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Electron Transfer Reactions within Zeolites: Radical Cation from Benzonorbornadiene

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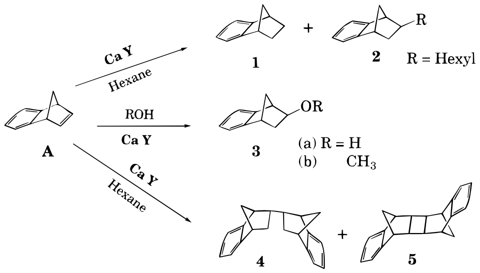
Zeolites are being used as solid acid catalysts in a number of commercial processes.[1] Occasionally zeolites are also reported to perform as electron transfer agents.[2] Recently, we observed that radical cations of certain olefins and thiophene oligomers can be generated spontaneously within ZSM-5 zeolites.[3] We noticed that these radical cations generated from diphenyl polyenes and thiophene oligomers were remarkably stable (at room temperature) within ZSM-5 and can be characterized spectroscopically at leisure. Synchrotron X-ray powder diffraction structural studies of *trans*-stilbene−ZSM-5 and bithiophene−ZSM-5 complexes, reported recently by us,[4] strengthened our original view that their stability derives from their unique arrangements within the channels of ZSM-5. While this high stability is useful for structural and spectroscopic characterizations, lack of reactivity restricted their chemical utility. With this as the background, we have initiated a program on electron transfer processes within large pore zeolites.[5] The basis of this approach is that once a cation radical is generated within a large pore zeolite, it will have sufficient room to undergo a molecular transformation. Our aim is to identify a condition under which electron transfer can be routinely and reliably carried out within large pore zeolites such as faujasites. To our great surprise, when benzonorbornadiene **A** and a number of olefins were included in divalent cation exchanged faujasites, they were transformed into products very quickly (<15 min). This observation allowed us to explore the use of zeolites as oxidants. Results of our studies on benzonorbornadiene are presented in this communication.[6]

The experimental procedure consisted of stirring known amounts of benzonorbornadiene **A** and activated Ca Y in hexane.[7] The solution turned yellowish in color immediately upon addition of **A** to hexane containing Ca Y. However, within minutes, the color faded significantly suggesting that **A** has been transformed into products. The solution was stirred for several hours at room temperature, filtered, and washed with hexane. The combined hexane washings showed neither the presence of **A** nor any other products. However, extraction of the zeolite with methylene chloride and GC analyses of the extract showed several products (Scheme 1). Such a reaction did not occur when **A** was stirred with monovalent cation (Na, K, Rb, and Cs) exchanged X and Y zeolites. A careful study revealed that this reaction is unique to Mg, Ca, and Sr Y zeolites. While dark reaction occurred in Mg, Ca, and Sr X zeolites, it was slow and incomplete. Both Ba X and Ba Y were found to be inert. No such oxidation occurred within Ca-exchanged LS X zeolites. The difference between X, Y, and LS X zeolites is only in the Si/Al ratio that constitutes the framework of the zeolite; the Si/Al ratio for Y, X, and LS X, respectively, are 1.54, 1.24, and 1.0.[8]

Scheme 1



The exact product distribution (Scheme 1, Figure 1) was dependent on the condition of inclusion. When the zeolite and the solvent hexane were very dry and the loading level of **A** was less than 0.25 (one molecule per four supercages), only reduction and solvent addition products **1** (>90%) and **2** (<10%) were obtained. When the addition was conducted under wet conditions (six molecules of water per supercage was adsorbed onto the previously dried Ca Y) *exo*-benzonorborneol **3a** was obtained as the sole product. The ratio of **3** to **(1 + 2)** can be controlled by regulating the amount of water present within the supercage. When the inclusion was conducted in methanol, **3b** was obtained as the only product. When the loading level was greater than 1 (more than one molecule per supercage), products **4** and **5** were formed in addition to **1** and **2**. In all cases, products accounted (isolated yield) for >90% of the disappearance of **A**. Our routine experiments were carried out on a 50 mg of **A** in 300 mg of Ca Y scale. In every case we were able to isolate ∼45 mg of products. Products **1**, **3**, **4**, and **5** were isolated and identified by comparing their spectral data with the literature reports.[9] Product **2** was obtained as a mixture of several addition products of hexane and was identified only by mass spectral data.

A general mechanism for the formation of **1**−**5** from **A** within Ca Y is presented in Scheme 2. We suggest that the reactions listed in Scheme 1 are initiated by an electron transfer process. This proposition is supported by the fact that diffuse reflectance spectra of several olefins (1,1-diphenylethylene, *trans*-stilbene, *trans*-*p*,*p*′-dimethoxystilbene, and 1,4-diphenylbutadiene) included in Ca Y agreed with those of the corresponding radical

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[1] (a) Corma, A. *Chem. Rev.* **1995**, *95*, 559. (b) Farneth, W. E.; Gorte, R. J. *Chem. Rev.* **1995**, *95*, 615.

[2] (a) Brouwer, D. M. *J. Catal.* **1962**, *1*, 372. (b) Chen, F.; Guo, X. *J. Chem. Soc., Chem. Commun.* **1989**, 1682. (c) Dollish, F. R.; Hall, W. K. *J. Phys. Chem.* **1965**, *69*, 4402. (d) Dollish, F. R.; Hall, W. K. *J. Phys. Chem.* **1967**, *71*, 1005. (e) Flockhart, B. D.; Scott, J. A.; Pink, R. C. *Trans. Faraday Soc.* **1965**, *61*, 730. (f) Hirschler, A. E.; Barmby, D. S.; James, R. L. *Catalysis* **1965**, *4*, 628. (g) Kortum, G.; Schlichemaier, X. *Z. Phys. Chem., Neue Folge* **1966**, *48*, 267. (h) Kurita, Y.; Sonoda, T.; Sato, M. *J. Catal.* **1970**, *19*, 82. (i) Roberts, R. M.; Barter, C.; Stone, H. *J. Chem. Phys.* **1959**, *63*, 2077. (j) Ronney, J. J.; Pink, R. C. *Trans. Faraday Soc.* **1962**, *58*, 1632. (k) Stamires, D. N.; Turkevich, J. J. *J. Am. Chem. Soc.* **1964**, *86*, 749. (l) Takimoto, K.; Miura, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2231. (m) Tokunaga, H.; Ono, Y.; Keii, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3569. (n) Yamamoto, Y.; Yamada, H. *J. Raman Spectrosc.* **1982**, *12*, 157.

[3] (a) Caspar, J. V; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600. (b) Ramamurthy, V.; Caspar, J. V; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 594.

[4] (a) Parise, J. B.; Hriljac, J. A.; Cox, D. E.; Corbin, D. R.; Ramamurthy, V. *J. Chem. Soc., Chem. Commun.* **1993**, 226. (b) Eylem, C.; Hriljac, J. A.; Ramamurthy, V.; Corbin, D. R.; Parise, J. B. *Chem. Mater.* **1996**, *8*, 844.

[5] A report on the use of Na Y as an electron transfer agent has appeared in the literature: Ghosh, S.; Bauld, N. L. *J. Catal.* **1985**, *95*, 300.

[6] Other olefins investigated thus far include stilbenes, diphenylbutadienes, 1-phenyl-3,4-dihydronaphthalene, 2-phenyl-3,4-dihydronaphthalene, 1,1-diphenylethylene, indene, and dibenzobarrelene. Every one of these molecules was cleanly converted to products. Results will be published shortly.

[7] Zeolites X and Y were activated at 450 °C, and LS X was activated at 350 °C. LS X is not stable at higher temperatures.

[8] For background information on zeolites, see: (a) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*; John Wiley and Sons: New York, 1974. (b) Dyer, A. *An Introduction to Zeolite Molecular Sieves*; John Wiley and Sons: New York, 1988.

[9] (a) Tori, K.; Muneyuki, R.; Takano, Y.; Tsuji, T.; Tanida, H. *Can. J. Chem.* **1964**, *42*, 926. (b) Goto, T.; Tatematsu, A.; Hata, Y.; Muneyuki, R.; Tanida, H.; Tori, K. *Tetrahedron* **1966**, *22*, 2213. (c) Katz, T. J.; Carnahan, J. C.; Boecke, R. *J. Org. Chem.* **1967**, 32, 1301. (d) Sandman, D. J.; Mislow, K.; Giddings, W. P.; Dirlam, J.; Hanson, G. C. *J. Am. Chem. Soc.* **1968**, *90*, 4877.

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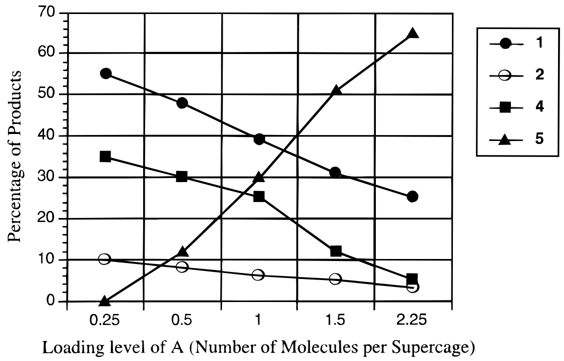
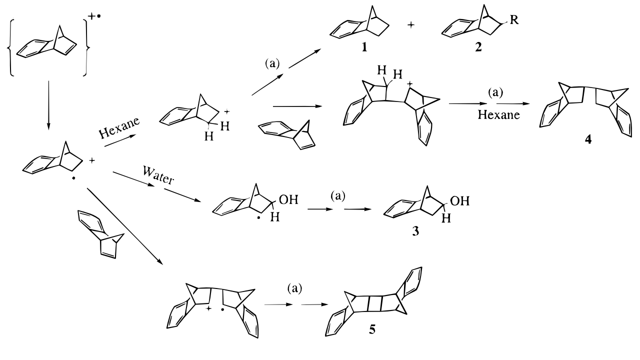


Figure 1. Loading level dependent product distribution upon inclusion of benzonorbornadiene within Ca Y. For product structures corresponding to numbering, see Scheme 1.

Scheme 2



(a) Back Electron Transfer from Zeolite to the Intermediate and further reaction.

cations.[10] Since the radical cation spectrum of benzonorbornadiene is not available in the literature, we are unable to provide unequivocal evidence in favor of radical cation formation in this case. Indirect support in favor of radical cation formation come from experiments carried out to probe whether protonation by Bronsted acid sites present within Ca Y is the initiating process. When benzonorbornadiene was included in H Y zeolite (Bronsted acid form of Y), none of the above products were obtained. Benzonorbornadiene was found to be stable in aqueous HCl. These two observations suggest that protonation may not be the primary step.

Reactions of benzonorbornadiene radical cation have not been reported in the literature. However, radical cation from norbornene, a molecule similar to benzonorbornadiene, undergoes hydrogen abstraction from solvent acetonitrile.[11] Considering the behavior of norbornene, the formation of **1** and **2** from benzonorbornadiene is not surprising. It is known that depending on the medium, the radical cation can react from either the cation or the radical end.[12] The addition of water and methanol, we believe, occurs from the trapping of the cationic part of the radical cation.

Speculations abound regarding the nature of the oxidizing site.[2] A Bronsted acid site, Lewis acid site, and an extra lattice aluminum site have been suggested as possible sites of oxidation.[13] The role of oxygen in generating oxidizing sites is also a subject of speculation.[14] It is not clear how these oxidizing sites are generated. Although we are unable to provide any insight into the nature of the oxidizing site, results obtained within X, Y, and LS X zeolites are noteworthy. While Y with a Si/Al ratio of >1.5 is very active, X with a Si/Al ratio of ~ 1.24 is moderately active, and LS X with a Si/Al ratio of 1.0 is not active at all. Further, while divalent cation exchanged Y zeolite is active, monovalent cation exchanged zeolite Y is inert as an electron transfer agent. Also, among divalent cation exchanged zeolites, Ba Y is inert. These observations are consistent with the model that defect/strain is generated on the framework of the zeolite when divalent cation balances two distantly located negative charges on the zeolite surface. As the Si/Al ratio decreases, the negative charges are located closer to each other, and less defect/strain is generated. This is supported by the fact that when high aluminum is present on the framework (LS X) the zeolite is inert even with Ca^{2+} as the cation. Also, when the cation is large in size such as Ba^{2+}, balancing the distantly located negative charges on the framework becomes easier, and no defect/strain on the framework results. What is surprising is that we are able to oxidize quantitatively more than 50 mg of substrate per 300 mg of the zeolite. This corresponds to 2.5 molecules per supercage. Such a large conversion is against our speculation of defect sites being responsible for the oxidation process. We are in the process of examining the role of oxygen in the electron process within zeolites.[15]

It is clear that the divalent cation exchanged zeolites are to be treated cautiously when they are used as the reactive media for photochemical reactions. What is significant with this zeolite-mediated electron transfer pathway is its simplicity and the mild conditions needed to achieve this. We are in the process of examining the nature of the oxidizing site and expanding the systems that can be subjected to mild oxidation within zeolites.[16]

Acknowledgment. V.R. thanks ACS-PRF and Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy, for support of this program.

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[10] (a) Shida, T. *Electronic Spectra of Radical Ions*; Elsevier: Amsterdam, 1988. (b) The solid sample of Ca Y included with benzonorbornadiene showed an intense ESR signal both at room and at liquid nitrogen temperature. The signal was unresolved at both temperatures. We thank G. Turner and M. Bakker of University of Alabama for help with ESR experiments.

[11] (a) Bruno, J. W.; Marks, T. J.; Lewis, F. D. *J. Am. Chem. Soc.* **1982**, *104*, 5579. (b) When cyclohexane was used as the solvent, two products similar to **2** in which cyclohexyl fragment has been introduced were isolated (exo and endo addition products). Similarly, when perdeuterated cyclohexane was used as the solvent, addition of deuterium to one carbon and perdeuterated cyclohexyl fragment to the other carbon of the olefin occurred.

[12] (a) Mattes, S. L.; Farid, S. *Org. Photochem.* **1983**, *6*, 233. (b) Lewis, F. D. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Vol. C, p 1. (c) Mizumo, K.; Otsuji, Y. *Top. Curr. Chem.* **1994**, *169*, 301. (d) Roth, H. *Top. Curr. Chem.* **1992**, *163*, 131.

[13] (a) Kasai, P. H.; Bishop, R. J. In *Zeolite Chemistry and Catalysis*; Rabo, J. A., Ed.; American Chemical Society: Washington, DC, 1974; p 350. (b) Cano, M. L.; Corma, A.; Fornes, V.; Garcia, H. *J. Phys. Chem.* **1995**, *99*, 4241. (c) Li, X.; Iu, K. K.; Thomas, J. K.; He, H.; Klinowski, J. *J. Am. Chem. Soc.* **1994**, *116*, 11811.

[14] Chen, F. R.; Fripiat, J. J. *J. Phys. Chem.* **1992**, *96*, 819.

[15] Oxygen is most likely involved in the oxidation process. When activation of Ca Y was conducted under conditions where oxygen was completely eliminated, radical cation formation was significantly reduced. Under such conditions, introduction of oxygen enhanced the radical cation formation. Details will be presented shortly.

[16] We have recently observed with a number of olefins that Ca Y upon activation under aerated conditions generates both carbocation and cation radical. By controlling the activation process, one can control the generation of these two reactive intermediates. Both are long-lived within Ca Y at room temperature. We are in the process of examining the involvement of carbocation formation in the benzonorbornadiene system.