

REMARKABLE PRODUCT SELECTIVITY IN PHOTOCYCLOADDITION OF DIARYL COMPOUNDS AND IN PHOTOSENSITIZED OXIDATION OF ALKENES WITHIN SUPRAMOLECULAR SYSTEMS

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Abstract – Supramolecular photochemistry is concerned with systems where non-covalent interactions become significant or dominate in determining the chemistry of guest/host systems. The photocycloaddition of diaryl compounds and the photosensitized oxidation of alkenes included in zeolites, low-density polyethylene films and Nafion membranes is the subject of this report.

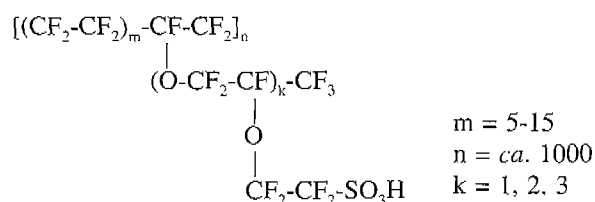
INTRODUCTION

Selectivity in organic phototransformation continues to be one of the main topics of current interest. Of the various approaches the use of supramolecular systems to control the reaction pathways has shown considerable promise.¹ Supramolecular system often possesses many of the features of guest-host complexes. The guest is often a small molecule of dimensions of several angstroms and the host is a larger molecule or a molecule aggregate of dimensions of tens of angstroms or larger. Among the many classes of hosts used in photochemical studies, molecular sieve zeolites and Nafion membranes are two outstanding members.

Molecular-sieve zeolites represent a novel and 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 molecular 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 cavities² (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 SO₃⁻ 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.

Another host we used for photochemistry study is low-density polyethylene (LDPE) films. LDPE is a very complex family of materials which consist of *ca.* 50% of crystalline regions and *ca.* 50% of amorphous or interfacial regions.⁴ A wide variety of organic molecules can be incorporated into

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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 and LDPE hosts control the pathways in photochemical reactions.

RESULTS AND DISCUSSION

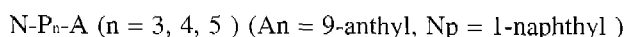
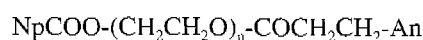
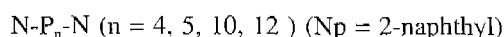
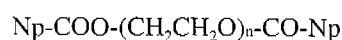
Zeolites and LDPE Films as Hosts for Preparation of Large-Ring Compounds: Intramolecular Photocycloaddition of Diaryl Compounds.

The construction of macrocyclic compounds continues to be an important topic of synthetic organic chemistry.⁵ 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, since the effective concentration for the reaction is kept constant by the function of a molecular chain linking the two functional groups. 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 1×10^{-5} M. This corresponds in a batch reaction to **1 × 10⁵ 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.

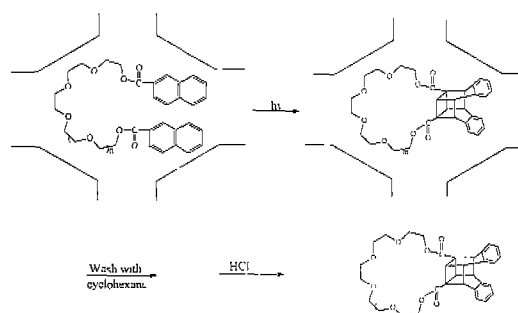
As mentioned above, each cavity of NaY zeolite can include 2 molecules of pyrene. Thus, one might expect that both aryl parts of a molecule with α, ω -diaryl groups separated by a flexible chain can be included in one supercage,

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 μ m diameter contains thousands of interconnected supercages, and the concentration of the supercages is *ca.* 500 μ 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 × 10⁴ 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 10³ 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. 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.



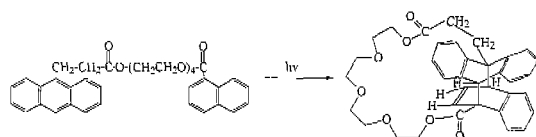
Irradiation of N-P_n-N in organic solutions, such as acetonitrile, can lead either to intra- or intermolecular photocycloadditions (Scheme 1). At concentrations higher than 10⁻³ M, the main product is the intermolecular photocyclomer. By contrast, irradiation of N-P_n-N adsorbed on NaY zeolite exclusively results in an intramolecular photocyclomer, as long as the loading level was kept at less than 50 μ 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 1). However,



Scheme 1.

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.** The yields of the intramolecular products were close to 100% based on the consumption of the starting material.

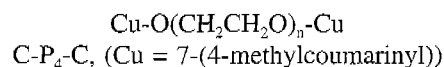
Although the photocycloaddition of anthracene and that of naphthalene have been extensively studied, until recently relatively little has been reported on the cross-photocycloaddition between an anthracene and a naphthalene moiety. The main reason for this is the large difference in the quantum yields between the photocycloaddition of anthracene and the cross-photocycloaddition of anthracene and naphthalene. Thus, bichromophoric molecules with anthryl as one chromophore and naphthyl as the other generally undergo intermolecular anthryl-anthryl cycloaddition rather than intramolecular cross-cycloaddition when irradiated. Irradiation of $1 \times 10^{-3} M$ N-P_n-A in acetonitrile gives the intermolecular photocyclomer of two anthracene groups. On the other hand, below $1 \times 10^{-3} M$, irradiation results in no photochemical reaction, because the lifetime of the singlet excited state of the anthryl (or naphthyl) is not long enough to allow it to encounter the other terminal chromophore of the N-P_n-A molecule (intramolecular reaction) or a chromophore of another molecule (intermolecular reaction). However, irradiation of N-P_n-A adsorbed on NaY zeolite with loading levels below $50 \mu\text{mol g}^{-1}$ yields the intramolecular $[4\pi+4\pi]$ photocyclomer exclusively (Scheme 2). The mass balance was > 90%, suggesting that any unidentified products must be minor.



Scheme 2.

We also studied the photocycloaddition of diaryl compounds included within LDPE films. 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, intermol-

ecular reactions should be inhibited, while intramolecular reactions still can occur. We found that this is indeed the case for the photocyclizations of N-P_n-N or tetra(ethylene glycol) terminated by 7-(4-methylcoumarinyl) groups (C-P₄-C).

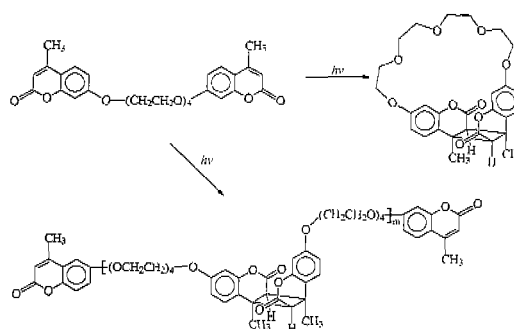


As in the case of NaY zeolite, irradiation of N-P_n-N in LDPE films yields the photocyclomers. Generally, after 5 h of irradiation, the conversion approached 100%. The products were extracted from the LDPE film with chloroform and analyzed by HPLC. Only the intramolecular ring-closure photocyclomers were evident; no intermolecular products were detected. The isolated yields of intramolecular products were > 90% based on consumption of the starting materials.

Due to the immiscibility of the polyether chains of the N-P_n-N with polyethylene, the maximal loading of N-P_n-N in LDPE film we could reach was *ca.* $1.2 \times 10^{-3} \text{ mol/g-film}$. Since the LDPE films employed are 42% crystalline, the actual volume in which the guest molecules reside is only *ca.* 60% of the total. As a result, the true concentrations in the amorphous regions are at least $1.7 \times 10^{-3} \text{ mol/g-film}$. In spite of this, the exclusive formation of intramolecular photocyclomers suggests that each occupied site contains one molecule of N-P_n-N.

The effect of stretching LDPE films doped with N-P_n-N on their photochemical reactivity was also examined. We cut a doped film into several pieces, half of which were stretched manually to 4.5 times their original length. We found that dimerization efficiency in the stretched films is *ca.* 1.4 times greater than in the unstretched ones. The interpretation advanced to explain these results is that film stretching decreases the average free volume of guest sites by aligning partially the polymethylene chains that constitute the cavity walls. Therefore, the two photoreactive groups of our substrates will reside, on average, closer to each other in stretched films than in unstretched ones; intramolecular photocycloaddition will be enhanced.

Similarly, C-P₄-C can undergo intra- and intermolecular photoreactions. Irradiation of $< 5 \times 10^{-4} M$ C-P₄-C in an organic solvent such as benzene results primarily in intramolecular *syn* head-to-tail cyclomer (Scheme 3), as demonstrated by mass spectral and NMR analyses. However, upon irra-



Scheme 3.

diation of more concentrated solutions, a large amount of oligomeric material was formed. For example, at concentration of $1 \times 10^{-5} M$, ca. 20% of oligomers were present in the product mixture.

As observed in the case of the N-P_n-N, irradiation of 1×10^{-2} mol/g-film C-P₄-C in LDPE resulted in conversion to intramolecular cyclomer. As in the case of irradiations in homogeneous solutions, only the *syn* head-to-tail cyclomer was detected. Since the material balance was > 90%, any unidentified products must be minor. Thus, at loading levels $< 1 \times 10^{-2}$ mol/g-film, each reaction cavity in LDPE must contain no more than one C-P₄-C molecule: intermolecular reaction is inhibited and intramolecular reaction is enhanced.

We also examined the effect of stretching the LDPE film on the photochemistry of C-P₄-C. Films doped with C-P₄-C was stretched manually to 4.5 times their original length and then irradiated. Again, at 1×10^{-2} mol/g-film C-P₄-C, only the intramolecular *syn* head-to-tail cyclomer was obtained. However, compared with the unstretched sample, the efficiency of the photocycloaddition is increased 1.2 times. This observation is consistent with the hypothesis that film stretching decreases the free volume of the reaction cavities and, thereby, enhances intramolecular reactions by forcing the reactive groups to reside nearer each other. Thus, LDPE complements zeolites, which we demonstrated above to serve a similar role in isolating molecules for intramolecular cyclizations. Each medium has its relative merits; now, it is possible to select the one which is more compatible with a particular reactant and cyclization reaction.

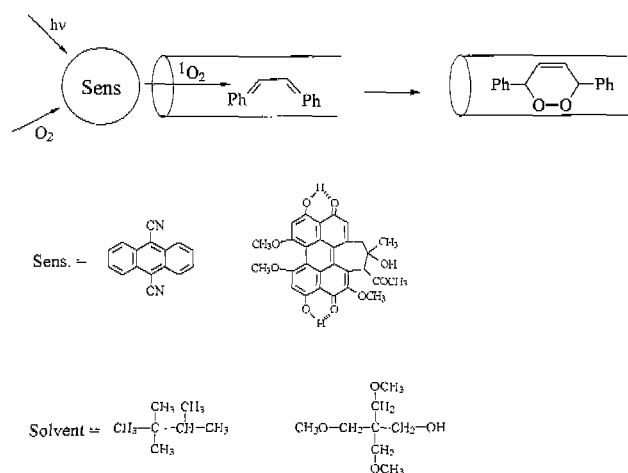
Photosensitized Oxidation of Alkenes Included in Pentasil Zeolite and Nafion Membrane

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.⁶

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. 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 electron transfer photosensitized oxidation electron-deficient sensitizers are generally used. Electron transfer from alkene to the sensitizer in its excited states results in alkene radical cation and sensitizer radical anion which subsequently reduces O₂ 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. *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

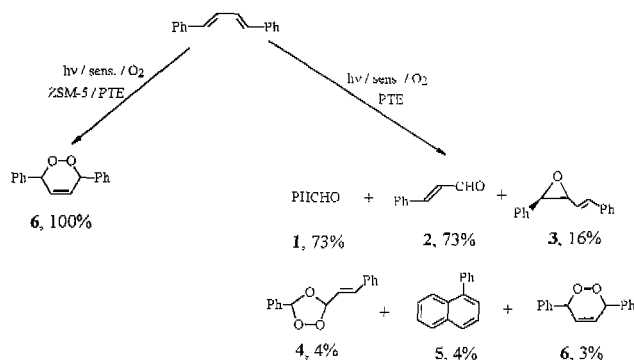
hypocrellin A (HA) were the sensitizers. The choice of the solvents and sensitizers was motivated by the desire that they were prevented from being sorbed into ZSM-5 channel due to their size and shape characteristics. Thus, the internal framework of ZSM-5 is "dry", and the substrate is protected from being extracted to the solution during photolysis. We trap the alkenes in the channels of ZSM-5 zeolites, and isolate the photosensitizers in the surrounding solution (Scheme 4).



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 photoxygenation.

Irradiation of oxygen saturated DPB solution in PTE containing DCA or HA with visible light gave benzaldehyde **1**, cinnamaldehyde **2**, epoxide **3**, ozonide **4** and endoperoxide **6** (Scheme 5). In addition, a small amount of 1-phenyl-



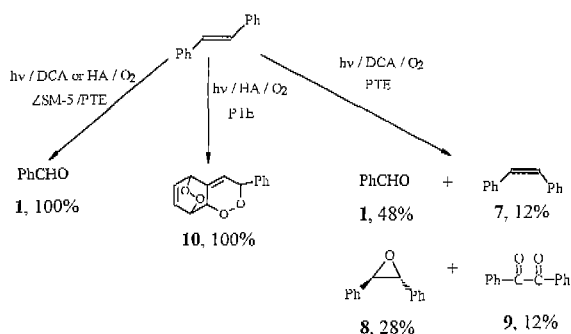
Scheme 5.

naphthalene **5** was detected. The product distribution is slightly dependent on the sensitizers and is shown on Scheme 5. In all cases, the main products are **1** and **2**. It has been established that DCA and HA can act both as singlet oxygen sensitizer and electron transfer sensitizer. Obviously, **6**

is a product of 1,4-cycloaddition of singlet oxygen (1O_2) 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 zeolites gave **6** as the unique product (Scheme 5). The yield of this product was 100% based on the consumption of the starting material. Evidently, the isolation of DPB within the zeolite channels from the sensitizer in the solution outside prevents them from undergoing electron transfer. Thus, no photooxidation products derived from electron transfer pathway were detected. On the other hand, 1O_2 can be formed in the solution by energy transfer from the triplet state sensitizer to the ground state oxygen. The species 1O_2 is small, uncharged and has relatively long lifetime and properties which allow it to diffuse freely from the surrounding solution to the internal framework of ZSM-5 zeolite. 1,4-Cycloaddition of 1O_2 to DPB in the internal surface of ZSM-5 results in endoperoxide **6**.

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 **1**, *cis*-stilbene **7**, *trans*-2,3-diphenyloxirane **8** and benzil **9** (Scheme 6). All these prod-



Scheme 6.

ucts were produced *via* the electron transfer pathway. However, at room temperature in CCl_4 using tetraphenylporphyrin as the sensitizer, the photooxidation of TS gave diendoperoxide **10** in a yield of 16% based on the reacted starting material. The other major product, benzaldehyde was produced in 80% yield. This reaction is proposed to proceed *via* energy transfer pathway. We found that in PTE using DCA as the sensitizer, the photooxidation products are the same as those obtained in the DCA-sensitized reaction in acetonitrile (Scheme 6), but the product distribution is slightly changed. On the other hand, in the same solvent using HA as the sensitizer, the main product is **10** (Scheme 6).

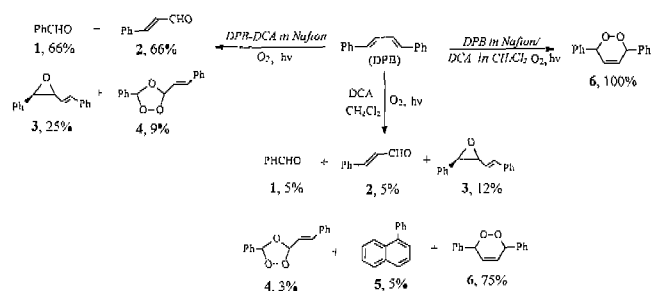
However, when TS is included within ZSM-5 zeolite and the sensitizer is solubilized in the surrounding solvent PTE, the photooxidation of TS sensitized by DCA or HA yields benzaldehyde as the unique product (Scheme 6). The mass

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* 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 **10** was not produced. This observation is contrary to the result of the reaction for TS with singlet oxygen in solution. The absence of **10** 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 **10**.

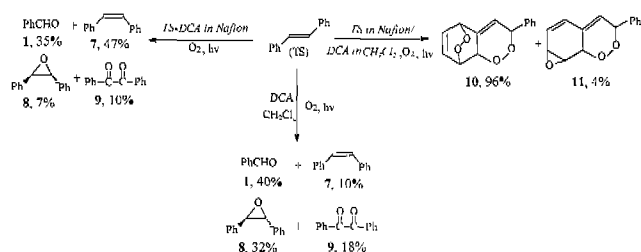
We extend the study to Nafion medium to establish the scope of this approach. The photosensitized oxidation was performed in two modes. The first one involves irradiation of DCA in dichloromethane solution ($5 \times 10^{-5} M$) in which the water-swollen Nafion sample incorporating the substrate is immersed (*substrate in Nafion/DCA in CH_2Cl_2*). Since dichloromethane can not swell Nafion and is insoluble in water, the substrate and water within Nafion can not be extracted into the solution, and CH_2Cl_2 and DCA in the solution can not 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_2Cl_2* , only the products derived from the energy transfer pathway were detected. The sensitized photooxidation of DPB gave **6** as the unique product (Scheme 7), while that of TS yielded **10** and **11** (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, **1**, **2**, **3**, and **4**. No singlet oxygen product, **6**, 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 **1**, **7**, **8** and **9** (Scheme 8).

The loading levels used in the present study were one DCA molecule per *ca.* 200 water clusters, and 4.2 alkene mole-



Scheme 7.



Scheme 8.

cules 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 can not compete with the quenching process by alkene. Thus, the subsequent triplet energy transfer to O_2 can not 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.⁷ 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.

CONCLUSION

We have shown that the photochemical reactions of the guest in a supramolecular system usually show deviation of product distribution from its molecular photochemical reactions and in some case result in the occurrence of reaction pathways that are not otherwise observed. In our case, these effects are attributed to (i) isolation of the substrate molecules with each other by the host, (ii) separation of the substrate with the sensitizer in photosensitization reaction.

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