactors and the substrate molecules. All these results demonstrate the utility of micoreactors to control the product selectivity in organic photochemical reactions.

### INTRODUCTION

Selectivity in organic phototransformation continues to be one of the main topics of current interest. Of the various approaches, the use of micoreactors to control the reaction pathways has shown considerable promise [1]. Micoreactors refer to organized and constrained media where the chemical reactions occur. The substrate is usually a small molecule of dimensions of several angstroms, and the micoreactor often has its size of tens of angstroms or larger. Thus, micoreactors are also known as nanoreactors. Among the many classes of micoreactors used in photochemical studies, molecular-sieve zeolites, Nafion membranes, vesicles, and low-density polyethylene films are outstanding members.

Molecular-sieve zeolites represent a unique class of materials [2]. This material may be regarded as open structures of silica in which silicon has been substituted by aluminum in a well-defined fraction of the tetrahedral sites. The frameworks thus obtained contain pores, channels, and cages of different dimensions and shapes. The pores and cages can accommodate, selectively according to size/shape, a variety of organic molecules of photochemical interest, and provide restrictions on the motions of the included guest molecules and reaction intermediates. For example, the internal surface of ZSM-5, a member of the pentasil family, consists of two types of pore systems (channels) [2]: one is sinusoidal with a near-circular cross-section of *ca.* 5.5 Å, and the other is straight and perpendicular to the sinusoidal channels. The straight channels are roughly elliptical with dimensions of *ca.* 5.2 × 5.8 Å. These channels of ZSM-5 can allow the adsorption of benzene and other molecules of similar molecu-

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lar size, but prevent molecules which possess a larger size/shape from being sorbed into the internal framework. On the other hand, the structure of Y-type zeolite consists of an interconnecting three-dimensional network of relatively large spherical cavities [2] (supercages) with a diameter of about 13 Å. Each supercage is connected tetrahedrally to four other supercages through 7.4-Å diameter windows or pores. As an indication of their volume, each supercage can include 5 molecules of benzene, 2 molecules of naphthalene, or 2 molecules of pyrene.

Nafion is a family of polymers which consists of a perfluorinated backbone and short pendant chains terminated by sulfonic groups. When swollen in water, the structure of Nafion is believed to resemble that of an inverse micelle [3]. The hydrated  $\text{SO}_3^-$  head-groups 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 that water-swollen Nafion can incorporate high concentrations of aromatic hydrocarbons and organic dyes, thus raising the possibility of obtaining high local concentration of organic molecules and inorganic cations. These optically transparent membrane systems are readily amenable to spectroscopic and photochemical investigations.

Vesicles are widely used as simplified models of cell membranes [4]. 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 [4]. This phenomenon arises from the strong electrostatic interaction between the oppositely charged head-groups of the components. 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 photosensitized oxidation of alkenes.

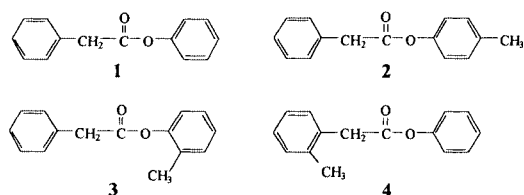
Another class of microreactors we used for photochemistry study is low-density polyethylene (LDPE) films. LDPE is a very complex family of materials which consists of *ca.* 50% of crystalline regions and *ca.* 50% of amorphous or interfacial regions [5]. A wide variety of organic molecules can be incorporated into LDPE by soaking its films in a swelling solvent containing the guest. The swelling process by which species are introduced "opens" the network of polymethylene chains in the amorphous and interfacial regions; when the swelling liquid is removed, the nearby chains move into van der Waals contact with the reactive guest molecules that have been left behind. It has been established that guest molecules are excluded from the crystalline portions of LDPE at temperatures below the melting transition. Their principal locations are the amorphous parts and the interfacial regions between crystalline and amorphous domains. Due to its anisotropic nature, LDPE has been used as a reaction medium to control the reaction pathways of a variety of guest molecules.

In the present work, we use the compounds, whose molecular photochemistry has been well established, as probes to show how the zeolite, Nafion, LDPE, and vesicle hosts control the pathways in photochemical reactions.

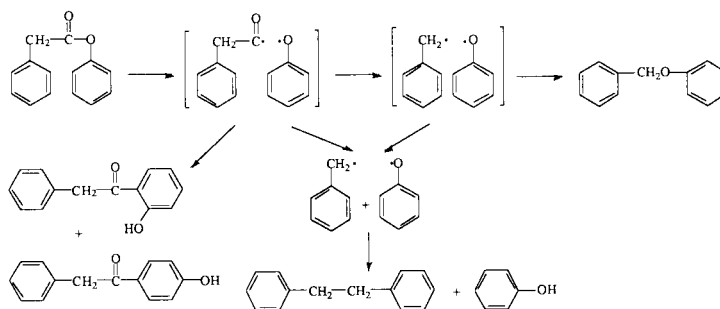
## PHOTOCHEMISTRY OF PHENYL PHENYLACETATES INCLUDED WITHIN ZEOLITES AND NAFION MEMBRANES

The photochemistry of esters **1–4** (Scheme 1) is expected to be analogous to that of phenyl acetate whose photochemistry in homogeneous solution has been well investigated [6]. Scheme 2 gives the photochemical reactions of these esters with **1** as the example. Upon photoradiation, **1** undergoes the C–O bond homolytic cleavage to give two-paired radicals. This geminate radical pair in cage recombines to form the starting ester or *ortho*- and *para*-hydroxyphenones. The latter reaction is known as the photo-Fries rearrangement. The phenylacetyl radical may undergo decarbonylation in cage to produce the secondary radical pair, which in turn produces phenyl benzyl ether. Thus, the hydroxyphenones and phenyl benzyl ether may be viewed as "cage" products. The radical pair may also undergo diffusive sep-

aration to give free phenoxy and phenylacetyl radicals. The active phenoxy radical would easily abstract a hydrogen atom to form phenol. The phenylacetyl radical can be expected to decarbonylate, generating benzyl radical, which in turn couples with each other to yield diphenylethane. Thus, phenol and diphenylethane are the “escape” products. The cage effect is defined as a fraction of the yields of hydroxyphenones and phenyl benzyl ether in the total yield of all of the products. Restriction on the diffusion of the radicals would increase the cage effect. Suppression of the rotation of the radicals would decrease the yield of the photo-Fries rearrangement products and enhance the ratio of the *ortho*- to the *para*-hydroxyphenone, since formation of a *para* rearrangement product requires a greater extent of the rotation of the radical than in the formation of a *ortho* product. Thus, one can use the cage effect and the ratio of *ortho*- to *para*-hydroxyphenone as probes for investigating the diffusibility and rotational mobility of radicals, respectively, in microreactors.



Scheme 1



Scheme 2

Photolysis of **1–4** in homogeneous solution results in the formation of diphenylethanes (5 ~ 15%), phenols (5 ~ 15%), *ortho*- (40 ~ 60%) and *para*-hydroxyphenones (20 ~ 25%). A small amount of phenyl benzyl ethers (3 ~ 8%) were also detected [6a]. However, photolyses of all of the four esters on NaY zeolite and Nafion only produce *ortho* rearrangement products. Molecular models suggest that esters **1–4** can enter into NaY zeolite internal surface and the inverse micelle of Nafion. We believe that the preference for formation of *ortho*-hydroxyphenones in the products is a consequence of the restriction on diffusional and rotational motion of the geminate radical pair.

For samples photolyzed on ZSM-5 zeolite, the product distributions of **1** and **2** are dramatically different from those photolyzed in homogeneous solutions. First, the rearrangement products were totally suppressed. Second, diphenylethane resulted from coupling of benzyl radical was not found. Only phenols and toluene were detected. In contrast, photolyses of **3** and **4** on ZSM-5 follow strikingly different pathways. Both photo-Fries rearrangement and decarbonylation products were formed. These results can be understood from consideration of size- and shape-selective sorption combined with restriction on the mobility of the substrates and reaction intermediates imposed by the pentasil pore system.

The structures of **1** and **2** are similar to *p*-xylene, and they are expected to diffuse into and be adsorbed within the internal surface of the pentasil. In the pentasil internal channels, **1** and **2** can only adopt a linear conformation to orientate themselves with the long axis of the molecules coinciding with the straight framework channels. The homolytic cleavage of the C–O bond of the excited state of esters

results in the production of two paired radicals. The kinetic pore diameter of the ZSM-5 framework channels is about 6 Å, and the benzene ring has a kinetic diameter of 5.85 Å. Thus, the fit inside the channels would be very tight. Such a tight fit and interaction between the radicals and the surfaces of ZSM-5 would restrict both diffusional and rotational motions of the radicals within the channels of ZSM-5. As observed, restriction on rotational motions of the radicals, which are required for Fries-rearrangement, would inhibit formation of *p*- and *o*-hydroxyphenones. Abstraction of a hydrogen atom for the phenoxy radical to form phenol is faster than its diffusion to access the benzyl radical and to couple each other, although the two geminate radicals are separated only by a small distance. Since the diffusion of the benzyl radical generated by decarbonylation of the phenylacetyl radical is also seriously inhibited, this radical has enough time to abstract a hydrogen atom before encountering another benzyl radical. Thus, toluene rather than diphenylethane was produced. In this sense toluene and phenol can be viewed as the cage products.

In contrast to **1** and **2**, the structures of **3** and **4** resemble *o*-xylene and possess a size/shape that inhibits them from diffusing into the ZSM-5 channel system. Thus, they are adsorbed on the external surfaces of ZSM-5. Molecules and intermediates on the external surfaces are expected to experience much less restriction to their diffusional and rotational motions. Therefore, both rearrangement and escape products are expected to be produced. Indeed, photolysis of **3** or **4** adsorbed on ZSM-5 zeolite results in both Fries rearrangement and decarbonylation products. However, close inspection of the product distribution reveals that both the cage effect and the ratio of *ortho*-hydroxyphenone to *para*-hydroxyphenone for photolysis of **3** or **4** on ZSM-5 are evidently greater than those for photolysis in homogeneous solution. This observation suggests that the external surface of ZSM-5 significantly restricts the diffusional and rotational motions of the photogenerated radicals.

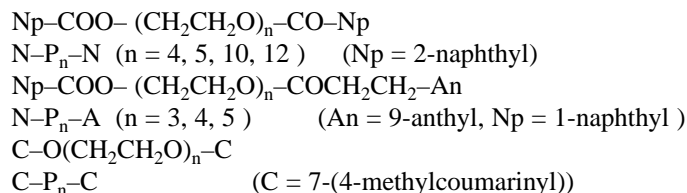
## **ZEOLITES AND LDPE FILMS AS HOSTS FOR PREPARATION OF LARGE-RING COMPOUNDS: INTRAMOLECULAR PHOTOCYCLOADDITION OF DIARYL COMPOUNDS**

The construction of macrocyclic compounds continues to be an important topic of synthetic organic chemistry [7]. A bifunctional molecule may undergo either intramolecular or intermolecular reactions. Intramolecular reaction gives macrocyclic ring-closure products, while intermolecular reaction results in dimers, oligomers, and polymers. Thus, the cyclization reaction suffers from the competition of the polymerization reaction. The rates of the latter are dependent on the concentration of the substrate, while those of the former are not. Hence, high substrate concentrations favor polymerization, while cyclization proceeds in good chemical yields only at low concentrations. In general, the syntheses of many-membered rings are performed at substrate concentrations as low as  $1 \times 10^{-5}$  M. This corresponds in a batch reaction to  **$1 \times 10^5$  liters of solvent for each mole of substrate!** We report a new approach to synthesize large-ring compounds in high yields under high substrate concentrations. The approach involves microporous solids as templates and hosts for the cyclization reactions. The size of the micropore has been chosen to permit only one substrate molecule to fit within each. Thus, intermolecular reactions are hindered, and cyclization can occur without competition under conditions of high loading. We find that Y-type zeolites and LDPE films can be used as such micro-vessels for intramolecular photocycloadditions of diaryl compounds with long flexible chains.

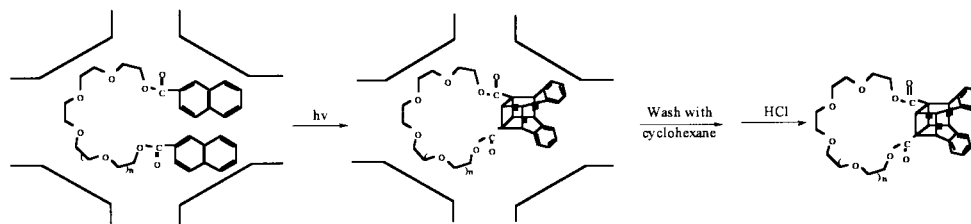
As mentioned above, each cavity of NaY zeolite can include 2 molecules of pyrene. Thus, one might expect that both aryl parts of a molecule with  $\alpha,\omega$ -diaryl groups separated by a flexible chain can be included in one supercage, and the intramolecular reactions between the two aryl groups should be enhanced. On the other hand, according to a Poisson distribution, as long as the loading level is less than one guest molecule per 10 supercages, there is less than a 5% probability to find two substrate molecules in one supercage, and the intermolecular reactions should be inhibited. The unit cell of NaY zeolite crystal is cubic with a dimension of *ca.* 25 Å. Thus, a typical particle of 1  $\mu\text{m}$  diameter contains thousands of interconnected supercages, and the concentration of the supercages is *ca.* 500  $\mu\text{mol}$  per

gram of zeolite. Assuming that a loading level of one substrate molecule per 10 supercages inhibits completely intermolecular reaction (*vide infra*), while cyclization still proceeds, only  $2 \times 10^4$  g of zeolite are needed for each mole of substrate! This corresponds to 40 g of NaY zeolite for each gram of substrate whose molecular weight is 500. This amount of zeolite is more than  $10^3$  times smaller compared with that of the solvent in solution-phase reactions that allow cyclization to dominate.

We have investigated the intramolecular photocycloadditions of diaryl compounds as shown below upon their inclusion in supercages of NaY zeolites [7a]. As expected from the analysis above, at loading levels less than 1 molecule of a diaryl compound per 10 supercages of NaY zeolite only intramolecular photocycloaddition is observed.



Irradiation of N-P<sub>n</sub>-N in organic solution, such as acetonitrile, can lead either to intra- or intermolecular cycloadditions (Scheme 3). At concentrations higher than  $10^{-3}$  M, the main product is the intermolecular photocyclomer. By contrast, irradiation of N-P<sub>n</sub>-N adsorbed on NaY zeolite results in an intramolecular photocyclomer, as long as the loading level was kept at less than *ca.* 50  $\mu\text{mol}$  of substrate per gram of zeolite (*ca.* 1 molecule per 10 supercages). Once formed, the photocyclomer is trapped inside the supercage of the zeolite, since the 7.4-Å window is too narrow to allow it to escape (Scheme 3).



**Scheme 3**

However, the aluminosilicate framework of Y zeolite can be dissolved in strongly acidic media so that the photocyclomer is released into solution and can be subsequently isolated. Thus, we first extracted the unreacted starting material with dichloromethane or cyclohexane, and then isolated the product by dissolving the zeolite framework in concentrated HCl followed by extraction with ether. Generally, the products were obtained in high purity by this procedure. **Only the intramolecular ring-closure photocyclomers were obtained, and no intermolecular products were detected by HPLC [7a].**

Irradiation of N-P<sub>n</sub>-A included in NaY zeolite also only results in intramolecular photocyclomers. Thus, we obtained the cross-photocyclomers of anthracene and naphthalene derivatives (a process not observed in homogeneous solution) in high yields.

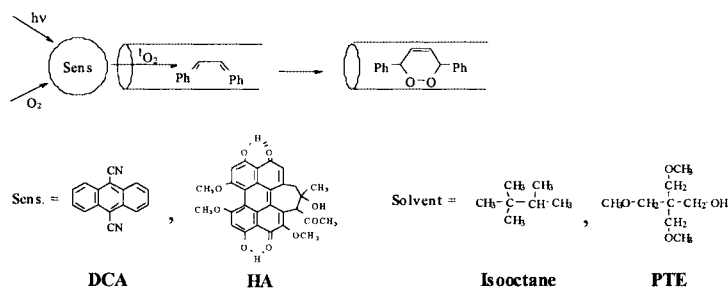
We also studied the photocycloaddition of diaryl compounds included within LDPE films [7b]. As mentioned above, organic molecules can be incorporated into the amorphous parts of LDPE by soaking its film in a swelling solvent containing the guest. In this way, the free volume of the reaction sites can be made sufficiently large to accept a molecule with two reactive groups linked by a flexible chain, yet small enough to force the two terminal groups in proximity. Furthermore, if the loading level is less than one guest molecule per 10 reaction cavities, there is less than a 5% probability to find two

guests in one cavity. As long as this condition is met and the rate of site exchange by guests is slower than that of conformational changes of the guest molecule, intermolecular reaction should be inhibited, while intramolecular reactions still can occur. We found that this is indeed the case for the photocyclizations of N-P<sub>n</sub>-N or C-P<sub>n</sub>-C.

### PHOTOSENSITIZED OXIDATION OF ALKENES INCLUDED IN PENTASIL ZEOLITE, NAFION MEMBRANES AND VESICLES

The dye-sensitized photooxidation of alkenes has been extensively investigated. There are two well-established types of such photooxidation: energy-transfer pathway and electron-transfer pathway [8]. The energy-transfer pathway involves energy transfer from the triplet sensitizer to the ground-state oxygen to generate singlet oxygen, then the generated singlet oxygen reacts with the substrate. In electron transfer, photosensitized oxidation electron-deficient sensitizers are generally used. Electron transfer from alkene to the sensitizer in its excited state results in alkene radical cation and sensitizer radical anion, which subsequently reduces O<sub>2</sub> to give superoxide radical anion. The generated superoxide radical anion reacts with the alkene radical cation to yield the oxidation products. In many cases, the two types of photooxidation occurs simultaneously, and the selectivity of the oxidation reactions is low.

We have studied the photosensitized oxidation of alkenes on ZSM-5 zeolites [8a]. *trans*, *trans*-1,4-Diphenyl-1,3-butadiene (DPB) and *trans*-stilbene (TS) were selected as the represents of alkenes, and 9,10-dicyanoanthracene (DCA) and hypocrellin A (HA) were the sensitizers. The choice of the solvents and sensitizers was motivated by the desire that they were prevented from being sorbed into ZSM-5 channel due to their size and shape characteristics. Thus, the internal framework of ZSM-5 is “dry”, and the substrate is protected from being extracted to the solution during photolysis. We trap the alkenes in the channels of ZSM-5 zeolite and isolate the photosensitizers in the surrounding solution (Scheme 4). The isolation of the substrate within the zeolite from the sensitizer in the solution outside inhibits the electron transfer to occur. 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 observed that the photosensitized oxidation proceeds with a high degree of selectivity, which is not observed in the solution photooxygenation.

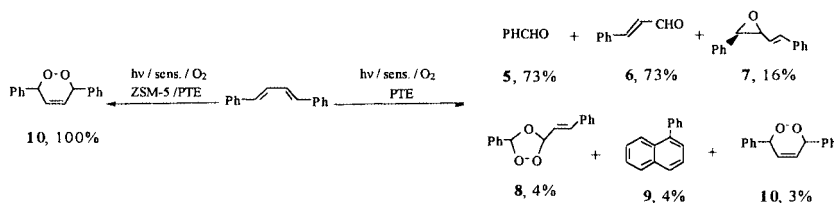


**Scheme 4**

Irradiation of oxygen-saturated DPB solution in PTE containing DCA or HA with visible light gave benzaldehyde **5**, cinnamaldehyde **6**, epoxide **7**, ozonide **8**, 1-phenylnaphthalene **9**, and endoperoxide **10** (Scheme 5). The product distribution is shown on Scheme 5. The main products are **5** and **6**. It has been established that DCA and HA can act both as singlet oxygen sensitizer and electron transfer sensitizer. Obviously, **10** is a product of 1,4-cycloaddition of singlet oxygen (<sup>1</sup>O<sub>2</sub>) to DPB. The other products are presumably derived via the electron-transfer pathway.

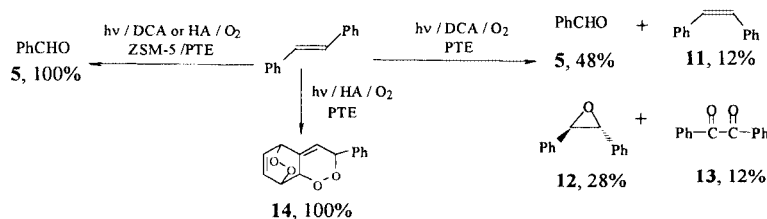
In contrast, the DCA- and HA-sensitized photooxidation of DPB adsorbed on the internal surface of ZSM-5 zeolite gave **10** as the unique product (Scheme 5). The yield of this product was 100% based

on the consumption of the starting material. Indeed, the isolation of DPB within the zeolite channels from the sensitizer in the solution outside prevents the formation of the products derived from the electron-transfer pathway, and only the  $^1\text{O}_2$ -mediated product was produced.



**Scheme 5**

As observed in the case of DPB, the photooxygenation of TS sensitized by DCA or HA differed significantly when included in ZSM-5 zeolite compared to that in homogeneous solution. The oxidation products in homogeneous solution are remarkably dependent on the sensitizers and conditions used. In acetonitrile using DCA as the sensitizer, the oxidation products were benzaldehyde **5**, *cis*-stilbene **11**, *trans*-2,3-diphenylloxirane **12**, and benzil **13** (Scheme 6). All these products were produced via the electron-transfer pathway. In PTE using DCA as the sensitizer, the photooxidation products are the same as those obtained in acetonitrile, but the product distribution is slightly changed. On the other hand, in the same solvent using HA as the sensitizer, the main product is diendoperoxide **14** (Scheme 6). This reaction is proposed to proceed via the energy-transfer pathway.



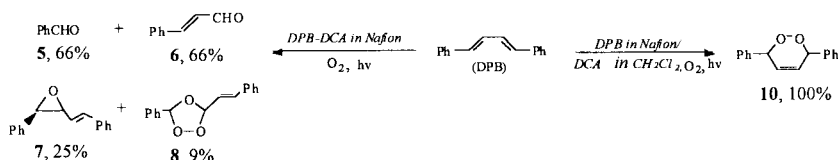
**Scheme 6**

However, when TS is included within ZSM-5 zeolite and the sensitizer is solubilized in the surrounding solvent PTE, the photooxidation of TS sensitized by DCA or HA yields benzaldehyde as the unique product (Scheme 6). The mass balances of this reaction for the two sensitizers are all close to 100%. As in the case of DPB, the isolation of TS within the zeolite from the sensitizer in the solution outside prevents electron transfer between the substrate and the sensitizer to occur. Thus, no superoxide anion is expected to be produced. Obviously, benzaldehyde is derived via the energy-transfer pathway. The singlet oxygen generated in solution diffuses into the internal framework of ZSM-5 and reacts with TS to form 3,4-diphenyl-1,2-dioxetane, which would decompose to yield benzaldehyde under reaction condition. We note that in the HA-sensitized photooxidation diendoperoxide **14** was not produced. This observation is contrary to the result of the reaction for TS with singlet oxygen in solution. The absence of **14** in the oxidation products within the zeolite is probably due to the constrained space within ZSM-5 channels, which is not big enough to accommodate the molecule of **14**.

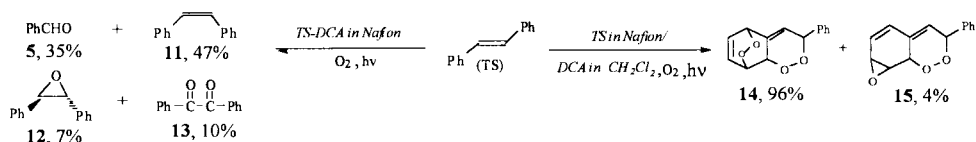
We extend the study to Nafion medium to establish the scope of this approach [8b]. The photo-sensitized oxidation was performed in two modes. The first one involves irradiation of DCA in dichloromethane solution ( $5 \times 10^{-5}$  M) in which the water-swollen Nafion sample incorporating the substrate is immersed (*substrate in Nafion/DCA in CH<sub>2</sub>Cl<sub>2</sub>*). Since dichloromethane cannot swell Nafion and is insoluble in water, the substrate and water within Nafion cannot be extracted into the solution, and CH<sub>2</sub>Cl<sub>2</sub> and DCA in the solution cannot diffuse into the Nafion. Thus, the substrate and sensitizer are isolated from each other during irradiation. The second mode involves irradiation of the

water-swollen Nafion sample, which has incorporated both the substrate and the sensitizer (*substrate-DCA in Nafion*).

As in the case of ZSM-5 zeolite sample, in *substrate in Nafion/DCA in CH<sub>2</sub>Cl<sub>2</sub>*, only the products derived from the energy-transfer pathway were detected. The sensitized photooxidation of DPB gave **10** as the unique product (Scheme 7), while that of TS yielded **14** and **15** (Scheme 8). 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, **5**, **6**, **7**, and **8**. No singlet oxygen product, **10**, was detected (Scheme 7). Material balance was near 100%. Similarly, the photosensitized oxidation of TS in *TS-DCA in Nafion* mode only produced the electron-transfer-mediated products **5**, **11**, **12**, and **13** (Scheme 8).



**Scheme 7**



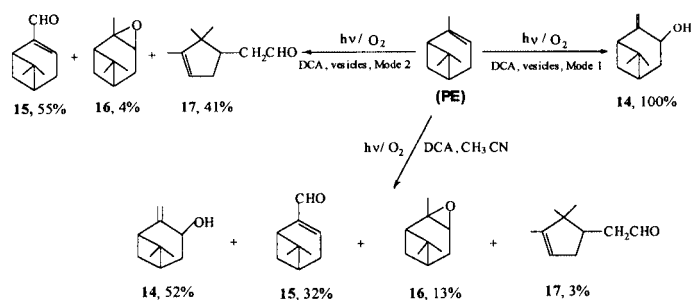
**Scheme 8**

The loading levels used in the present study were one DCA molecule per *ca.* 200 water clusters, and 4.2 alkene molecules per water cluster of Nafion. Thus, each DCA molecule is surrounded by a number of the alkene molecules. The high “local concentration” of the alkene and the close contact between DCA and the alkene molecules in the confined cluster of Nafion lead to efficient quenching of the singlet excited state of DCA by the alkene 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 alkene. Thus, the subsequent triplet energy transfer to O<sub>2</sub> cannot occur, and no singlet oxygen-mediated product was produced. On the other hand, the concentration of oxygen inside Nafion is more than ten times higher than in organic solvents [8b]. The DCA radical anion generated above would efficiently undergo electron transfer to oxygen to produce superoxide radical anion, which subsequently reacts with the alkene radical cation to yield electron transfer-mediated products.

The product selectivity in the photosensitized oxidation of alkenes included in zeolite or Nafion, as described above, originates from the isolation or close contact of the substrate and sensitizer molecules. Based on this idea, we also carried out the photooxidation of alkenes in mixed surfactant vesicles [8c,d]. The photosensitized oxidation was performed in two modes. In the first mode, 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. Thus, the photosensitized oxidation process in this mode involved the generation of <sup>1</sup>O<sub>2</sub> in one vesicle and reaction with alkene molecules in other vesicles. In the second mode, both the sensitizer and the substrate were incorporated in the bilayer of the same set of vesicles. Generally, the concentration of the olefins was  $\sim 1.0 \times 10^{-3}$  M, corresponding to thousands of substrate molecules in each vesicle, while the concentration of the sensitizer was generally  $\sim 1.0 \times 10^{-4}$  M. Thus, each sensitizer molecule is sur-



rounded by a number of alkene molecules in the confined bilayer of vesicles. We have examined the oxidation of  $\alpha$ -pinene (PE) sensitized by DCA in these vesicles. 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 **14** and the non-ene products myrtenal **15**, epoxide **16**, and aldehyde **17**, as shown in Scheme 9. The ene product and the non-ene products have been proposed to be derived from the energy-transfer and electron-transfer pathways respectively [8d]. The product distribution in acetonitrile is given in the scheme.



**Scheme 9**

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 the first mode followed by mixing the sample with a sodium sulfite aqueous solution to reduce the reaction mixture exclusively produced the ene product **14**. No trace of the non-ene products **15–17** was detected. In contrast, the photooxidation in the second mode exclusively gave the non-ene products **15–17** (Scheme 9). No product derived from the energy-transfer pathway was detected. These observations demonstrate 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.

## CONCLUSION

We have demonstrated that the photochemical reactions of organic compounds in microreactors usually show deviation of product distribution from their molecular photochemical reactions and, in some cases, result in the occurrence of reaction pathways that are not otherwise observed. These effects are attributed to (i) size and shape inclusion selectivities, (ii) restriction on rotational and translational motions of the included molecules and intermediates imposed by the microreactor, (iii) compartmentalization of the substrate molecules in the microreactors, and (iv) separation or close contact of the substrate with the sensitizer in photosensitization reaction.

## ACKNOWLEDGMENTS

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