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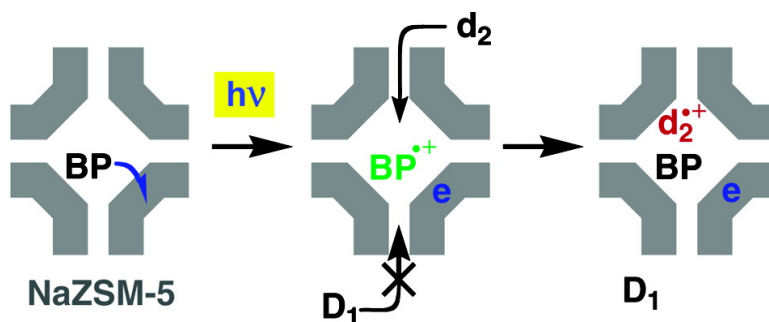# Selective Solid State Photooxidant

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Selective Solid State Photooxidant

Tracy L. Morkin,† Nicholas J. Turro,*,† Mark H. Kleinman,† Cheyenne S. Brindle,†
Wolfgang H. Kramer,‡ and Ian R. Gould*,‡

*Contribution from the Department of Chemistry, Columbia University, 3000 Broadway,
New York, New York 10027 and Department of Chemistry and Biochemistry,
Arizona State University, Tempe, Arizona 85287-1604*

Received June 23, 2003; E-mail: njt3@columbia.edu

Abstract: Irradiation of biphenyl encapsulated in the cavities of a NaZSM-5 zeolite framework has been reported to result in the formation of an extremely long-lived radical cation. Here, we show that such zeolite encapsulated radical cations can act as irreversible one-electron oxidants for simple alkenes and dienes, in a solid-state analogue to solution-phase cosensitization. Compared to the well-known semiconductor photooxidizers, such as titanium dioxide, the NaZSM-5 zeolite-based solid photooxidants exhibit enhanced selectivity based on oxidation potential, molecular size and shape, and Lewis base character.

Introduction

Photoinduced one-electron-transfer reactions represent the primary step in a wide variety of important natural and technological processes. Historically, photosynthesis, artificial solar energy conversion, and various imaging processes have been among the more obvious examples of these processes.[1] More recently, one-electron oxidation processes involving semiconductor substrates have found application in the remediation of organic waste materials.[2] Excitation of the semiconductor, commonly TiO_2, results in the formation of a valence hole and conduction band electron that can initiate redox reactions leading to destruction of organic materials. In many cases, complete oxidation to carbon dioxide can be achieved.[2] Oxidation of the organic material can be initiated either by the generation of oxidizing species such as hydroxyl radicals, or by direct one-electron oxidation of the absorbed organic compound D to form its radical cation.[2] The radical cation reaction products can be further oxidized by this, or other mechanisms. In common with all photoinduced electron-transfer processes,[1,3] the utility of these semiconductor-based oxidation processes are controlled to a large extent by the efficiency of trapping of the initially formed excited state (in this case, a valence band hole), and energy wasting return electron transfer (in this case, from the conduction band to the valence band) to reform the starting species.[2b]
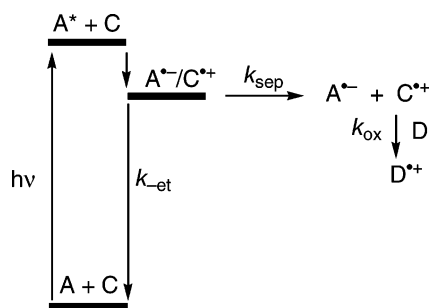
In homogeneous solution, these problems have been circumvented to some extent by the use of cosensitizers.[3,4] The concept is illustrated in Scheme 1. Excitation of an electron acceptor (A) results in electron transfer from the cosensitizer (C) to form a geminate pair consisting of the acceptor radical anion and the cosensitizer radical cation ($A^{•-}/C^{•+}$). The cosensitizer is chosen so that separation in the geminate pair is much faster than return electron transfer (i.e., k_{sep} is much larger than k_{-et}, Scheme 1). In this way, the efficiency of formation of separated radical ions ($A^{•-} + C^{•+}$) is very high.[3] The separated $C^{•+}$ can then oxidize the donor to form $D^{•+}$ in a second step, k_{ox}. The overall efficiency for formation of $D^{•+}$ is high because formation of separated $C^{•+}$ occurs with high efficiency, and the follow-up oxidation process of D is irreversible. Furthermore, the concentration of the D can be low because it does not have to react with a short-lived excited state, A*, but with the relatively long-lived $C^{•+}$.[3,5] An ideal cosensitizer C has a high oxidation potential, both to ensure a small k_{-et} as a consequence of the Marcus inverted region effect, and also so that the $C^{•+}$ can oxidize as wide a range of D molecules as possible,[3] and importantly, a long lifetime. The most widely used cosensitizer in solution has been biphenyl.[3,4] With 9,10-dicyanoanthracene as the electron acceptor, biphenyl has one of the highest yields of separated radical ions in polar solution yet measured.[3] Biphenyl also has a relatively high oxidation potential, ca. 2 V vs SCE.[3] Because the biphenyl radical cation is also relatively long-lived in solution, even endothermic oxidations of donor molecules in solution have been observed.[5] An obvious question is whether the solution phase cosensitization concept can be extended to a solid-state photooxidation system. Consequently, our attention was drawn to reports of long-lived photogenerated biphenyl radical cations in zeolites.[6] We wondered whether these

† Department of Chemistry, Columbia University.
‡ Department of Chemistry and Biochemistry, Arizona State University.

(1) See, for example: (a) *Electron Transfer in Chemistry, Vols. 1−5*; Balzani, V., Ed.; Wiley-VCH: New York, 2001. (b) *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; Jai Press: Greenwich, CT, 1991−1994, Vols. 1−4. (c) *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988. (d) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(2) (a) *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F.; Al-Ekabi, H., Eds.: Elsevier: New York, 1993. (b) Thurnauer, M. C.; Rajh, T.; Dimitrijevic, N. M. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: New York, 2001; Vol. 5, p 695.

(3) (a) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290. (b) Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522.

(4) Schaap, A. P.; Siddiqui, S.; Prasqad, G.; Palomino, E.; Lopez, L. *J. Photochem.* **1984**, *25*, 167. (b) Arnold, D. R.; Snow, M. S.; *Can. J. Chem.* **1988**, *66*, 3012. (c) Majima, T.; Pac. C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499.

(5) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233.

Scheme 1. Mechanism of Solution-Phase Cosensitization

Figure 1. Apparatus for EPR study of radical cations in zeolites. S, stopcock; V, vacuum joint. The biphenyl and zeolite are heated, then irradiated in bulb B and transferred to EPR tube E for analysis. The donor is subsequently introduced from bulb D and any reaction products are analyzed again in E.

species could be used to oxidize electron donor compounds in an analogous manner to solution phase cosensitization.[7]

Previous work on related systems suggested that this should be possible. Photoinduced reactions in zeolites, including bimolecular processes, are well-known,[8] and many studies of bimolecular electron transfer reactions involving excited state donors and acceptors have been reported.[9] Studies of radiation induced and thermal processes have demonstrated intermolecular hole transfer and electron transfer within zeolite cages,[10] including an example demonstrating size selectivity,[10c] and another involving electron transfer to biphenyl radical cation from a coadsorbed amine.[10f] In this and other work on organic radical ions in zeolites,[11] however, no systematic study of secondary oxidation processes corresponding to solid-state cosensitization has been reported.

The present work sets out to address a variety of issues. Although our primary interest is in extending the cosensitization concept from solution to the solid state, the ultimate goal is to explore the utility of zeolite-encapsulated organic radical cations as solid-state photoactivatable oxidizing substrates. Although
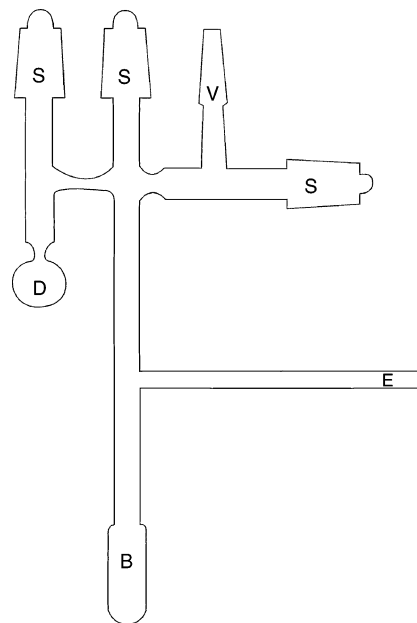
complete oxidation of organics may be desirable in some applications, control over the oxidizing power of a solid-state photooxidant may allow the development of selective partial oxidizing agents.[12] The use of different organic radical cations would allow much finer control over oxidizing power than that available via manipulation of a semiconductor band levels.[2b] Furthermore, by taking advantage of the known size and shape selectivity of zeolites,[8,13] we hoped to gain further control and selectivity on the oxidation process beyond that possible in solution or on the surface of a semiconductor particle.[2]

In this paper, we demonstrate all of these. Biphenyl radical cation has been photochemically generated in sodium cation exchanged ZSM-5 zeolites, and selective irreversible oxidation of a series of simple alkenes and dienes as electron donors demonstrated. Fine control of the oxidation based on size, shape and the Lewis basicity of the alkene is demonstrated. The oxidation process is much more selective than the corresponding process in homogeneous solution.
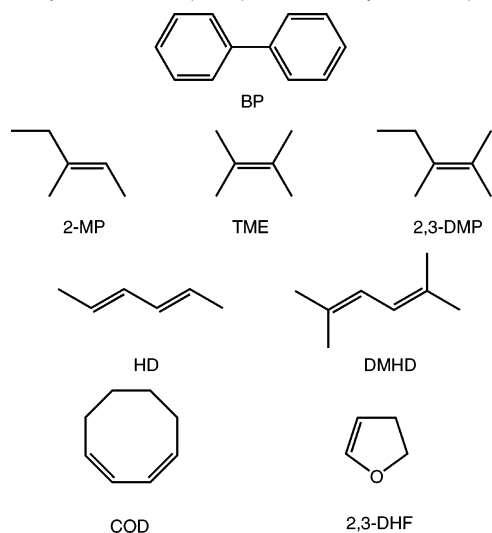
Experimental Approach and Selection of Electron Donors

To confirm oxidation of the donors in NaZSM-5, we need to first observe formation of the BP[•+] in the zeolite, demonstrate reaction of the donor molecules with the BP[•+], and confirm that the product of this reaction is the radical cation of the donor, D[•+]. EPR spectroscopy was chosen as the preferred method for detection of the radical cations in the solid state. An EPR cell was designed (Figure 1) to allow the study of photochemical

(6) (a) Gener, I.; Buntinx, G.; Moissette, A.; Bremard, C. *J. Phys. Chem. B* **2002**, *106*, 10 322. (b) Gener, I.; Moissette, A.; Vezin, H.; Patarin, J.; Bremard, C. *Stud. Surf. Sci. Catal.* **2001**, *38*, 1819. (c) Bremard, C.; Buntinx, G.; De Waele, V.; Didierjean, C.; Gener, I.; Poizat, O. *J. Mol. Struct.* **1999**, *480−481*, 69. (d) Gener, I.; Buntinx, G.; Bremard, C. *Angew. Int. Ed. Engl.* **1999**, *38*, 1819−1822. (e) Gener, I.; Buntinx, G.; Bremard, C. *Micropor. Mesopor. Mat.* **2000**, *41*, 253−268. (f) Erickson, R.; Lund, A.; Lindgren, M. *Chem. Phys.* **1995**, *193*, 89. (g) Mao, Y.; Zhang, G.; Thomas, J. K. *Langmuir* **1993**, *9*, 1299−1305.
(7) For other approaches to photooxidative processes in zeolites, see: Vasenkov, S.; Frei, H. *Mol. Supramol. Photochem.* **2000**, *5*, 295.
(8) See, for example: (a) Ramamurthy, V.; Robbins, R. J.; Thomas, J. K.; Lakshminarasimhan, P. H. In *Organized Molecular Assemblies in the Solid State*; Wiley: New York, 1999, p. 62. (b) Scaiano, J. C.; Garcia, H. *Acc. Chem. Res.* **1999**, *32*, 783. (c) Turro, N. J. *Acc. Chem. Res.* **2000**, *33*, 637. (d) Ramamurthy, V. *J. Photochem. Photobiol., C* **2000**, *1*, 145. (e) Thomas, J. K. *International Journal of Photoenergy* **2002**, *4*, 27. (f) Tung, C.-H.; Wu, L.-Z.; Zhang, L.-P.; Chen, B. *Acc. Chem. Res.* **2003**, *36*, 39. (g) Hashimoto, S. *J. Photochem. Photobiol. C* **2003**, *4*, 19.
(9) See, for example: (a) Yoon, K. B. *Chem. Rev.* **1993**, *93*, 321. (b) Thomas, J. K. *Chem. Rev.* **1993**, *93*, 301. (c) Liu, X.; Mao, Y.; Ruetten, S. A.; Thomas, J. K. *Solar Energy Materials and Solar Cells* **1995**, *38*, 199. (c) Dutta, P. K.; Ledney, M. *Prog Inorg. Chem.* **1997**, *44*, 209. (d) Zhang, G.; Liu, X.; Thomas, J. K. *Radiat. Phys. Chem.* **1998**, *51*, 135. (e) Yoon, K. B. *Mol. Supramol. Photochem.* **2000**, *5*, 143. (f) Garcia, H.; Roth, H. D. *Chem. Rev.* **2002**, *102*, 3947. (g) Vaidyalingam, A. S.; Coutant, M. A.; Dutta, P. K. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: New York, 2001; Vol. 4, p 412. (h) O'Neill, M. A.; Cozens, F. L.; Schepp, N. P. *J. Phys. Chem. B* **2001**, *105*, 12 746.
(10) (a) Crockett, R.; Roduner, E. *Stud. Surf. Sci. Catal.* **1994**, *84*, 527. (b) Barnabas, M. V.; Trifunac, A. D. *Chem. Phys. Lett.* **1992**, *193*, 298. (c) Yoon, K. B.; Park, Y. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 12 710. (d) Werst, D. W.; Han, P.; Trifunac, A. D. *Chem. Phys. Lett.* **1997**, *269*, 333. (e) Vitale, M.; Castagnola, N. B.; Ortins, N. J.; Brooke, J. A.; Vaidyalingam, A.; Dutta, P. K. *J. Phys. Chem. B* **1999**, *103*, 2408. (f) Zhang, G.; Thomas, J. K. *J. Phys. Chem. B* **2003**, ASAP.
(11) (a) Werst, D. W.; Han, P.; Trifunac, A. D. *Radiat. Phys. Chem.* **1998**, *51*, 255. (b) Park, Y. S.; Lee, K.; Lee, C.; Yoon, K. B. *Langmuir*, **2000**, *16*, 4470. (c) Folgado, J.-V.; Garcia, H.; Marti, V.; Espla, M. *Tetrahedron*, **1997**, *53*, 4947. (d) Erikson, R.; Benetis, N. P.; Lund, A.; Lindgren, M. *J. Phys. Chem. A* **1997**, *101*, 2390. (e) Hashimoto, S. *J. Photochem. Photobiol. C* **2003**, *4*, 19−49.
(12) (a) Zaera, F. *J. Phys. Chem. B* **2002**, *106*, 4043. (b) Rafelt, J. S.; Clark, J. H. *Catalysis Today* **2000**, *57*, 33. (c) Heller, A. *Acc. Chem. Res.* **1995**, *28*, 503. (d) Pichat, P. *Catal. Today* **1994**, *19*, 313. (e) Zhan, B.-Z.; White, M. A.; Sham, T.-K.; Pincock, J. A.; Doucet, R. J.; Ramana, K. V.; Robertson, K. N.; Cameron, T. S. *J. Am. Chem. Soc.* **2003**, *125*, 2195.
(13) (a) Dwyer, F. G. *Stud. Surf. Sci. Catal.* **1991**, *67*, 179. (b) Corbin, D. R.; Herron, N. *J. Mol. Catalysis* **1994**, *86*, 343. (c) De Vos, D. E.; Jacobs, P. A. *Catal. Sci. Series* **2002**, *3*, 261.

Scheme 2. Structures and Abbreviations for Cosensitizer Biphenyl (BP) and Electron Donors: 2-Methylpentane (2-MP), Tetramethylethylene (TME), 2,3-Dimethyl-2-pentene (2,3-DMP), 2,4-Hexadiene (HD), 2,4-Dimethyl-2,4-hexadiene (DMHD), *cis,cis*-1,3-Cyclooctadiene (COD) and 2,3-Dihydrofuran (2,3-DHF)

Table 1. Oxidation Potentials, Reaction Free Energies, Rate Constants, and Reactivity in Zeolites for Oxidation of Electron Donors with Biphenyl Radical Cation in Solution and in Na-ZSM-5 Zeolites

donor[a]	dimensions[b] (Å)	E_{ox}^D (V vs SCE)	ΔG_{et}^c (eV)	k_{ox} (M^{-1} s^{-1})	quenching in Na-ZSM-5[d]
2-MP	4.4 × 6.4	1.98[16a]	0.02	4.0 × 10^8	no
COD	6.1 × 6.4	1.90[16b]	−0.06	5.5 × 10^9	no
HD	4.4 × 8.4	1.82[16a]	−0.14	9.5 × 10^9	yes
TME	5.4 × 5.8	1.56[16a]	−0.40	7.5 × 10^9	yes
2,3-DMP	5.9 × 5.9	1.35[e]	−0.61	5.8 × 10^9	no
2,3-DHF	3.8 × 4.0	1.26[f]	−0.70	1.0 × 10^{10}	no
DMHD	5.1 × 8.7	1.33[16a]	−0.63	1.5 × 10^{10}	yes

[a] See Scheme 2 for structures. [b] Cylindrical dimensions of the molecule, estimated as described in the text and the Experimental Section. The smaller dimension represents the diameter of the cylinder, the second, its length. The corresponding dimensions for biphenyl are 5.4 × 10.4 Å. [c] Calculated using eq 1, with a value of 1.96 V vs SCE[3a] for E_{ox}^C. [d] Indicates whether quenching of the biphenyl radical cation EPR signal is observed upon addition to BP•+@Na-ZSM-5. [e] Estimated from IP[16c] according to correlation in ref 16e. [f] Estimated from IP[16d] according to correlation in ref 16e.

formation of the BP•+ first, and then the effects of subsequent addition of a potential electron donor.

In a typical experiment, biphenyl is loaded into the zeolite under vacuum (see the Experimental Section for details) and BP@NaZSM-5 is irradiated. The irradiated zeolite mixture is transferred into the EPR tube part of the apparatus and the spectrum is recorded. The apparatus is removed from the EPR spectrometer, and the donor is allowed to mix with the BP@NaZSM-5. The tube is then returned to the EPR spectrometer to look for any possible reactions.

For secondary oxidation in NaZSM-5 zeolites, electron donors that would be sufficiently volatile to be loaded into the zeolites using the experimental apparatus were required. To investigate the possible factors controlling oxidation, ready manipulation of the donor structure was required. A series of small unsaturated electron donors with a maximum of eight carbons, that include a range of oxidation potentials, shapes, and atomic composition were chosen, i.e., 2-methyl-2-pentene (2-MP), tetramethylethylene (TME), 2,3-dimethyl-2-pentene (2,3-DMP), 2,4-hexadiene (HD), 2,5-dimethyl-2,4-hexadiene (DMHD), *cis,cis*-1,3-cyclooctadiene (COD), and 2,3-dihydrofuran (DHF). Their structures are summarized in Scheme 2. We have also measured the solution-phase rate constants for one-electron oxidation of these donors with biphenyl radical cation using laser flash photolysis, to compare the results with those we obtained in the zeolite environment.

Results

Solution Phase Oxidation. Pulsed laser excitation of 9,10-dicyanoanthracene in acetonitrile in the presence of biphenyl resulted in the observation of absorptions due to separated DCA•− and BP•+, as described previously.[3] In the presence of oxygen, the DCA•− undergoes rapid pseudo-first-order decay due to electron transfer to oxygen. The decay of the BP•+ is unaffected by added oxygen, and decays by mainly pseudo-first-order processes under the experimental conditions with a lifetime of ca. 1.5 μs. Such behavior is quite common for radical cations of compounds with relatively high oxidation potential,

such as biphenyl. The decay is presumably due to oxidation of low-oxidation potential impurities, or perhaps attack by adventitious nucleophiles such as water.[5]

The oxidation process in solution can be characterized by the quantum efficiency of formation of the separated C•+ (Scheme 1), and the bimolecular rate constant for the secondary oxidation step, k_{ox}. Under the experimental conditions, the quantum yield for formation of separated C•+ has a value of ca. 0.7 and obviously does not vary with the alkene donor, D.[3a] Summarized in Table 1 are the bimolecular rate constants measured in acetonitrile solvent for the various donors, k_{ox}, together with their oxidation potentials, E_{ox}^D. Bimolecular electron transfer between the C•+ and the D should be close to diffusion controlled for reactions that are more exothermic than the reaction reorganization energy.[14] The thermodynamics of the oxidation reactions, ΔG_{et}, are given by the difference between the oxidation potential of the electron donor (E_{ox}^D) and that of the biphenyl cosensitizer (E_{ox}^C), eq 1. Reactions that are more exothermic than ca. 0.5 eV (i.e., $-\Delta G_{et} > 0.5$ eV) are usually close to diffusion controlled, although exothermicities close to 1 eV may be required to actually reach this limit.[14,15] However, thermodynamically meaningful oxidation

$$\Delta G_{et} = E_{ox}^D - E_{ox}^C \qquad (1)$$

potentials are difficult to obtain (the errors in the potentials given in Table 1 are not known), because electrochemical oxidation is usually not reversible for simple alkenes such as those in Scheme 2 due to fast follow-up reactions on the electrochemical time scale. Furthermore, the solvent reorganization is not well-defined for diffusive bimolecular reactions in solution, and indeed may vary within a series of reactions depending upon the exothermicity.[15] Nevertheless, the expected behavior is roughly observed for the present data. The oxidation reaction of the trisubstituted alkene 2-MP is slightly endothermic, its $-\Delta G_{et}$ is significantly smaller than the solution reorganization energy, and its rate constant significantly smaller than diffusion

(14) (a) Marcus, R, A. *J. Chem. Phys.* **1957**, *26*, 872. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (c) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(15) Gould, I. R.; Young, R. H.; Mueller, L. J.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8176.
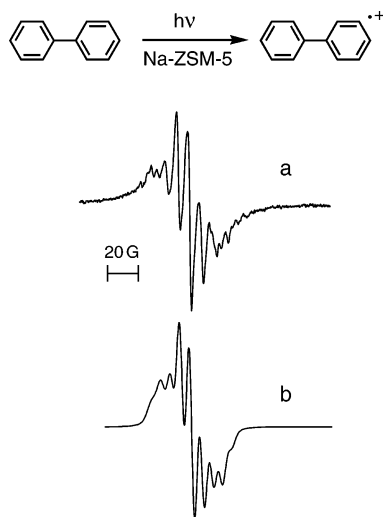
Figure 2. EPR spectra showing formation of biphenyl radical cation upon UV irradiation in Na-ZSM-5 zeolite. (a) Experimentally measured spectrum; (b) simulated spectrum.

Figure 3. EPR spectrum observed upon addition of 2,4-dimethyl-2,4-hexadiene to biphenyl radical cation in Na-ZSM-5 zeolite.

controlled. The other reactions are all exothermic and their rate constants exhibit a small increase with increasing reaction exothermicity, with the most exothermic reactions approaching the diffusion controlled limit.

Solid-State Oxidation. When biphenyl (BP) is sublimed into activated NaZSM-5 under vacuum, the zeolite crystals remain colorless. Irradiation of the BP occluded NaZSM-5 using a Rayonet Reactor (254 nm) at 298 K caused the zeolite to turn bright green. This color change has been described previously, and a diffuse-reflectance UV−vis spectrum of the irradiated zeolite matches that previously observed, and attributed to the radical cation of biphenyl.[6d] EPR analysis of the sample gave rise to the spectrum given in Figure 2a. The coupling constants and line widths are consistent with literature values for BP[•+] reported previously.[6d,e] A simulation of the EPR spectrum of BP[•+] is given in Figure 2b. The close match between the observed and calculated spectra, and the similarity to previous observations confirm generation of the BP[•+] in the NaZSM-5 zeolite channels.

In contrast to the behavior in acetonitrile solvent (above), and as observed previously, the EPR signal due to the BP[•+] is quite long-lived, and is stable on a time scale of many hours, even days, in the absence of any added potential reactants. This is a remarkable considering the high oxidizing power and potential reactivity of this species. As discussed above, its lifetime in acetonitrile solvent is shorter by more than *10 orders of magnitude*! Presumably, the zeolite cage protects the BP[•+]@NaZSM-5 from unwanted reaction with adventitious nucleophiles and reductants. If this is true, then the zeolite cage also has the potential to prevent the desired redox reactions of the BP[•+] with the donors of Scheme 2. However, subsequent addition of the electron donors demonstrated this not to be the case (Table 1), although the reactions *were* found to be highly selective.

Addition of the two linear dienes, 2,4-hexadiene (HD) and 2,5-dimethyl-2,4-hexadiene (DMHD) to the BP[•+]@NaZSM-5 resulted in rapid fading of the characteristic green color of the BP[•+]@NaZSM-5 within a few seconds. Presumably, irreversible electron transfer occurred from the dienes to the BP[•+] within the zeolite channels. Measurement of the EPR spectrum
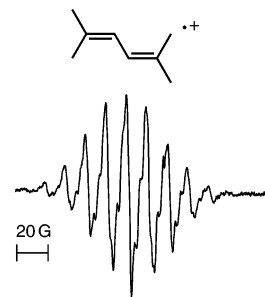
confirmed complete quenching of the BP[•+] in each case. With DMHD, the BP[•+] signal was replaced by a new EPR spectrum similar to that previously attributed to the DMHD[•+] on H-mordenite, Figure 3.[17] This spectrum is stable for at least 24 h. However, control experiments showed that the same spectrum is also observed upon loading the DMHD into NaZSM-5 in the absence of BP[•+] and without irradiation. With HD, no new paramagnetic signals are observed after addition of the diene. The HD obviously reacts with the BP[•+], but in this case, any HD[•+] that is formed must have a lifetime of less than 60 s, otherwise we would have expected to observe it under the experimental conditions. It is possible that significant broadening of the signal could occur in the presence of the added donor such that the radical cation might not be detected. However, the disappearance of the characteristic green color is further evidence to support the finding that the radical cation has indeed been quenched.

Corresponding addition of the alkene 2-MP to the BP[•+]@ NaZSM-5 did not quench the color, or reduce the intensity of the BP[•+] EPR spectrum, indicating that this electron donor does not react with the BP[•+]. Interestingly, no significant decrease in the BP[•+] EPR intensity is observed even 24 h after addition of this donor, i.e., any reaction is at least 3 orders of magnitude slower than the corresponding reactions for HD and DMHD. Oxidation of 2-MP by BP[•+] is essentially thermoneutral and slow in solution (Table 1), and so the lack of reactivity is perhaps not surprising in this case.

Addition of the alkene 2,3-DMP, diene COD, and enol ether 2,3-DHF also resulted in no detectable quenching of the BP[•+] EPR signal. These observations are considerably more surprising, because in each case reaction with BP[•+] in solution is exothermic, and their k_{ox} are all within an order of magnitude of the diffusion controlled limit. In these cases, factors other than reaction exothermicity must be important in determining reactivity.

When tetramethylethylene is added to the BP[•+]@NaZSM-5, quenching of both the color and the BP[•+] EPR signal is observed. In this case, appearance of a new EPR spectrum is observed, that is consistent with that reported previously for TME[•+].[18] Within 10 minutes of the addition of TME to BP[•+], the absorptions attributed to BP[•+] have disappeared and the

(16) (a) Schepp, N. P.; Johnston, L. J. *J. Am. Chem. Soc.* **1996**, *118*, 2872−2881. (b) Lew, C. S. Q.; Brisson, J. R.; Johnston, L. J. *J. Org. Chem.* **1997**, *62*, 4047. (c) Masclet, P.; Grosjean, D.; Mouvier, G.; *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 225. (d) Bernhard, K.; Geimer, J.; Canle-Lopez, M.; Reynisson, J.; Beckert, D.; Gleiter, R.; Steenken, S. *Chem. Eur. J.* **2001**, *7*, 4640−4650. (e) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.
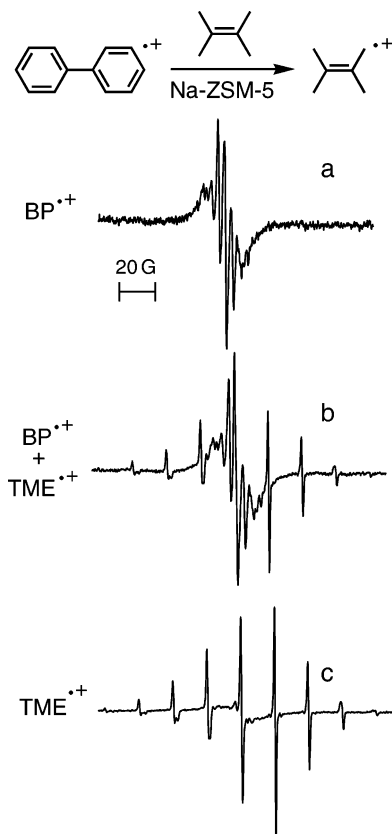(17) Roduner, E.; Wu, L. M.; Crockett, R.; Rhodes, C. J. *Catal. Lett.* **1992**, *14*, 373.

Figure 4. EPR spectra showing reduction of biphenyl radical cation (BP•+) by tetramethylethylene (TME) in Na-ZSM-5 zeolite, and formation of the TME•+. (a) Spectrum of BP•+ formed by irradiation of BP in Na-ZSM-5, (b) spectrum observed 2 min after addition of TME; (c) spectrum observed 6 min after addition of TME.

spectrum of the TME•+ persists for several hours. Control experiments show that TME does not spontaneously ionize on NaZSM-5 at room temperature under our conditions, indicating that reaction with BP•+ in the zeolite is necessary for the oxidation of TME to occur. The spectra recorded during the reaction are shown in Figure 4.

Discussion

The reactivity of supramolecular systems can be discussed in terms of four main criteria.[19] Topology describes the shape of the three-dimensional space in which the components of the supramolecular assembly are found. For example, the MFI family of zeolites to which NaZSM-5 belongs defines a reaction space of parallel channels intersecting with sinusoidal channels.[13] Geometry describes the actual dimensions of that topology in terms of size and angles. Structure encompasses the chemical features of the species involved, including thermodynamics and binding affinity of the guest molecules to various sites within the zeolite environment. Finally, chemical dynamics that describe the motion of the molecules within the restricted reaction space must also be considered. With these four criteria in mind, we can address the overall reactivity of "guest@host" assemblies, or in our case, BP•+@ZSM-5.

A general mechanism for the intrazeolite oxidation is given in Scheme 3. Irradiation of the biphenyl leads to ejection of an

(18) (a) Corio, P. L.; Shih, S. *J. Phys. Chem.* **1971**, *75*, 3475. (b) Chemerisov, S. D.; Werst, D. W.; Trifunac, A. D. *Chem. Phys. Lett.* **1998**, *291*, 262. (c) Roduner, E.; Crockett, R.; Wu, L. M. *J. Chem. Soc. Far. Trans.* **1993**, *89*, 2101.

Scheme 3. General Mechanism for Photooxidation of Donors by Biphenyl Included and Irradiated NaZSM-5 Zeolites

electron. It has been proposed that the electron can be trapped in the form of a Na_4^{3+} species.[20] The second step involves subsequent transfer of a single electron from the electron donor, D to the BP•+ (via more than one possible mechanism, see further below). Whether this process actually occurs depends on a number of factors.

Apart from the higher oxidation potential donor 2-MP, the efficiencies of the reactions between BP•+ and the donors in acetonitrile solution vary over a fairly limited range (Table 1).

On the other hand, the efficiencies of the reactions between BP•+ and the donors in NaZSM-5, as given by the observation of quenching of the BP•+ EPR signal, vary dramatically (Table 1), and clearly depend on other factors in addition to oxidation potential. A quantitative comparison of the solution phase second-order rate constants k_{ox} with the EPR quenching observations in the solid state is clearly not possible, but it is obvious that the variation in reaction efficiency is much larger in the zeolite than in solution, to the extent that either reaction occurs rapidly (seconds to minutes), or not at all over a time period of days.

The alkene TME and the two dienes HD and DMHD all quench the BP•+ signal, but the alkene 2-MP does not. As discussed above, the lack of reaction with the latter can be explained as a consequence of the fact that electron transfer is slightly endothermic in this case, and is exothermic for the others, and thus the lack of reaction is not surprising.

It is interesting that the difference in reactivity between the exothermic and endothermic reactions may be greater in the zeolite, compared to solution. Although the present data do not allow these to be distinguished, possible reasons for this include differences in diffusion rates and/or reorganization energies in the two media. Nevertheless, we conclude that when the thermodynamics of electron transfer are favorable, electron transfer *may* occur efficiently. The interesting cases are those reactions that *do not occur*, even when thermodynamically favorable. These reactions are presumably controlled by one or more of the other criteria mentioned above, including the topology, geometry and atomic composition of the zeolite.

The known size and shape selectivity of zeolites prompted us to estimate the molecular dimensions of the donors. These were defined in terms of the minimum cylindrical dimensions, i.e., the dimensions of the smallest cylinder that will accommodate the most reasonable conformation of the molecule. The molecules were first subject to a molecular dynamics annealing process to obtain a rough lowest energy conformation, which was followed by a molecular mechanics energy minimization.[21] The "length" of the cylinder was then assigned to the length of the longest axis of the resulting structure, determined by visual inspection, that was consistent with providing the appropriate minimum orthogonal width. It is assumed that the molecule will orient with the long axis aligned with the zeolite channel, which

(19) Turro, N. J.; Barton, J. K.; Tomalia, D. A. *Acc. Chem. Res.* **1991**, *24*, 332.
(20) Liu, X.; Zhang, G.; Thomas, J. K. *J. Phys. Chem.* **1995**, *99*, 10 024.
(21) Calculations were performed using Chem3D-Pro, Cambridgesoft Corp., Cambridge, MA. Details are given in the Experimental Section.
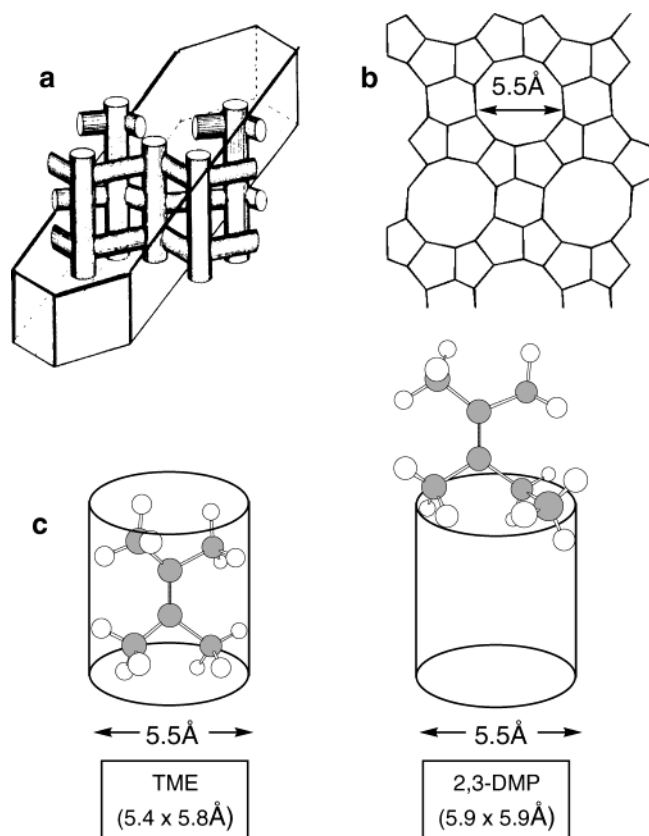
Figure 5. Crystal structure of ZSM-5, showing both the straight and sinusoidal channels. (b) Top view of ZSM-5 showing the straight channel diameter where substrates can enter the internal surface of the zeolite. (c) Molecular dynamics and mechanics minimized conformations for (left) tetramethylethylene (TME) and (right) 2,3-dimethyl-2-pentene (2,3-DMP), compared to the dimensions of the straight channel of ZSM-5. The estimated molecular cylindrical dimensions are included in brackets (see text).

means that the width of the cylinder defines the size of the molecule that the channel must accommodate. The dimensions were determined as equivalent internuclear length and width distances, plus 1Å to account for the size of the exterior hydrogen atoms.[22] The results are shown in Figure 5, for the examples of 2,3-DMP and TME, and summarized in Table 1 for all of the donors. Several points should be noted. First, the dimensions are of the most reasonable (low energy) conformers, and not necessarily the "smallest" conformers. More compact conformations can be attained, however, only *at an energy cost*. Second, the longest axis is not necessarily along one of the obvious dimensions, e.g., the carbon−carbon double bond. For example, the length of the cylinder for 2-MP is longer than that for 2,3-DMP, corresponding to a quite different axis, because in this way, a smaller width dimension can be obtained. Third, the dimensions determined in this way are clearly somewhat arbitrary; however, we believe that they represent a relative ranking that is adequate for the present purposes.

The kinetic width of the channels in NaZSM-5 are estimated to be 5.5 Å.[23] The cyclic COD was not expected to react with the BP•+, based on the fact the eight-membered ring was

assumed to be too large to fit into the NaZSM-5 channels, and is consistent with the cylindrical width of 6.1Å, Table 1.[24] Indeed, no reaction can be detected, despite the fact that the reaction occurs in solution with a similar rate constant to TME (Table 1). Presumably, the zeolite can accommodate much smaller quantities of this diene compared to the smaller donors, although we have no way of determining the extent to which the donors are actually absorbed. The fact that no reaction is also observed for the 2,3-dimethyl-2-pentene (2,3-DMP), however, was initially surprising. The thermodynamics of this oxidation are very similar to those for TME, and the additional methyl group compared to TME was not expected to have a large influence. However, the cylindrical width of the 2,3-DMP is significantly larger than that for TME (5.9 vs 5.4Å), which evidently is sufficient to restrict access to the BP•+ to such an extent that no reaction can be observed!

More than one mechanism has been proposed for bimolecular electron-transfer reactions in zeolites,[25] from those involving direct contact between the reactants, to electron transfer "at a distance", with the zeolite frame mediating electron transfer between nondirectly interacting reactants.[9h] For example, it has been proposed that electron migration could occur over the electron deficient sites in the zeolite, such as cations,[25d] cation clusters, and tri-coordinated aluminum centers.[9h] Alternatively, hole migration (redistribution of positive charge) could occur via electron rich sites, such as oxygen sites in the zeolite framework.[6a,d] The current data do not provide any direct evidence as to the exact mechanism of electron transfer; however, some of the observations are interesting in this regard. Quenching of the BP•+ occurs within seconds with the dienes, but takes several minutes with TME. If direct contact between the BP•+ and the donor is required, then mutual diffusion of one or both partners is required. In this case, diffusion of the dienes is presumably significantly faster than that of TME. The cylindrical widths, i.e., 4.4 and 5.1 Å for the dienes and 5.4 Å for TME support this suggestion. Alternatively, the dienes and the TME may quench by different mechanisms. For example, spontaneous ionization of the DMHD certainly can occur, and transfer of this ionized electron to the BP•+ (perhaps via the zeolite framework) could account for the observations. The TME does not spontaneously ionize, and it is possible that diffusion to direct contact between the TME and the BP•+ is required, which would be consistent with the considerably slower reaction in this case. The estimated widths for TME and BP are, in fact, identical (5.4Å); however, their relative mobilities may be controlled more by electronic effects with the framework.

Computational evidence from Bremard et al. suggests that the preferred binding site for BP is close to the intersections between the straight and sinusoidal channels of NaZSM-5.[6d] For electron transfer to occur in contact, either the donor must migrate to this site, or the BP•+ must migrate from this site. EPR simulations of the hyperfine anisotropy in the EPR spectra of TME•+ and DMHD•+ in HZSM-5 suggest restricted motion for these radical cations,[18c] perhaps as a consequence of the terminal methyl groups, and a location near the ellipsoid

(22) (a) 1Å was chosen as a rough compromise between the hydrogen covalent (0.4) and van der Waals radii (1.1−1.3Å).[22b] (b) Cotton, F. A.; Wilkinson, G *Advanced Inorganic Chemistry*; Interscience: New York, 3rd ed.; 1972; pp. 116−119.
(23) Olson, D. H.; Kokotallo, G. T.; Lawton, S. L.; Meier, W. M. *J. Phys. Chem.* **1981**, *85*, 2238.

(24) Kokotailo, G. T.; Lawton, S. L.; Olson, D. H.; Meier, W. M. *Nature* **1978**, *272*, 437.
(25) See, for example: (a) Turberville, W.; Robins, D. S.; Dutta, P. K. *J. Phys. Chem.* **1992**, *96*, 5024. (b) Liu, X.; Iu, K.-K.; Thomas, J. K. *J. Phys. Chem.* **1989**, *93*, 4120. (c) Iu, K.-K.; Thomas, J. K. *Langmuir*, **1990**, *6*, 471. (d) Wernette, D. P.; Ichimura, A. S.; Urbin, S. A.; Dye, J. L. *Chem. Mat.* **2003**, *15*, 1441−1448.

intersections of the straight and sinusoidal channels of the zeolite. If the TME, indeed experiences restricted motion within the zeolite framework, then diffusive motion may well be slow, as observed.

Because of its relatively small width (3.8 Å), a size effect seems unlikely to be the reason for the lack of reactivity for the enol ether DHF. Note that this donor has the second lowest oxidation potential of all of the donors included in the present study. It is possible that the preferred location of the oxygen-containing DHF in the zeolite is very different from that of the hydrocarbons discussed thus far. Two possible consequences of the basic oxygen can be envisioned. First, the lone pair electrons on the oxygen could interact in a partially bonding manner with the cations in the zeolite framework. One of our groups has already shown that the lone pairs on the carbonyl oxygen of a phenyl ketone derivative can coordinate with the metal cations located on the external surface of the zeolite,[26] and recently an interaction between the nonbonding electrons on THF and the sodium ions in ZSM-35 was reported.[27] The coordination of the ketone was found to inhibit its diffusion into the channels of the ZSM-5 zeolite. It is possible that it is the restricted diffusive or orientational molecular motion of the DHF in the zeolite framework that inhibits the reaction in this case, either as a result of a corresponding coordination process, or simply because of its larger dipole moment compared to the other donors. Alternatively, interaction of the nonbonding electrons on the enol ether with Lewis acid sites in the framework, or with extraframework Na^+ ions, will also increase the oxidation potential of the enol ether. The effect on oxidation potential of coordination to Na^+ ions has been demonstrated in electrochemical studies.[28] Whether as a result of restricted motion, or less favorable thermodynamics, it is clear that the oxidative ability of $BP^{\bullet+}@NaZSM$-5 can also be controlled via the Lewis basicity of the electron donor.

The product of electron transfer is $D^{\bullet+}$, and these radical cations are observed for two of the three donors that react with the $BP^{\bullet+}$. Although the mechanism of formation of the $DMHD^{\bullet+}$ is ambiguous, there is no doubt that the $TME^{\bullet+}$ is formed by electron transfer to $BP^{\bullet+}$. One question is why $HD^{\bullet+}$ is not observed? As discussed above, EPR spectra for both $DMHD^{\bullet+}$ and $TME^{\bullet+}$ have been observed previously on H-ZSM-5, but EPR detection of $HD^{\bullet+}$ has not been reported. This presumably reflects the fact that the lifetime of this particular radical cation is too short under the experimental conditions. The factors that control the reactivity and lifetimes of the radical cations of simple alkenes on zeolites have not yet been completely described.[9f,11a,29] It has been suggested that a "tight fit" of the substrate within the zeolite pores or channels is essential for generating a long-lived radical cation.[29] On the basis of the width estimates, HD should certainly have the "loosest" fit of any of the simple alkenes and dienes, which may result in a more mobile radical cation that can undergo, for example, deprotonation or even dimerization reactions.[30]

Summary

The generation of $BP^{\bullet+}$ and analogous radical cations in NaZSM-5 zeolites represents an example of a new class of supramolecular solid-state irreversible photooxidizers. Evidence is provided for one-electron oxidation of simple organic electron donors in this manner. The oxidation reactions exhibit high selectivity, and can be controlled by the thermodynamics of the reactions (via the oxidation potential of the donor or a substituted biphenyl), and also the molecular size, shape, and Lewis basicity of the donors. In those cases where oxidation is observed, complete quenching of the $BP^{\bullet+}$ EPR signal indicates that the reactions are quantitative and thus efficient in a chemical sense. An important unanswered question, however, relates to the photochemical efficiency, which is controlled by the as yet unknown quantum yield of formation of the $BP^{\bullet+}$. Studies to further address this and other factors that control the selectivity, reactivity, and product distributions in these systems are ongoing in our laboratories.

Experimental Section

Sodium-exchanged ZSM-5 (Si/Al = 20) was a Chemie Uetikon product obtained as a generous gift from Dr. V. Ramamurthy, Department of Chemistry, Tulane University, New Orleans, LA. Biphenyl was obtained from the Aldrich Chemical Co. and sublimed prior to use. Tetramethylethylene, 3-methyl-2-pentene, 2,3-dimethyl-2-pentene, 2,3-dihydrofuran, *cis*,*cis*-1,3-cyclooctadiene, 2,5-dimethyl-2,4-hexadiene, and 2,4-hexadiene were obtained from Aldrich and used as received. 9,10-Dicyanoanthracene was available from previous studies.[3]

The EPR spectra of the radical cations in the zeolites were recorded using a Bruker EMX-EPR spectrometer operating at X-band (9.5 GHz). The radical cations in solution were detected using a transient absorption apparatus that has been described previously.[3]

Typical sample preparation for study in the zeolites involved the calcination of NaZSM-5 in a furnace at 500°C for 12 h prior to use. A 9-mg portion of biphenyl and a 300-mg portion of hot zeolite were placed in a custom-made EPR tube equipped with a small bulb attachment containing the alkene (Figure 1). An equimolar amount of alkene was placed in the small bulb on the side of the tube. All stopcocks were closed, and the sample was placed on a vacuum line. The portion of the tube containing the zeolite and biphenyl was evacuated to 5×10^{-5} Torr. After the evacuation was complete, the zeolite-biphenyl mixture was heated at 70 °C to sublime the biphenyl into the channels of the zeolite, typically for a period of 12 h. The contents of the small bulb then underwent 3 freeze−pump−thaw cycles to deaerate the alkene. EPR spectra were measured before and after irradiation was carried out in a Rayonet reactor equipped with 16 254-nm lamps. Each sample was irradiated for 10 min. The extent of inclusion of the biphenyl or the added donor into the zeolite is not known.

Experiments in solution were performed in acetonitrile solvent (Omnisolv Spectro grade, used as received). Typically, 9,10-dicyanoanthracene (ca. 10^{-4} M) was excited at 355 nm using a nanosecond laser in the presence of 0.15 M biphenyl. The absorption of the biphenyl radical cation was monitored at 670 nm. The pseudo-first-order decay of the biphenyl radical cation was measured as a function of added donor to yield the bimolecular rate constant for reaction, k_{ox}.

(26) Turro, N. J.; Lei, X.; Niu, S.; Liu, Z. *Org. Lett.* **2000**, *2*, 3991.

(27) Lin, D.-C.; Zhou, W.-Z.; Guo, J.; He, H.-Y.; Long, Y.-C. *J. Phys. Chem. B.* **2003**, *107*, 3798.

(28) Bard, A. J.; Faulkner, L. R. Chapter 8 *In Electrochemical Methods; Fundamentals and Applications*, 2nd ed.; Wiley and Sons: New York, 2001.

(29) Ramamurthy, V.; Caspar, V. J.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 594.

(30) (a) Crockett, R.; Roduner, E. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1503. (b) Werst, D. W.; Piocos, E. A.; Tartakovsky, E. E.; Trifunac, A. D. *Chem. Phys. Lett.* **1994**, *229*, 421. (c) Leu, T. M.; Roduner, E. *Stud. Surf. Sci. Catal.* **2001**, *135*, 2014. (d) Ramamurthy, V.; Lakshminarasimhan, P.; Grey, C. P.; Johnston, L. J. *Chem. Commun.* **1998**, 2411. (e) Garcia, H.; Marti, V.; Casades, I.; Fornes, V.; Roth, H. D. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2955.

The cylindrical widths were estimated by first performing a molecular dynamics annealing calculation on the molecules using the program Chem3D-Pro, from CambridgeSoft. The cooling rate was 1 kcal/atom/ps, and the final temperature was 300 K. An additional molecular mechanics optimization was performed to a minimum RMS gradient of 0.1. The relevant axes were then determined by visual inspection. Equivalent atomic center-to-center distances were measured graphically, and 1.0Å was added to this distance to take into account the dimensions of the exterior hydrogen atoms. Repeated calculations of this type gave dimensions that were reproducible to ca. 0.15Å.