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# Photooxidations in zeolites. Part 2: A new mechanistic model for reaction selectivity in singlet oxygen ene reactions in zeolitic media

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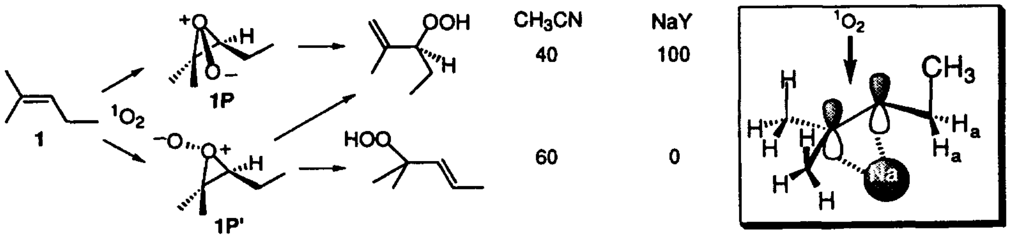
**Abstract**

The singlet oxygen ene reaction in Methylene Blue doped NaY was examined. A new mechanism is proposed which involves complexation of the sodium cation to the pendant oxygen in the perepoxide intermediate. It is argued that this complexation leads to greater positive charge on the carbon framework and to steric interactions between the sodium and the groups on the proximal side of the perepoxide. © 1999 Elsevier Science Ltd. All rights reserved.

The $^1O_2$ ene reaction (Scheme 1) was first introduced by Schenck in the late 1940s.[1] Subsequently, a large number of experimental and theoretical studies have established a novel two-step mechanism for the reaction, via perepoxide intermediates, **1P** and **1P′**.[2]



Scheme 1.

In 1996 Ramamurthy and coworkers[3,4] introduced the use of zeolites to enhance $^1O_2$ ene regioselectivity. For example, photooxidation of 2-methyl-2-pentene, **1**, in thionin doped NaY resulted in 100% regioselective formation of the allylic hydroperoxide formed in minor amount in solution (Scheme 1).[5] This dramatically enhanced regioselectivity was tentatively attributed to complexation of the olefin to a $Na^+$ compelling the sterically demanding allylic methyl group to rotate to the face approached by

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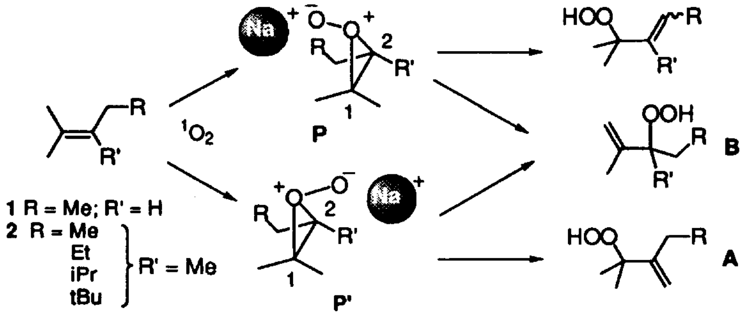
${}^1O_2$, thereby preventing access to the allylic hydrogens $H_a$ on the methylene carbon (Scheme 1). We now report that results from the photoxidations of tetrasubstituted olefins, **2**,[6] in Methylene Blue (MB) doped zeolite Y[7] are inconsistent with this mechanism. We also suggest a new mechanistic model for the reaction in the zeolite which provides a satisfying rationale for a diverse set of experimental data.

Photooxidations of olefins **2** (R=Me, Et, *i*Pr, and *t*Bu) (Scheme 2) were conducted by adding 0.3 g of dry NaY/MB, with an average occupancy ($\langle S \rangle$) of 0.01 molecules of MB per supercage, to 5 mL of hexane containing the substrate. The hexane slurries were saturated with $O_2$ and stirred for 15 minutes and then irradiated under continuous oxygen agitation with a 600 W tungsten-halogen lamp for 1 h through 1 cm of a 12 M $NaNO_2$ filter solution. All the photooxidations resulted in the formation of two allylic hydroperoxides, **2A** and **2B**, (Scheme 2) which were analyzed by GC after extraction from the zeolite and quantitative reduction to the alcohols by $Ph_3P$. The peak areas were adjusted with the appropriate GC response factor and the product ratios were compiled and are listed in Table 1 where they are compared to the analogous homogeneous photooxidations conducted in $CH_3CN$. No other products were observed by GC and the isolated yield in the case of **2** (R=Et) was 87.3%. The hydroperoxides formed in the photooxidation of **2** (R=*i*Pr) in solution could be introduced into the zeolite and extracted without decomposition or rearrangement. Finally, the product ratios in the photoxidations of **1** using MB absorbed on silica gel are identical to those observed in solution implying that these reactions are occurring in the supercages of the zeolite.



Scheme 2.

Table 1
A comparison of solution and zeolite photooxidations of olefins **2** (R=Me, Et, *i*Pr, *t*Bu)

| | Solution[a] | | | Zeolite[b] | | |
|---|---|---|---|---|---|---|
| R | %2A[c] | %2B[c] | 2A/2B | %2A | %2B | 2A/2B |
| Me | 32.9±3.3 | 67.1±3.3 | 0.49 | 39.5±3.7 | 60.5±3.7 | 0.65 |
| Et | 42.0±1.7 | 58.0±1.7 | 0.72 | 52.7±1.7 | 47.3±1.7 | 1.11 |
| iPr | 52.6±1.1 | 47.4±1.1 | 1.1 | 51.8±2.8 | 48.2±2.8 | 1.07 |
| tBu | 70.6±1.1 | 29.4±1.1 | 2.4 | 61.2±1.1 | 38.8±1.1 | 1.58 |

a. Olefins (4 - 7 x $10^{-2}$M) in $CH_3CN$ containing 2 x $10^{-4}$M MB were irradiated to 100% completion through 1cm of a 12M $NaNO_2$ filter solution. b. NaY doped with MB <S> = 0.01. c. From integration of hydroperoxy protons in the ${}^1H$ NMR spectra.

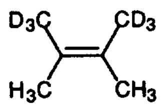
The ene regiochemistries of **2** in solution ($CH_3CN$) are very sensitive to the size of the allylic substitutent, R. As the size increases the proximal $C_2$–O bond in perepoxides **2P** and **2P′** lengthen and weaken inducing cleavage and predominate hydrogen abstraction from the methyl group geminal to the substituent (intramolecular steric effect). If the mechanistic model in the interior of the zeolite operates as depicted in Scheme 1, this large group effect should be amplified in the supercage. Examination of Table 1 reveals that indeed the **2A**:**2B** ratio increases for R=Me and R=Et. However, the ratio is approximately the same for R=*i*Pr and is significantly smaller than in $CH_3CN$ when R=*t*Bu. These results are inconsistent with the olefin complexation model (Scheme 1).

As an alternative (Scheme 2) we suggest that the pendant oxygen in the perepoxides interact with the electrostatic field generated by the cations in the supercage. This interaction has two consequences: (1) it induces a greater charge transfer from the olefin to $O_2$ in comparison to that observed in homogeneous reactions. As a result, inductive and/or resonance stabilization of the positive charge on the perepoxide carbon framework becomes a more important factor, in comparison to its importance in homogeneous reactions, in determining the regiochemistry of the reaction, and (2) steric interactions between the cation and the *cis* substituents become important in determining the perepoxide diastereomer population. For example, addition of $^1O_2$ to **1** or **2** in the zeolite can potentially generate two perepoxides, **P** and **P′**, the latter of which is more stable since the pendant oxygen and associated cation are on the least sterically congested side of the olefin.

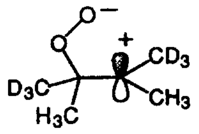
Perepoxides **1P** and **1P′** (R′=H) adopt unsymmetrical structures with long $C_1$–O and shorter $C_2$–O bonds reflecting the enhanced stabilization of the positive charge on $C_1$. As a consequence, trisubstituted olefins such as **1** will react preferentially by abstraction of hydrogen from the more highly substituted ($C_1$) end of the olefin. Tetrasubstituted olefins **2** will also preferentially form the least congested perepoxide **2P′**, however, it will be more symmetrical than **1P** or **1P′** since both $C_1$ and $C_2$ are tertiary carbons. Both these factors will result in an **2A**:**2B** ratio in the zeolite closer to 1.0 than observed in solution. This is exactly what was observed experimentally for all the tetrasubstituted olefins (Table 1).

This new mechanistic model for singlet oxygen ene reactions in the supercages of NaY also receives support from, and provides satisfying explanations for, other experimental observations. For example:

(i) the isotope effect ($k_H/k_D$) for the photoxidation of *Z*-2,3-dimethyl-1,1,1,4,4,4-hexadeutero-2-butene, **3**, was 1.04±0.02. This is consistent with a perepoxide intermediate and completely inconsistent with an open zwitterion, **4**, which would be expected to collapse to the hydroperoxide with a significant discrimination for hydrogen abstraction ($k_H/k_D > 1$);

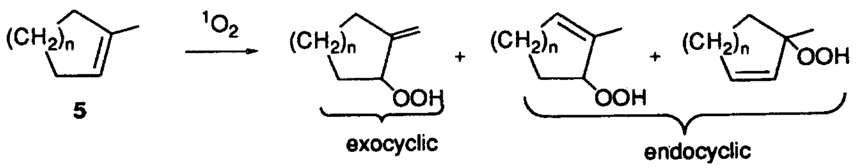


**3**

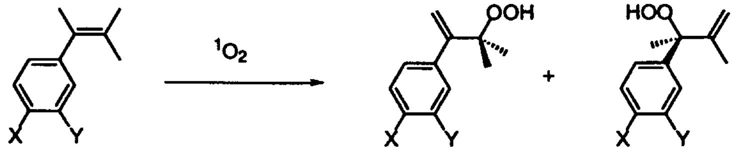


**4**

(ii) the shift from endocyclic to exocyclic hydrogen abstraction in the ene reactions of 1-methylcycloalkenes, **5**,[3] as the reaction is moved from solution to the interior of the zeolite is consistent with severe steric interactions in over-the-ring complexation in the perepoxide.



(iii) the regiochemistries of the singlet oxygen ene reactions of $\alpha,\beta,\beta'$-trimethylstyrenes, **6**, are nearly independent of aryl substituent in homogeneous photooxidations conducted in $CH_3OH$ with 2% pyridine.[8] We have also verified a lack of a substituent effect in solution ($CH_3CN$) with a Hammett $\rho=-0.016$ when $\log[(\%\mathbf{6A}_{X\text{ or }Y})/(\%\mathbf{6A}_H)]$ is plotted versus $\sigma^+$ for *para* substituents X and versus $\sigma_m$ for *meta* substituents Y ($r$=0.77604), corresponding to a change from 72% **6A** in the reactions of **6** (X=H; Y=Cl) to 74% **6A** in the reaction of **6** (X=MeO; Y=H). In contrast, the same plot for photooxidations in NaMBY gives a Hammett plot ($\rho=-0.17$; $r$=0.97034) corresponding to a change from 58.6% **6A** in the reactions of **6** (X=H; Y=Cl) to 95.2% **6A** in the reaction of **6** (X=MeO; Y=H) revealing a dramatic affect of aryl substituents. These results are consistent with a greater buildup of charge on the carbon framework in the zeolite in comparison to solution photooxidations in $CH_3CN$. Carbocation rearrangements similar to those reported for *p*-methoxystyrene in CaY were not observed in the reactions of **6** in the NaMBY environment used in this study.[9]



**6** **6A** **6B**

This new mechanistic model to predict singlet oxygen ene stereo- and regiochemistry provides a powerful new tool for the rational synthetic design of important naturally occurring allylic hydroperoxides.

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## References

1. Schenck, G. O.; Eggert, H.; Denk, W. *Liebigs Ann. Chem.* **1953**, *584*, 177–181.
2. Frimer, A. A.; Stephenson, L. M. *Singlet $O_2$. Reaction Modes and Products*; A. A. Frimer, Ed.; CRC Press: Florida, 1985; Vol. 2, pp. 67–91.
3. Li, X.; Ramamurthy, V. *J. Am. Chem. Soc.* **1996**, *118*, 10666–10667.
4. Robbins, R. J.; Ramamurthy, V. *Chem. Commun.* **1997**, 1071–1072.
5. Results observed in our zeolitic medium for the photooxidation of **1**, identical to those reported by Ramamurthy and coworkers,[3,4] verify the similarity of batches of NaY used in our laboratories.
6. Clennan, E. L.; Chen, X.; Koola, J. J. *J. Am. Chem. Soc.* **1990**, *112*, 5193–5199.
7. Ramamurthy, V.; Sanderson, D. R.; Eaton, D. F. *J. Am. Chem. Soc.* **1993**, *115*, 10438–10439.
8. Foote, C. S.; Denny, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5162–5167.
9. Ramamurthy, V.; Lakshminarasimhan, P.; Grey, C. P.; Johnston, L. J. *Chem. Commun.* **1998**, 2411–2424.