

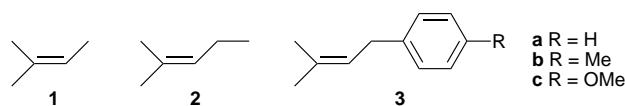
Generation and reactivity of singlet oxygen within zeolites: remarkable control of hydroperoxidation of alkenes

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A highly selective oxidation of alkenes included within a Y zeolite is achieved by generating singlet oxygen *via* excitation of a monomeric dye exchanged within a zeolite; conformational control brought forth by the medium is suggested to be responsible for the observed remarkable selectivity.

One well known reaction of singlet oxygen is the hydroperoxidation of alkenes containing allylic hydrogens, often referred to as the 'ene' reaction or Schenk reaction.¹ Reaction with substrates containing several distinct allylic hydrogens produces several distinct products. Although the peroxidation *via* singlet oxygen has found much synthetic application, regio- and stereo-control are still difficult issues.² We show here that the interior of a zeolite offers one possible solution to this important problem. When the oxidation of alkenes **1–3** is conducted within the supercages of faujasite Y type zeolite a remarkable selectivity of the hydroperoxidation is observed.

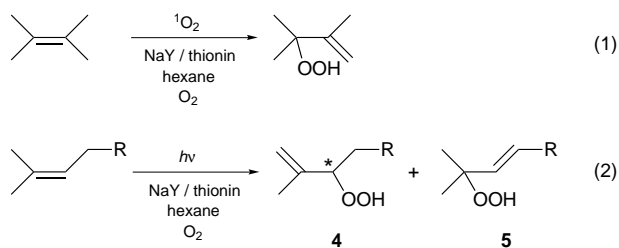


Although the mechanistic details of the ene reaction are still being debated, certain trends have been identified.³ Experiments by several groups have brought out the importance of the geometrical arrangement of the allylic hydrogens with respect to the attacking singlet oxygen during the hydroperoxide formation.⁴ This suggested to us that if one succeeds in controlling the conformation of the alkene and thus the accessibility of the allylic hydrogen(s) to the reagent, singlet oxygen, one might be able to achieve selectivity in the oxidation process. We have already established that one can use zeolite as a medium to achieve conformational control on ketones that undergo Norrish type reactions.⁵ With this in mind, we set out to use a similar strategy to demonstrate that zeolite can play a vital role in oxidation processes initiated by singlet oxygen. Indeed, this strategy has yielded remarkable results in terms of obtaining predominantly a single hydroperoxide from the alkenes **1–3** within the supramolecular assembly of alkene, thiazine dye, oxygen and zeolite.

In our system, generation of singlet oxygen entails irradiation of a thiazine dye located within the supercages of the zeolite lattice. These dyes (thionin, methylene blue and methylene green) are placed within the zeolite *via* a cation-exchange process.⁶ The exchange involves dropping the zeolite (*e.g.* 600 mg unactivated NaY) in a prestirred aqueous solution of thionin (2 mg in 250 ml of water). Continuous stirring for 3 h followed by filtration and aqueous washes (or Soxhlet extraction) yields a pink zeolite. The presence of water in the zeolite has a dramatic effect on the state of aggregation of the organic dye within the zeolite cage. With coadsorbed water or in 'wet' zeolite, thionin exists as a dimer, whereas in 'dry' zeolite the organic dye exists as a monomer and as a result the zeolite turns blue.⁶ It is only the monomeric form of the dye which functions as a sensitizer and generates singlet oxygen. Initial experimentation showed that in the absence of alkene, irradiation of

'dry' Na Y/thionin/oxygen generated an emission at 1268 nm corresponding to ¹O₂. Irradiation of the dye-exchanged zeolite in the presence of 2,3-dimethylbut-2-ene, a standard alkene known to react with singlet oxygen, gave the same hydroperoxide as in the isotropic solution medium [Scheme 1, eqn. (1)].⁷ This demonstrated that not only was ¹O₂ generated in the zeolites, but that it was reactive as well.

Having established that generation of singlet oxygen within a zeolite is feasible, we tested our conformational control proposition with the alkenes **1–3a–c**. Irradiation took place in a Kimax tube containing a zeolite and alkene as a slurry in hexane. Product hydroperoxide(s) were extracted from the zeolite with tetrahydrofuran and were analysed by GC and NMR after reduction with PPh₃. The only products obtained are those reported. The isolated yield ranged between 65 and 75%. Products were compared and found consistent with literature reports.⁸ Table 1 compares the ratio of secondary (**4**) to tertiary



Scheme 1

Table 1 A comparison of the ratio of secondary to tertiary hydroperoxides in various media

Alkene	Conditions	Secondary hydroperoxide 4	Tertiary hydroperoxide 5
1	Thionin/MeCN	51	49
	Rose Bengal/MeCN	50	50
	NaY/thionin	72	28
2	Thionin/MeCN	40	60
	NaY/thionin	100	—
3a	Thionin/MeCN	50	50
	Rose Bengal/MeCN	54	46
	LiY/thionin	100	—
	NaY/thionin	85	15
	RbY/thionin	80	20
3b	CsY/thionin	66	34
	Rose Bengal/MeCN	56	44
	LiY/thionin	100	—
	NaY/thionin	100	—
3c	RbY/thionin	94	6
	CsY/thionin	92	8
	Rose Bengal/MeCN	52	48
	LiY/thionin	100	—
	NaY/thionin	100	—
RbY/thionin	100	—	
CsY/thionin	100	—	

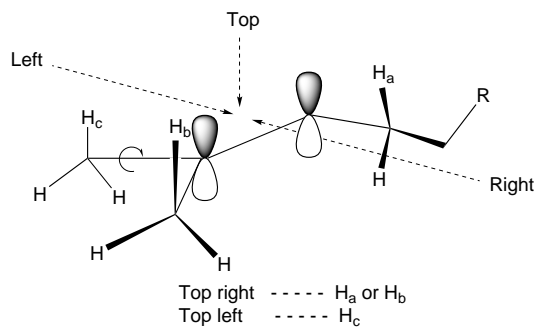


Fig. 1

(5) hydroperoxides obtained in an acetonitrile solution to that obtained in the zeolite oxidation reaction. For additional confirmation, the tertiary alcohol product of **3a** was independently synthesized as an authentic sample. Retention times and NMR of the authentic samples are consistent with the observed products. Also, the hydroperoxides generated from Rose Bengal sensitized oxidation were stirred overnight in a slurry of hexane and NaY/thionin. Both products were recovered in the same ratio as prior to zeolite treatment. These control experiments confirmed that the observed unprecedented selectivity is not an experimental artifact.

Formation of both hydroperoxides **4** and **5** in solution has been rationalized on the basis that singlet oxygen attacks the alkene from the top-right side (Fig. 1).⁴ In such an approach, the transition state is stabilized by secondary interactions between the oxygen and the allylic hydrogens which are situated parallel to the π -p orbitals. As per this accepted model the methyl group on the top-left side (Fig. 1) does not participate in the oxidation process. Results within the zeolites clearly suggest that the methylene hydrogens H_a of **2** and **3** (Fig. 1) are not abstracted by the singlet oxygen. While the lack of formation of **5** within zeolites is an indication that the methylene hydrogens are excluded from the reaction, selective formation of **4** does not indicate which of the two (or both) methyl groups participates in the oxidation process. Without further experiments that would distinguish between the *gem* dimethyl groups, we can only provide a tentative model for the observed selectivity.

We suggest that the R group in the alkene (Fig. 1) plays a crucial role in the type of product(s) formed. While in solution, the most favoured conformation places both the methyl and methylene hydrogens in an appropriate geometry for abstraction (Fig. 1), it is quite likely that such a conformation may not be favoured within a zeolite. In a supramolecular assembly one will have to consider the interactions that arise between the adsorbent/guest and the environment. We speculate that within a zeolite, the alkene will be adsorbed to the surface *via* cation- π interactions.⁹ A rotation of the C³-C⁴ bond might result under such conditions to relieve the steric strain that develops between the bulky R group and the surface. Such a rotation will place the methylene hydrogens away from the incoming singlet oxygen (Fig. 2) and therefore no tertiary hydroperoxide would be formed. The extent of steric repulsion between the surface and the R group may depend on the distance between the group and the surface. Larger cations such as Cs ion may place the alkene slightly further from the surface and thus reduce the steric strain between the surface and the R group. Formation of small amounts of tertiary hydroperoxide **5** in the case of **3a** and **3b** is

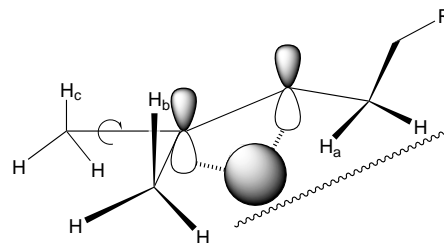


Fig. 2

consistent with this speculation. A comparison of the product distribution from **1** and **2** (and **3**) makes it clear that in order to achieve selectivity it is necessary to replace at least one hydrogen of the methyl group (in **1**) by a larger group such as methyl or phenyl. We recognize that the above model is only a working hypothesis and further experiments are needed to understand this unusual selectivity. The use of zeolite as a medium to achieve selective oxidation has been established and we are in the process of exploring this strategy with other alkenes. The ability to generate singlet oxygen and to achieve regioselective hydroperoxidation of alkenes within a zeolite has prompted us to consider stereoselective hydroperoxidation of alkenes with zeolite as the medium.¹⁰

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Footnote

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