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Selective Oxidation of Olefins within Organic Dye Cation-Exchanged Zeolites

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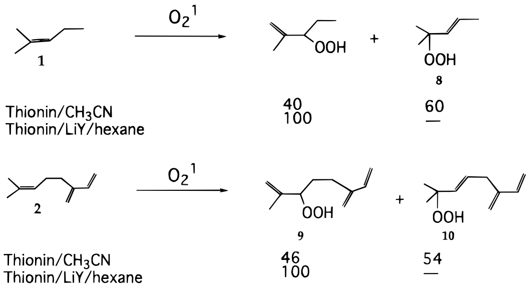
In the present paper, we report an unprecedented selectivity in the products during singlet oxygen mediated oxidation of olefins included within dye-exchanged X and Y zeolites.[1,2] Singlet oxygen is generated within a zeolite by irradiating a thiazine dye exchanged into zeolites.[3] Oxazine and thiazine dye molecules can be readily exchanged for alkali cations present in the interior of faujasite (X and Y) zeolites.[4] Depending on the status of hydration, these dye molecules exist either in monomeric or dimeric forms. We show below that when a thiazine dye molecule is present in its monomeric form within a zeolite, it serves as an excellent singlet oxygen sensitizer. Utilizing zeolite supercages as "active reaction cavities",[5,6] we have directed the reactive oxygen toward a particular face of the olefin and obtained a high selectivity in the products of oxidation.

The general procedure for exchanging oxazine and thiazine dye molecules[4a] consisted of stirring known amounts of the dye (0.1 mg) and the zeolite (300 mg) in aqueous solution (10 mL) for 3 h at room temperature. Filtration and exhaustive washing or Soxhlet extraction with water (until the aqueous wash was colorless) gave a lightly colored zeolite. Normally, the loading level of the dye was maintained near 1 dye molecule/100 supercages. Dye-exchanged zeolites were dried at ~100 °C on a vacuum line (10^{-4} Torr) and used for further studies. Under such conditions, as per diffuse reflectance spectra, the dye existed as monomer. Of the various dyes investigated (thionin, methylene blue, methylene green, oxazine-170, oxazine-1, pyronin-Y, Nile blue-A, acridine orange, rhodamine-6G, safranin, and crystal violet), only the first three provided results of interest to this paper.

Excitation of thionin, methylene blue, or methylene green exchanged Na X or Na Y gave fluorescence in the expected visible region. More importantly, an emission, the intensity of which was dependent on the water content of the zeolite, due to singlet oxygen was also observed at 1268 nm.[7] The observation of singlet oxygen emission prompted us to investigate the reactivity of singlet oxygen within a zeolite. The oxidation of olefins **1**−**6** (Schemes 1 and 2) was investigated. A typical method consisted of exposing a dry hexane solution (5 mL) containing known amounts of the dry dye-exchanged zeolite (~300 mg) and the olefin (~5 mg) to visible radiation (>450 nm) for about 15−30 min.[8] Generally, quantitative conversion was reached within an hour of irradiation. Products were extracted with ether and analyzed by GC after addition of excess triphenylphosphine. Results are shown in Schemes 1 and 2. For comparison, solution irradiations were conducted in acetonitrile, and the results obtained were identical to the literature reports.[9]

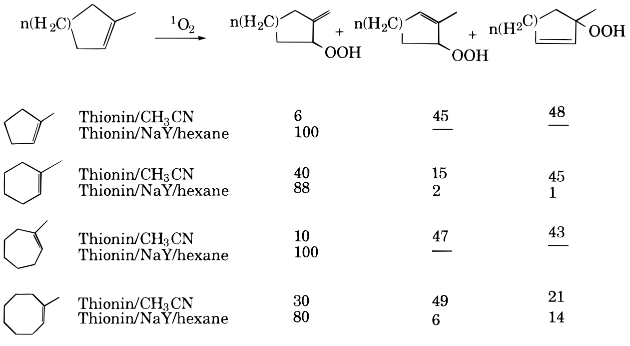
Scheme 1



	1		**8**
Thionin/CH$_3$CN		40	60
Thionin/LiY/hexane		100	—

	2	**9**	**10**
Thionin/CH$_3$CN		46	54
Thionin/LiY/hexane		100	—

Scheme 2



3	Thionin/CH$_3$CN	6	45	48
	Thionin/NaY/hexane	100	—	—
4	Thionin/CH$_3$CN	40	15	45
	Thionin/NaY/hexane	88	2	1
5	Thionin/CH$_3$CN	10	47	43
	Thionin/NaY/hexane	100	—	—
6	Thionin/CH$_3$CN	30	49	21
	Thionin/NaY/hexane	80	6	14

For both cyclic and acyclic olefins, oxidation within zeolites resulted in a single major product (Schemes 1 and 2). Selectivities similar to the one reported with thionin were also observed with methylene blue and methylene green as sensitizers. By following control experiments, we established that the selectivity obtained is not due to any experimental artifacts. In every case, products were independently synthesized and tested for their stability and retention within zeolites. They were stable and had no unusual affinity for zeolite interior. Also, none of them were converted either to any other products or to the isomer that was isolated as the major product. Mass balance in oxidation experiments was excellent (>90%) indicating the absence of any side reactions. The following experiments indicate that the reactive species is singlet oxygen. Oxidation was quenched by singlet oxygen quenchers such as β-carotene, Dabco (1,4-diazabicyclo[2.2.2]octane), and *N*,*N*-dimethylaniline. When the electron transfer sensitizer 9,10-dicyanoanthracene was used, no selectivity was obtained with both β-myrcene (**2**) and 2-methyl-2-pentene (**1**) (Scheme 1).[10,11]

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[1] (a) *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979. (b) *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vols. 1−4.

[2] For a few selected reviews, see: (a) Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104. (b) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395. (c) Adam, W.; Prein, M. *Acc. Chem. Res.* **1996**, *29*, 275.

[3] Recently, elegant examples of oxidation upon visible excitation of olefin−oxygen complex in zeolite has been reported by Frei and co-workers: (a) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1993**, *115*, 7501. (b) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 1812. (c) Sun, H.; Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 7951. (d) Blatter, F.; Moreau, F.; Frei, H. *J. Phys. Chem.* **1994**, *98*, 13403. (e) Blatter, F.; Sun, H.; Frei, H. *Catal. Lett.* **1995**, *35*, 1. (f) Blatter, F.; Sun, H.; Frei, H. *Chem. Eur. J.* **1996**, *2*, 113.

[4] (a) Ramamurthy, V.; Eaton, D. F.; Sanderson, D. R. *J. Am. Chem. Soc.* **1993**, *115*, 10438. (b) Calzaferri, L. G.; Gfeller, N. *J. Phys. Chem.* **1992**, *96*, 3428. (c) Wohrle, D.; Schulz-Ekloff, G. *Adv. Mater.* **1994**, *6*, 875.

[5] Weiss, R. G.; Ramamurthy, V.; Hammond, G. S. *Acc. Chem. Res.* **1993**, *26*, 530.

[6] (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. (c) van Bekkum, H.; Flanigen, E. M.; Jansen, J. C. *Introduction to Zeolite Science and Practice*; Elsevier: Amsterdam, 1991.

[7] Kasha, M.; Brabham, D. E. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 1.

[8] Excitation (>450 nm) of olefins **1**−**5** in Na Y in the absence of the dye did not give any products.

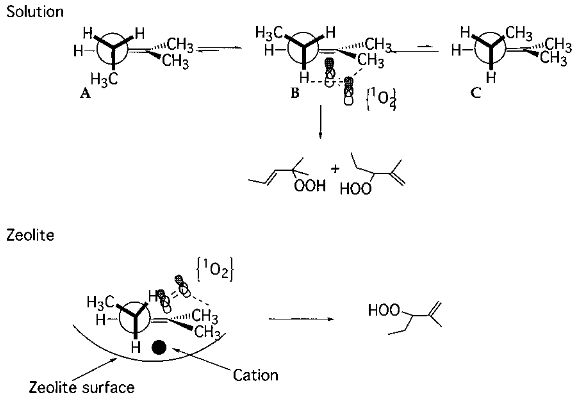
[9] (a) Foote, C. S.; Wexler, S.; Ando, W.; Higgins, R. *J. Am. Chem. Soc.* **1968**, *90*, 975. (b) Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5168. (c) Foote, C. S. *Pure Appl. Chem.* **1971**, *27*, 635.

[10] 9,10-Dicyanoanthracene (DCA) has been established to act both as an electron transfer and energy transfer sensitizer during the oxidation of olefins: (a) Foote, C. S. *Tetrahedron* **1985**, *41*, 2221. (b) Kanner, R. C.; Foote, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 678, 682. (c) Arakai, Y.; Dobrowolski, D. C.; Goyne. T. E.; Hanson, D. C.; Jiang, Z. Q.; Lee, K. L.; Foote, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 4570.

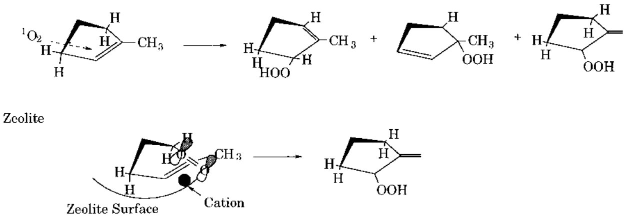
[11] A few of the olefins investigated here have been established to quench the excited singlet of DCA by an electron transfer process (ref 9c).

S0002-7863(96)02372-4 CCC: $12.00

Scheme 3



Scheme 4



The following experiments established that the selectivity reported here is the result of oxidation within zeolite and not due to reaction on the external surfaces or in solvent hexane. When either methylene blue or rose Bengal adsorbed on silica gel were used as the sensitizer, no selectivity resulted. Furthermore, when C_{60}, which due to its large size can only adsorb on the external surfaces of Na Y, was used as the sensitizer no selectivity was observed.[12-14] Similarly, no selectivity resulted when a hexane slurry of methylene blue adsorbed on silica gel, olefin, and dry Na Y was irradiated under oxygen atmosphere. These experiments establish that in order to achieve selectivity it is important to have both the olefin and the sensitizer included within the same zeolite particle.

The proposed models to rationalize the selective oxidation of olefins are illustrated in Schemes 3 and 4. The reactivities of **1**−**6** in solution are understood on the basis of preferred mode of interaction between the singlet oxygen and the reactant olefin.[15] It has been suggested that, in the absence of steric problems, the singlet oxygen prefers to attack the olefin from the side which allows for maximum stabilization due to interaction with allylic hydrogens. We believe that the role of the zeolite is to alter the geometry of attack. As illustrated in Scheme 3, the most favored conformer for 2-methyl-2-pentene (**1**) is B.

When **1** adsorbs on the surface of the zeolite, it would be expected to adsorb from the less-hindered side, as illustrated in Scheme 3 (i.e., the molecule will adsorb from the side which is normally attacked by singlet oxygen in solution). Under such conditions, the oxygen would be forced to attack the molecule from the face substituted by hydrogen and a methyl group. Such an attack would not result in the formation hydroperoxide **8** (Scheme 1) derived from abstraction of allylic H from the ethyl group. Indeed, this is the case. We suggest that the cation plays an important role in keeping the olefin in the above geometry on the surface of the zeolite. An interaction between a monovalent cation and the π-cloud is a well-established phenomenon.[16] The strength of binding would be expected to depend on the size of the cation, and the smaller cations such as Li^+ and Na^+ are expected to bind much more strongly than larger cation such as Cs^+. Indeed, when the cation size is increased from Li^+/Na^+ to Cs^+, lesser selectivity resulted.[17] For example, in the case of β-myrcene (**2**), the product distribution (**9**:**10**) changed from 100:1 in Li Y to 61:39 in Cs Y. A similar trend was observed with olefins **1** and **3**−**6** as well.

An argument similar to the one proposed above rationalizes the observed remarkable selectivity for cyclic olefins **3**−**6**. Although, at this stage, we are not certain that this model is fully valid, we utilize this to plan further experiments. The illustration provided in Scheme 4 for **3** highlights the proposed model. In solution, the singlet oxygen prefers to attack 1-methylcyclopentene from the ring side due to secondary stabilization with allylic hydrogens. This ring side attack would not be favored when **3** is adsorbed on zeolite surface due to lack of interaction with the allylic hydrogens and to steric hindrance provided by the methylene unit. Under such circumstances, the attack would be expected to occur from the methyl side, leading to the observed product. We wish to emphasize that the selectivity observed here is not obtained when either silica or alumina was used as the support. The cation plays a critical role of maintaining the molecule in a particular conformation for a much longer time.

In conclusion, this study illustrates that a supramolecular assembly made up of dye, olefin, oxygen, and zeolite can provide unprecedented opportunities to conduct selective oxidation of olefins. We are in the process of extending the studies to other olefins to establish the limitation of this approach. An insight into the mechanistic origin of selective oxidation is expected to be gained through the use of partially deuterated olefins. Such experiments are underway. Zeolite is also being explored as a medium to synthesize enantioselective chiral hydroperoxides.[18]

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(13) Foote, C. S. *Top. Curr. Chem.* **1994**, *109*, 347.

(14) (a) The authors thank Dr. Y. P. Sun for a gift of C_{60} and Dr. K. Pitchumani for performing oxidation studies with C_{60}/Na Y. (b) In these experiments, the olefin remained outside the zeolite. Because of its size, once the C_{60} plugged all entrances to the zeolite, the oxidation occurred in hexane solution.

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(17) Independent of the cation, most of the olefin remained within the zeolite. However, in no case were all olefin molecules adsorbed within the zeolite. Also, at the end of the reaction no product remained in hexane portion.

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