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Cation controlled singlet oxygen mediated oxidation of olefins within zeolites

Lakshmi S. Kaanumalle, J. Shailaja, Rebecca J. Robbins, V. Ramamurthy*

Department of Chemistry, Tulane University, New Orleans, LA 70118, USA

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Dedicated to Prof. K. Venkatesan on the occasion of his 70th birthday

Abstract

Oxidation of trialkyl olefins has been performed within zeolites employing thionin as the singlet oxygen sensitizer. Unusual selectivity in favor of secondary hydroperoxides is observed within zeolites. In light of the fact that in solution such a selectivity is never observed the selectivity reported here is of great significance. Based on computational results the observed selectivity is attributed to conformational control of the reactant olefins by cations present in zeolites. Cation-π interaction seems to control the behavior of the olefins towards singlet oxygen within zeolites.

Keywords: Olefins; Oxidation; Zeolites

1. Introduction

A decade ago three research groups independently developed methods to include dyes such as thionin and methylene blue within Y and L zeolites, and investigated their spectroscopic properties with different aims [1–3]. Calzaferri et al. focussed their studies on using dye included L zeolites for the purpose of light harvesting [4]. Schulz-Ekloff et al. directed their investigations towards developing dye included zeolites for electro-optical applications [5]. Our group concentrated its efforts in using thionin exchanged zeolites as media for selective oxidation of olefins [6]. We demonstrated in 1996 that there is regioselectivity during the singlet oxygen mediated oxidation of trialkyl alkenes (Scheme 1, Eq. (1)) [6,7]. Because of the absence of ‘cis effect’, within LiY and NaY one obtains the secondary hydroperoxides as the major products instead of equal amounts of secondary and tertiary hydroperoxides. Such a type of selectivity is rarely observed during the singlet oxygen mediated oxidation of trialkyl alkenes in solution [8]. In light of this rarity, the observed behavior within zeolites is unique and this prompted the attention of the singlet oxygen community, especially that of Stratakis et al. [9], Clennan and Sram [10], and Stratakis and co-workers [11]. In a remarkable set of experiments Clennan and Sram while confirming our results showed that singlet oxygen attacks the olefin from both sides (singly substituted and doubly substituted) with nearly equal ease to yield the secondary hydroperoxide as the major product (Scheme 1, Eq. (2)) [10]. Studies by Stratakis and co-workers also showed that the oxidation in favor of secondary hydroperoxides occurs within thionin doped NaY zeolites [11]. At this stage the remarkable selectivity in favor of secondary hydroperoxides and absence of ‘cis effect’ within zeolites seem secure. However, the potential synthetic use of this reaction is suppressed by the fact that the product hydroperoxides and the dye themselves are photochemically less stable within zeolites [12]. Independent of this drawback, the mechanistic understanding of this process is challenging and intrinsically interesting.

Two fundamental questions need to be addressed: (a) Why does the ‘cis effect’ not operate within a zeolite? (b) What drives the electrophilic singlet oxygen to attack a cation bound olefin which is electron deficient? It has been established that singlet oxygen prefers to attack the trialkyl olefins from the doubly substituted side (in solution) due to better secondary orbital interaction with two α C–H bonds as opposed to one from the less substituted side (Scheme 2a). We postulated that within NaY zeolite steric interaction between zeolite bound cation and olefin would prevent one of the two α C–H bonds (more substituted alkyl group) from becoming parallel to the π-orbitals (Scheme 2b) [12]. This phenomenon removes the advantage of singlet oxygen attacking the olefin from the more substituted side. However,

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* Corresponding author. Tel.: +1-504-862-8135; fax: +1-504-865-5596.
E-mail address: murthy@tulane.edu (V. Ramamurthy).

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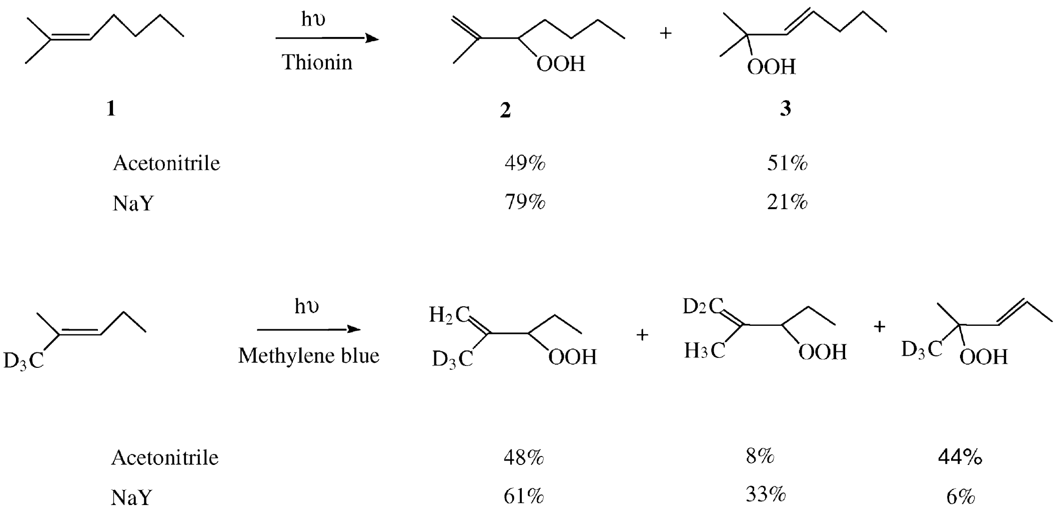


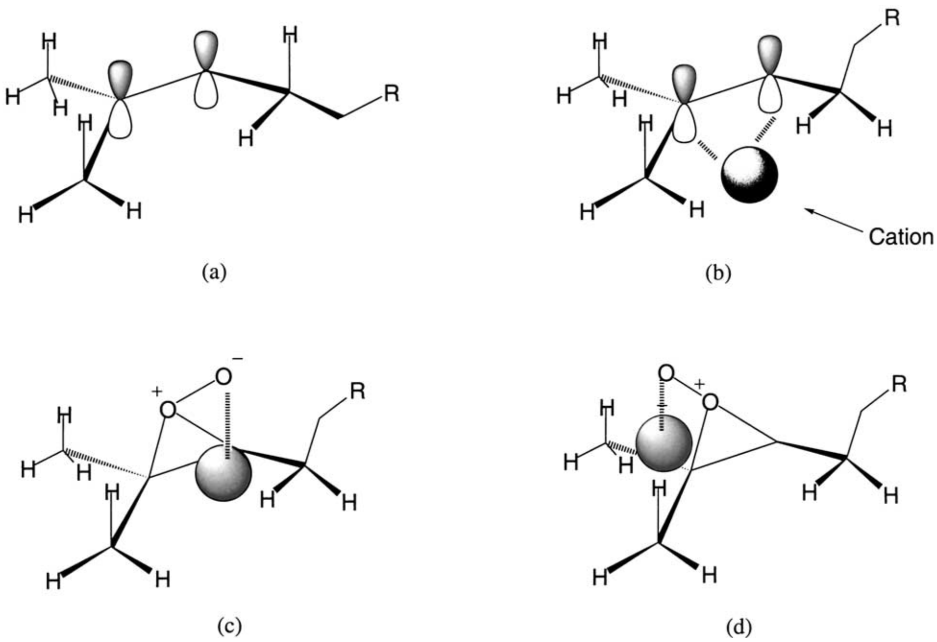
	2	3
Acetonitrile	49%	51%
NaY	79%	21%

Acetonitrile	48%	8%	44%
NaY	61%	33%	6%

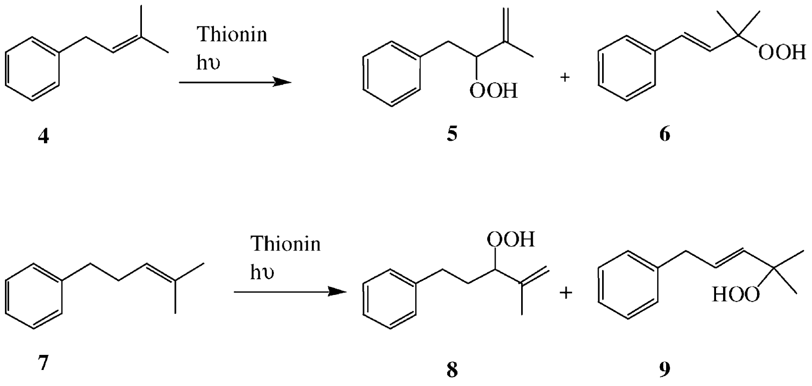
Scheme 1.

this model does not address the reactivity question. Clennan and co-workers have proposed that the transition state for the formation of perepoxide intermediate within zeolites would be lowered due to interaction between the perepoxide negatively charged oxygen and Na^+ ion (Scheme 2c and d) [10,13]. Thus in spite of the olefin being electron deficient the reaction would have lower activation energy due to stabilization of the perepoxide intermediate by Na^+ ion. A combination of ideas proposed by Clennan and us account for the observed selectivity during the oxidation of numerous olefins within zeolites [14].

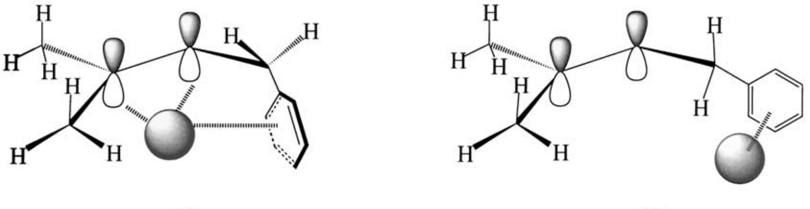
As discussed above, in trialkyl olefins such as **1** the selectivity is due to non-alignment of one of the α C–H bonds due to interaction between the surface of the zeolite and the bulky alkyl group (Scheme 2b). To further explore the conformational control model we have investigated the oxidation of olefins **4** and **7** that contain an aryl group (instead of alkyl) at the α or β positions (Scheme 3). In these systems we visualized that cation would either bind co-operatively to both olefin and aryl groups in which case the secondary hydroperoxide would be favored or preferentially bind to the aryl group in which case there would be no selectivity (Scheme 4). Preliminary results on olefin **4** presented by us earlier showed that this olefin also, similar to 2-methyl-2-heptene undergoes selective oxidation within Y zeolites [15]. Following the appearance of our prelimi-



Scheme 2.



Scheme 3.



(a) (b)

Scheme 4.

nary communication the same system has been investigated by Stratakis and Froudakis [16]. Results accumulated on olefins **4** and **7** in our laboratory are presented below. These should be of help in a comprehensive understanding of the cation controlled oxidation of olefins.

2. Results

In this study the oxidation behavior of two olefins (4-phenyl-2-methyl-2-butene **4**, and 5-phenyl-2-methyl-2-pentene **7**) within zeolites are examined. During our previous studies we had recognized that thionin decomposes within zeolites, especially within RbY and CsY [12]. Therefore, irradiations were carried out for less than 15 min. Further the product peroxides themselves were found to be unstable within zeolites under both thermal and photolytic conditions. This prompted us to examine the product ratios at 5 min irradiation time. Even 15 min irradiation resulted in decomposition of product hydroperoxides. Our main concern in this study is to examine the influence of zeolite on the product distribution with respect to that in solution. Results of these experiments are summarized in Table 1.

The experimental protocol adopted to achieve oxidation of alkenes within zeolites is as follows. The pink NaY/thionin sample (300 mg) was dried in an air oven at 120 °C for 24 h by which time the sample turned to blue color. The 'dry' NaY/thionin sample was dropped into a dry hexane solution (12 ml) containing the alkene (12 μl) of interest. The mixture was stirred, bubbled with oxygen and irradiated with a 450 W medium pressure mercury lamp fitted with a Corning filter CS #3.73 (>420 nm). Following 5 or 15 min irradiation, the slurry was filtered, the hexane filtrate analyzed for products and unreacted alkene by GC. The hydroperoxide products from the zeolite residue were extracted by stirring the residue with either acetonitrile or tetrahydrofuran-water (5%) mixture for about 12 h. For ease of GC analysis, the product hydroperoxides were converted to the corresponding alcohols by the addition of excess triphenyl phosphine. The oxidation products were characterized by ^{1}H NMR and by comparison with authentic samples prepared by solution irradiation and analyzed by GC. The recovery (mass balance) was estimated by GC using undecane or hexadecane as the calibration standards. The results obtained for 5 and 15 min irradiation times are provided in Table 1.

In solution both olefins **4** and **7** give secondary and tertiary hydroperoxides (Scheme 3) in nearly 1:1 ratio. However, within zeolites except in the case of CsY, the product ratios were not 1:1 but were in favor of secondary hydroperoxide. When the irradiations were conducted for longer than 30 min the product mixture contained only the secondary hydroperoxide. The mass balance estimated by GC using internal standard showed that it is better (>85%) for 5 min irradiations, but it dropped to less than 50% for 15 min irradiations. Because of this the ratios given for 5 min irradiations are mechanistically more significant than the 15 min data. This observation as well as that made on 2-methyl-2-heptene and 1-methylcyclooctene previously

Table 1
Photo-oxidation of 5-phenyl-2-methyl-2-pentene and 4-phenyl-2-methyl-2-butene

Medium	Relative ratio[a] (tertiary:secondary hydroperoxides) (5 min)	Mass balance (%)[b]	Relative ratio[a] (tertiary:secondary hydroperoxides) (15 min)	Mass balance (%)[b]
5-Phenyl-2-methyl-2-pentene				
CH_3CN/rose Bengal	49:51	98	50:50	95
LiY/thionin	5:95	85	0:100	41
NaY/thionin	10:90	85	7:93	50
KY/thionin	20:80	88	17:83	55
RbY/thionin	30:70	92	28:72	85
CsY/thionin	45:55	90	48:52	87
4-Phenyl-2-methyl-2-butene				
CH_3CN/rose Bengal	47:53	95	46:54	95
LiY/thionin	5:95	85	0:100	47
NaY/thionin	12:88	88	0:100	66
KY/thionin	18:82	90	12:88	71
RbY/thionin	30:70	95	17:83	68
CsY/thionin	48:52	95	42:58	80

In all cases the reactant olefin was found to be present completely inside the zeolite. None was present in the hexane solvent prior to irradiation.

[a] The alcohols were analyzed by GC (obtained by converting the peroxides using PPh_3); an average of three runs is provided with an error limit of ±3%.

[b] Mass balance calculated using internal standard (undecane or hexadecane) by GC analyses.

lead us to conclude that to obtain the true selectivity one needs to keep the time of irradiation short [12]. An important point to note is that the oxidation within a zeolite occurs with significant regioselectivity. Based on the data provided in Table 1 we believe that there is selectivity towards the secondary hydroperoxide within a zeolite. The observed regioselectivity depends on the M^+ ion. Generally, Li^+ and Na^+ ions give higher selectivity while Cs^+ gives lower selectivity.

An important point to note is that the two olefins investigated here remained inside the zeolite and none remained in the hexane layer. This is different from olefins such as 2-methyl-2-heptene with no aromatic groups which we investigated previously where only 10% of the olefin tended to remain within a zeolite [12]. The product hydroperoxide also preferred the zeolite surface over the hexane solvent. GC analyses at the end of the oxidation detected no hydroperoxide and the unreacted olefin in the hexane layer. Thus we believe that the oxidation of olefins **4** and **7** occurs truly within a zeolite. In order to be able to interpret the observed results with some confidence the thermal and photo stabilities of the hydroperoxides were independently tested and results are summarized in Table 2. Clearly the hydroperoxides from 4-phenyl-2-methyl-2-butene are much less stable than the ones from 5-phenyl-2-methyl-2-pentene. Also a point to note is that the hydroperoxides are much less stable within LiY and NaY than in other zeolites. Unfortunately, the selectivity in the oxidation occurs within the same zeolites where the hydroperoxides are also less stable. Since for experiments with 5 min irradiation the mass balance was fairly good (>85%) we believe that the selectivity in favor of secondary hydroperoxides observed within LiY and NaY are meaningful. We believe that when interpreting the results of long irradiations within zeolites one needs to be cautious. According to control experiments the tertiary hydroperoxides as well as tertiary alcohols tend to decompose within zeolites under both photolytic and thermal conditions. We did not pursue experiments to probe the origin of poor stability of these compounds within MY zeolites and also we did not characterize the products of decomposition of hydroperoxides.

In order to obtain more insight into the role of cations on the observed product distributions, ab initio and DFT calculations were carried out on olefins **4** and **7** by using the Titan program [17]. In view of the complexities involved in the reactions inside the zeolite cage, the goals of the computational work were necessarily limited to a few specific aspects. First, the magnitude of the interaction energies between various cations and olefins were quantified. These provide a measure of the potential role of different cations in altering the reactivity of the olefins with singlet oxygen. In addition to the energies, unsymmetrical distortions in the optimized geometries were analyzed.

The geometries of olefins **4** and **7** coordinated to different metal cations, Li^+, Na^+, K^+, Rb^+, and Cs^+ were optimized at the Hartree-Fock (HF) and hybrid HF and density functional method (B3LYP) levels. The 6-31G* basis set including polarization functions on all atoms (d for heavy atoms, p for hydrogens) was employed for all calculations. For the heavier elements, K, Rb, and Cs, psuedo-potentials (core potentials) basis sets were used. The computed interaction energies, without corrections for basis set superposition errors as well as zero point and thermal energy terms, are provided in Table 3. As expected, the strength of the interaction is relatively large for Li^+ and Na^+, and becomes progressively smaller for the heavier alkali metal cations [18]. The Cs^+ complex is very weakly bound. By placing the cation at various positions near the olefin one minimum

Table 2
Stability of the hydroperoxides of 5-phenyl-2-methyl-2-pentene and 4-phenyl-2-methyl-2-butene inside zeolite

Zeolite	Condition	Relative ratio after irradiaton[a,b] (tertiary:secondary hydroperoxides)	Mass balance (%)[c]
Hydroperoxides of 5-phenyl-2-methyl-2-pentene			
LiY/thionin	No ($h\nu$, O_2/N_2)	5:95	59
NaY/thionin		28:72	69
KY/thionin		40:60	95
RbY/thionin		42:58	94
CsY/thionin		48:52	97
LiY/thionin	$h\nu$, O_2	6:94	54
NaY/thionin		28:72	60
KY/thionin		45:55	94
RbY/thionin		48:52	95
CsY/thionin		46:54	87
Hydroperoxides of 4-phenyl-2-methyl-2-butene			
LiY/thionin	No ($h\nu$, O_2/N_2)	0:100	56
NaY/thionin		0:100	52
KY/thionin		33:67	85
RbY/thionin		30:70	80
CsY/thionin		40:60	85
LiY/thionin	$h\nu$, O_2	0:100	60
NaY/thionin		0:100	55
KY/thionin		28:72	61
RbY/thionin		26:74	74
CsY/thionin		38:62	66

[a] Initial ratio of tertiary:secondary hydroperoxides = 49:51.
[b] The peroxides were analyzed as alcohols by GC. An average of three runs is provided with an error limit of ±3%.
[c] Mass balance calculated based on GC using hexadecane as internal standard.

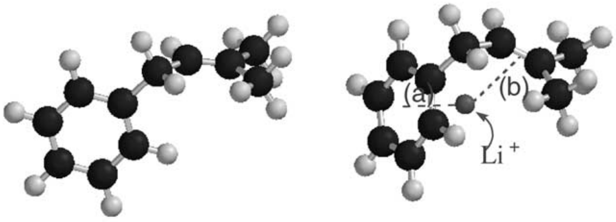
energy structure for cation bound olefin **4** and two for cation bound olefin **7** were obtained (Scheme 5). One point to note is that the cation bound simultaneously to olefinic and aromatic π-orbitals is more stable than to aromatic π-orbitals alone.

Within a zeolite, the cations are bound to oxygen counterions. As a result, the metal ions are likely to interact less effectively than usual with an olefin. Nevertheless, the trends in the relative binding energies are expected to be similar to those computed for the free cations. Of the cations examined,

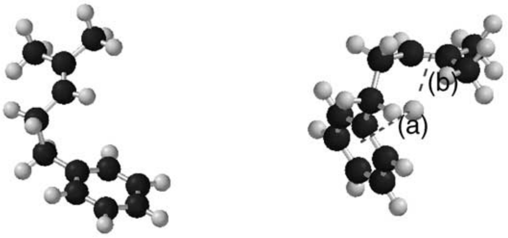
Table 3
Calculated distances between cation and aryl ring and C=C bond and interaction energies between action and olefins at two theoretical levels

Cation (M^+)	Benzene M^+[a] (Å)	C=C M^+[b] (Å)	Binding energy (kcal/mol)
5-Phenyl-2-methyl-2-pentene (unfolded form)			
Li	1.918 (1.852)	3.929 (3.872)	−44.80 (−46.75)
Na	2.438 (2.361)	4.064 (3.913)	−29.99 (−32.63)
K	3.014 (2.990)	4.185 (4.186)	−16.94 (−12.55)
Rb	3.116 (3.155)	4.291 (4.517)	−12.74 (−09.41)
Cs	3.475 (3.456)	4.682 (4.711)	−10.04 (−6.28)
5-Phenyl-2-methyl-2-pentene (folded form)			
Li	2.007 (1.942)	2.403 (2.351)	−51.76 (−56.79)
Na	2.478 (2.417)	2.789 (2.688)	−34.51 (−40.16)
K	3.016 (2.973)	3.409 (3.258)	−19.45 (−16.44)
Rb	3.265 (3.183)	3.588 (3.536)	−17.57 (−11.92)
Cs	3.534 (3.439)	3.845 (3.792)	−10.67 (−07.53)
4-Phenyl-2-methyl-2-butene (folded form)			
Li	2.013 (2.002)	2.727 (2.498)	−48.26 (−51.08)
Na	2.501 (2.449)	2.923 (2.772)	−33.26 (−37.65)
K	3.015 (2.973)	3.399 (3.336)	−23.22 (−17.57)
Rb	3.268 (3.200)	3.611 (3.530)	−18.19 (−12.55)
Cs	3.530 (3.461)	3.844 (3.785)	−11.92 (−09.60)

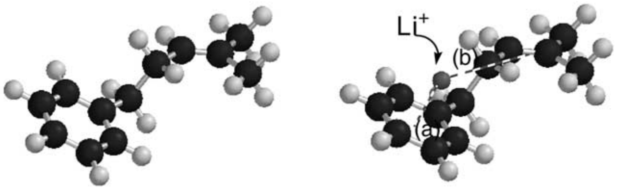
The numbers are obtained via HF 6-31G* for (Li and Na), and LACVP* for K, Rb and Cs. The numbers in parenthesis were obtained via B3LYP 6-31G* for (Li and Na), and LACVP* for (K, Rb and Cs).
[a] Distance marked (a) in Scheme 5.
[b] Distance marked (b) in Scheme 5.



4-Phenyl-2-methyl-2-butene-folded form



5-Phenyl-2-methyl-2-pentene-folded form



5-Phenyl-2-methyl-2-pentene - Unfolded form

Scheme 5. Distance between (a) Li^+ and the center of the benzene ring; and (b) Li^+ and the center of the C=C.

Li^+ and Na^+ are predicted to have the strongest interaction with alkenes. Considering the stronger binding of olefins **4** and **7** compared to 2-methyl-2-butene to cations (e.g. binding energy of Na^+ ion to 2-methyl-2-butene is −31.3, to olefin **4** −37.65, and to alkene **7** −40.16 kcal/mol), olefins **4** and **7** are expected to be adsorbed within zeolites more strongly than trialkyl ethylenes with no aryl substituents. Consistent with this prediction, for the same loading levels, olefins **4** and **7** were completely adsorbed within dry NaY, while trialkyl alkene such as 2-methyl-2-heptene was adsorbed only to the extent of 10% during the oxidation process.

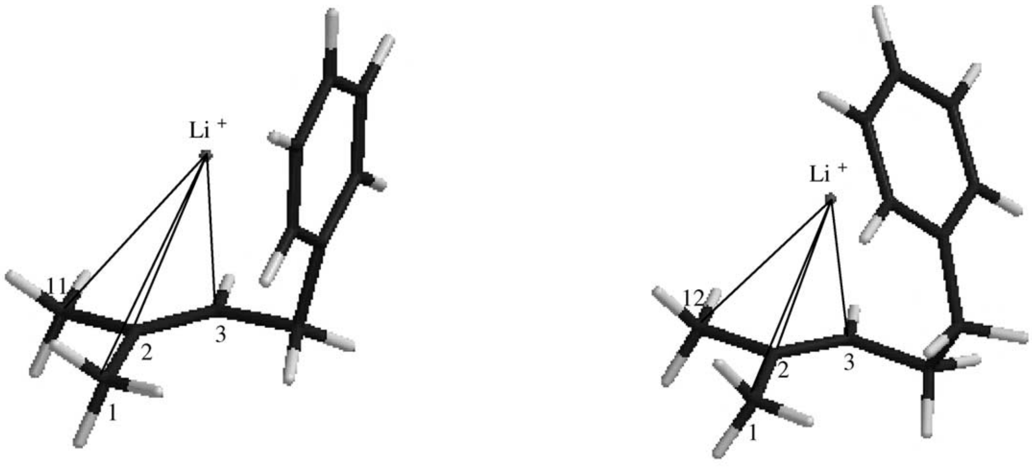
3. Discussion

Analysis of the results presented in Tables 1 and 2 reveal that singlet oxygen mediated oxidation of olefins **4** and **7** are more selective within Y zeolites than in solution. A nagging problem with oxidation studies in zeolites is that the product hydroperoxides are much less stable in zeolites than in solution. In spite of this problem, during short irradiation times selectivity in favor of the secondary hydroperoxides is observed.

Computational results are of considerable value in understanding the observed behavior within zeolites. We believe that the cation-π interaction holds the olefins **4** and **7** within MY zeolites [18]. As seen in Table 3, the interaction energies between cations such as Li^+ and Na^+, and the olefins are fairly large. Certainly the computed interaction energies in the case of olefins **4** and **7** are much higher than those computed earlier for olefins containing no aryl substituent [12]. For example, the interaction energies (B3LYP) between Li^+ and Na^+ to 2-methyl-2-butene are −31.3 and −21.5 kcal/mol, while that to olefin **7** are −56.79 and −40.16 and to olefin **4** are −51.08 and −37.75 kcal/mol, respectively. The higher interaction energies are due to co-operative interaction of olefin and aryl π-orbitals with the cation. As shown in Scheme 5 of the two structures identified in the case of olefin **7**, in only one the cation is bound both to olefin and aryl groups. In the unfolded structure where the cation is bound only to the aryl group the interaction energies are smaller than in the folded form (Li^+: −46.74 and Na^+: −32.63 kcal/mol). Because of higher interaction energies the folded structure shown in Scheme 5 for olefin **7** is the one that is likely to be important within zeolites. It is important to note that the computed interaction energies are for cation–olefin complexes in the gas phase. However, within zeolites the cations are bound to the framework of the zeolite. Whether the cation could be displaced from the wall to interact with the olefin would depend upon the difference in binding energies between the cation–wall and the cation–olefin interactions. It is also likely that the cation would be partially bound to the walls of the zeolite while interacting with the olefin. At this stage no experimental information on the structure of the cation–olefin complex within a zeolite is available. The binding energies of larger cations such as Rb^+ and Cs^+ to olefins **4** and **7** are small (Table 3), and therefore these cations are less likely to influence the oxidation behavior of olefins **4** and **7**. As seen in Table 1, the product distribution within CsY is similar to that in solution. The highest selectivity is observed in LiY and NaY, and it decreases with KY and RbY. This trend is consistent with the notion that cation–olefin binding plays an important role during the oxidation of olefins within zeolites.

Cation bound olefin is expected to be electron deficient and therefore one would expect them to be less reactive with electrophilic singlet oxygen [8]. From the product studies it is clear that the cation bound olefins are reactive towards singlet oxygen and expected hydroperoxides are formed. As suggested by Clennan the perepoxide is likely to be stabilized via interaction of the negatively charged oxygen with the cation (Scheme 2), and this feature is likely to make the cation bound olefin as reactive as a cation-free olefin [10].

Selectivity noted in Table 1 can be understood by examining the conformations of cation bound **4** and **7** (Scheme 5). As indicated earlier, the ‘cis effect’ in solution is a result of secondary orbital interaction between the incoming singlet oxygen and the two α-hydrogens (Scheme 2a) [7]. To be able to overlap with the π-orbitals of singlet oxygen the two α



4-phenyl-2-methyl-2-butene

	Li^+-C3	Li^+-C2	Li^+-C1	Li^+-C11
HF	2.71	3.10	3.81	3.82
B3LYP	2.50	2.87	3.63	3.60

The dihedral angle C_2-C_3-C_4-H: 20.9°

5-phenyl-2-methyl-2-pentene

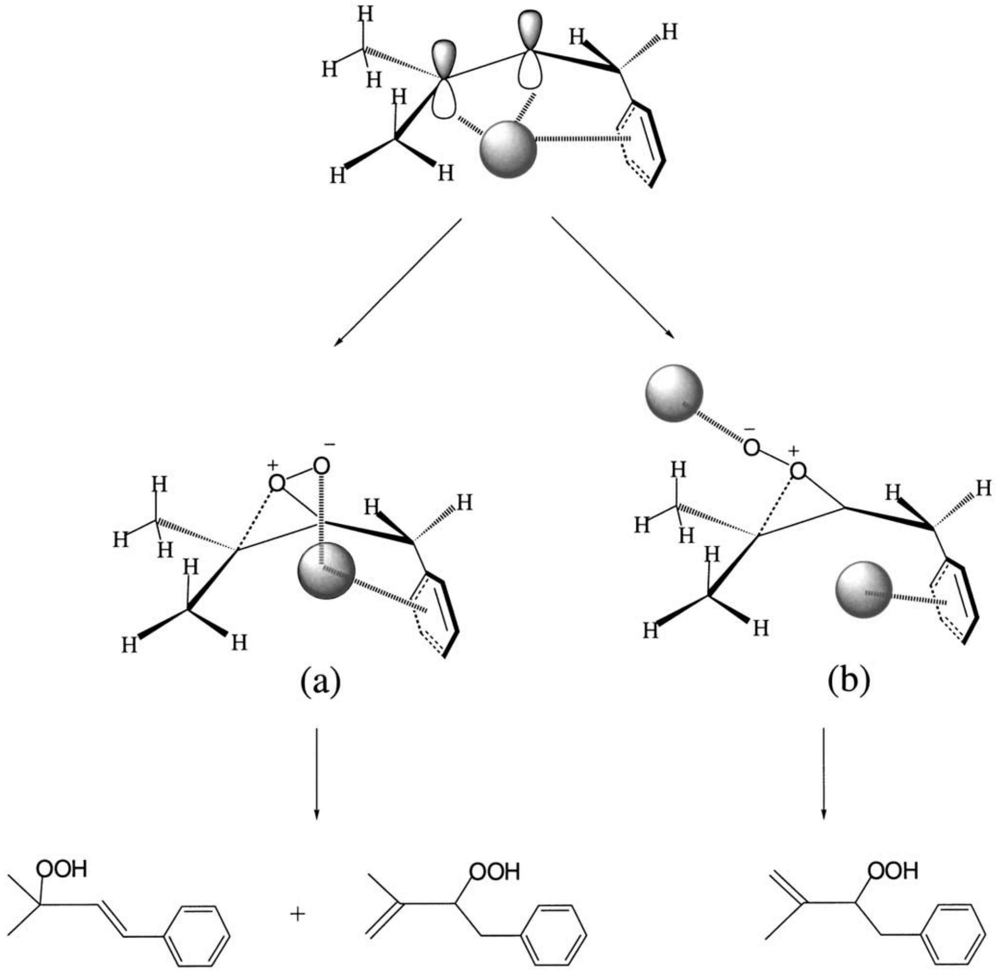
	Li^+-C3	Li^+-C2	Li^+-C1	Li^+-C12
HF	2.43	2.73	3.70	3.19
B3LYP	2.36	2.64	3.61	3.12

The dihedral angle C_2-C_3-C_4-H: 49.2°

Scheme 6. All distances are reported in Å.

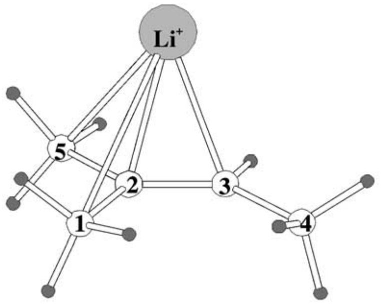
C–H bonds must align themselves perpendicular to the C–C bond, i.e. the H–C_4–C_3=C_2 dihedral angle must be close to 90°. Examination of the conformations of cation bound **4** and **7** show that the C_4–H is locked at a dihedral angle different from 90°; the dihedral angle in these two cases are 20.9 and 49.2°, respectively (Scheme 6). Although in the absence of cation these bonds are free to rotate to achieve the required alignment, in presence of cations the molecule is locked in a specific conformation and the C_4–H will not be able to achieve the required 90° angle. This would prevent the hydrogens present on C_4 from participating in the stabilization of the transition state during the formation of the perepoxide intermediate. Under such conditions there is no preference and the attack will occur from either side (less and more substituted sides). Only hydrogens that would participate in the reaction are the methyl hydrogens attached to C_2. The origin of selectivity in olefins **4** and **7** is slightly different from that noted earlier in the case of 2-methyl-2-heptene and related olefins [12]. In 2-methyl-2-heptene steric hindrance between the cation bound olefin and the surface of zeolite is believed to force the molecule to adopt a conformation in which the α-hydrogens present on C_4 have a dihedral angle different from 90° (H–C–C=C). In olefins **4** and **7** interaction of cation to both olefin and aromatic π-orbitals locks the molecule in a conformation in which the hydrogens present on C_4 have a dihedral angle that is not conducive for secondary orbital interaction with the incoming singlet oxygen.

By monitoring the isotope effect during the oxidation of *Z*-2,3-dimethyl-1,1,1,4,4,4-hexadeutero-2-butene, Clennan and Sram have established the involvement of perepoxide as an intermediate during singlet oxygen oxidation of zeolite bound olefins [10]. As indicated in Section 1 (Scheme 1, Eq. (2)) oxidation of appropriately deuterated olefin showed that both CH_3 and CD_3 are involved in hydroperoxidation. In the case of specifically deuterated olefin **4** a similar observation has been made by Stratakis and Froudakis [16]. These results are consistent with the model that two perepoxides (Scheme 7) are involved during the oxidation of olefins within a zeolite. An important difference between solution and zeolite as reaction media is that while in solution predominantly only one perepoxide (structure (a) in Scheme 7) is formed, within zeolites two ((a) and (b)) are formed. Whether the same cation bound to the olefin is also involved in the stabilization of the perepoxide is not clear. While in 2-methyl-2-heptene and related systems the cation initially bound to the olefin can move to stabilize the perepoxide, this is less likely in the systems investigated here. As illustrated in Scheme 8, the case of 2-methyl-2-butene, the cation bound to the olefin is slightly displaced towards the less substituted side. Once the olefin starts interacting with singlet oxygen it will loose its ability to bind to a cation. Under such conditions the cation is likely to move towards the negatively charged oxygen of the perepoxide. By this process both structures (a) and (b) (Scheme 7) could



Scheme 7.

be stablized by the zeolite cation. As illustrated in Scheme 6 even in 5-phenyl-2-methyl-2-pentene the cation bound to the olefin is displaced towards the less substituted side. In 4-phenyl-2-methyl-2-butene the cation is nearly at the top of the olefin π-bond. This may have to do with the fact that the methylene chain is not long enough to allow the phenyl to reach the less substituted side of the olefin **4**. A comparison of the computational results on olefins **4** and **7** suggest that the primary interaction of the cation is with the phenyl group. Therefore, in these two systems, even if the olefin reacts with singlet oxygen the cation will still be held in place by aryl-cation interaction. The fact that similar selectivity is obtained both in phenyl substituted olefins as well as in systems lacking phenyl substitution (compare 2-methyl-2-heptene and related systems with olefins **4** and **7**) suggests that the cation stabilization of the perepoxide intermediate is independent of the nature of the initial interaction between the cation and the olefin. Considering that zeolite supercage contains four type II cations, it is quite likely that a different cation might be involved in the stabilization of the structures (a) and (b). However, currently there are no experimental results to support this model.



	Li^+-C3	Li^+-C2	Li^+-C1	Li^+-C5
MP2	2.33	2.27	3.32	2.41
B3LYP	2.31	2.24	3.28	2.39

Scheme 8. Calculated key metal–carbon distances (Å) in Li^+ and Cs^+ complexes of trimethylethylene (for details see [12]).

The last topic concerns with the selectivity observed during the transformation of the perepoxide (a) (Scheme 7) to the products hydroperoxides. The fact that the secondary hydroperoxide is the major product suggests that the negatively charged oxygen end of the perepoxide (a) abstracts a proton from the methyl rather than the methylene end. We visualize two possibilities for this preference: (a) the two C–O bonds in perepoxide intermediate are not symmetrical and the bond connected to the carbon bearing two methyl groups is longer and/or (b) the methylene hydrogens are not properly aligned for abstraction due to binding of this end to the cation. Supported by ab initio calculations we had suggested that the electron density on the two olefinic carbons of cation bound 2-methyl-2-butene are not the same and the less substituted carbon is relatively more electron dense [12]. In Scheme 6 it can be seen that Li^+ is much closer to C3 than to C2 in both olefins **4** and **7**. Such a type of binding would polarize the olefin in such a way that the C3 end is electron rich. Due to this feature we believe that the transition state leading to the cation bound perepoxide would be unsymmetrical in olefins **4** and **7**, and the singlet oxygen will interact with C3 more than C2. Clennan has suggested that the structure of the perepoxide itself is unsymmetrical and this is the cause for the observed selectivity [14].

In the second model the selectivity results from the preference for singlet oxygen approach towards the olefin. In this case, the conformational control imposed on the olefin by the cation binding 'turns off' the preference for approach from the more substituted side. Even if the oxygen forms the perepoxide from the less substituted side, the methylene hydrogens would be free to realign itself to be abstracted by the negatively charged oxygen end. In this case once the olefin is transformed to the perepoxide there are no groups excepting the perepoxide oxygen that would be able to interact with the cation. This is not the case in olefins **4** and **7**. Phenyl substitution would restrict the mobility of the methylene group. The fact that the selectivity is observed in 2-methyl-2-heptene as well as in olefins **4** and **7** suggests that the main reason for the selective abstraction of the methyl rather than methylene protons is not the inability of the methylene hydrogens to align itself for abstraction. In all possibility the unsymmetrical structure of the perepoxide could be the main cause for the observed selectivity. At this stage this suggestion needs experimental verification.

We have shown in this report that the oxidation of olefins within a zeolite is selective and its origin is related to the cations present within the zeolite supercage. Computational results although deal with gas phase structures, provide an insight into the origin of selectivity within a zeolite. Conventional 'cis effect' observed during singlet oxygen oxidation in solution is suppressed within zeolites due to conformational restrictions enforced on the reactant olefin by cations through cation-π interactions. Cation binding to the perepoxide intermediate reduces the activation energy for the reaction of singlet oxygen with electron deficient cation bound olefin. Once the problems associated with oxidations in zeolites are addressed the regioselective oxidation of trialkyl olefins is likely to be synthetically useful.

4. Experimental

4.1. Materials

Hexane and acetonitrile (Fischer Scientific) were used without further distillation. Tetrahydrofuran (Fischer Scientific) was distilled over sodium to remove the peroxide impurities prior to use. Thionin (Aldrich) and NaY (CBV-100; Zeolyst International) were used as received. The olefins **4** and **7** were synthesized as described below.

4.2. Preparation of MY (M = Li, K, Rb, and Cs) zeolites from NaY

NaY zeolite (CBV-100; Zeolyst International) was exchanged with other alkali ions such as Li^+, K^+, Rb^+, and Cs^+ by refluxing 25 g of the unactivated NaY zeolite in 250 ml of 10% solution of the corresponding alkali metal nitrate for 24 h. The mixture was filtered, washed with de-ionized water and dried. The above procedure was repeated three times to ensure maximum exchange of cations of interest for Na^+ ions.

4.3. Preparation of thionin exchanged zeolites

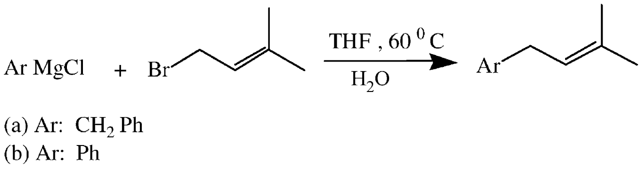
Thionin was exchanged into MY zeolite by stirring 5 g of the zeolite with 5 mg of the dye (thionin: 17.4 μmol) in 250 ml of de-ionized water for 24 h. The slurry was filtered and washed thoroughly with de-ionized water until the filtrate was colorless. The zeolite residue was air dried. The loading level was approximately one molecule in 100–150 supercages.

4.4. Synthesis of 5-phenyl-2-methyl-2-pentene and 4-phenyl-2-methyl-2-butene

The above two olefins were synthesized following the reactions outlined in Scheme 9.

4.5. Synthesis of 5-phenyl-2-methyl-2-pentene

In a dry nitrogen purged 250 ml three necked flask fitted with a reflux condenser, 60 ml of dry tetrahydrofuran, 8.6 ml of benzyl magnesium chloride (2.0 M solution in tetrahydrofuran from Aldrich) were added with the help of syringe under nitrogen atmosphere, followed by slow addition of 2.0 ml (17.4 mmol) of 4-bromo-2-methyl-2-butene



Scheme 9.

to the contents of the flask with constant stirring. Following refluxing for 2 h, water was added to the contents of the flask and the product was extracted with ethylacetate, the organic layer was dried with anhydrous magnesium sulfate and the solvent was removed in vacuum. The residue which was a colorless oil was purified by vacuum distillation to yield 5-phenyl-2-methyl-2-pentene (yield 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10–7.40 (m, 5H), 5.14–5.24 (m, 1H), 2.10–2.66 (t, 2H), 2.24–2.34 (m, 2H), 1.69 (s, 3H), and 1.56 (s, 3H).

4.6. Synthesis of 4-phenyl-2-methyl-2-butene

To a three necked flask fitted with a reflux condenser, 1.1 equivalent of magnesium, a pinch of iodine, 40 ml of dry tetrahydrofuran and bromobenzene (1 eq.) were added under nitrogen atmosphere. The mixture was refluxed for 3 h. 4-Bromo-2-methyl-2-butene (1 eq.) was added dropwise with a syringe and the mixture was refluxed 2 h more and then worked up with water. The olefin was extracted into ethyl acetate, dried over anhydrous magnesium sulfate and concentrated to yield the olefin, a colorless oil, which was purified by vacuum distillation to give 4-phenyl-2-methyl-2-butene in 50% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.10–7.50 (m, 5H), 5.25–5.40 (t, 1H), 3.36–3.40 (d, 2H), 1.70 (s, 3H), 1.83 (s, 3H).

4.7. Oxidation of 5-phenyl-2-methyl-2-pentene and 4-phenyl-2-methyl-2-butene in solution

Using rose Bengal as sensitizer, 12 μl of alkene in acetonitrile (5 ml) was irradiated using a 450 W medium pressure mercury lamp with a >420 nm filter (CS #3-73) with continuous purging of oxygen for duration listed in Table 1. The resulting hydroperoxides were converted to the corresponding alcohols by stirring with 25 mg (95 μmol) of triphenyl phosphine. The amounts of alcohols formed were estimated using GC with 2 μl (7.0 μmol) of hexadecane as calibration compound for **7** and undecane as calibration compound for **4**. The above reaction was repeated with deuterated acetonitrile in NMR tube. NMR analysis of the irradiated solution showed the presence of two distinct –OOH protons (δ 8.90 (s, 1H), 9.40 (s, 1H)) for hydroperoxides from **7** and (δ 9.05 (s, 1H), 9.45 (s, 1H)) for hydroperoxides from **4**. The alcohols prepared from hydroperoxides were identified based on their ^{1}H NMR and mass spectral data.

4.8. Oxidation of 5-phenyl-2-methyl-2-pentene and 4-phenyl-2-methyl-2-butene within zeolite

Thionin exchanged zeolite (300 mg) was dried in an oven at 120 °C for 24 h. The dried thionin exchanged zeolite was added to a test tube containing 12 ml of hexane and 12 μl of alkene. The hexane–zeolite/thionin slurry was irradiated (>420 nm filter (CS #3-73) using a 450 W medium pressure mercury lamp for durations listed in Table 1), while the solution was continuously purged with oxygen (dried using drierite). The slurry was then filtered and the filtrate (hexane supernatant) was analyzed by GC using internal standard (2 μl of hexadecane for **7**, or 2 μl of undecane for **4**) to estimate the amount of the unreacted alkene. The zeolite residue was then extracted three times with 5 ml of acetonitrile. The extracted hydroperoxides were converted to the corresponding alcohols by stirring with 25 mg (7.0 μmol) of triphenylphosphine. The amounts of alcohols formed were estimated by GC using 2 μl of calibration compound. The ^{1}H NMR and mass spectral data of the hydroperoxides were identical to the ones obtained during solution irradiation.

4.9. Testing thermal and photo stabilities of hydroperoxides within zeolites

Larger amounts (100 mg) of hydroperoxides from 5-phenyl-2-methyl-2-pentene and 4-phenyl-2-methyl-2-butene were prepared by the following procedure for testing their stability. Olefin (30 μl) in 10 ml of acetonitrile, 2 mg of rose Bengal were taken in a test tube and irradiated with 450 W medium pressure mercury lamp with light above $\lambda > 420$ nm (CS #3-73) with continuous purging of oxygen for 4 h. Solvent acetonitrile was evaporated, and hexane was added to the residue. The solution was filtered through a cotton plug to remove rose Bengal. The resulting solution containing hydroperoxides was divided into three fractions. To the first fraction triphenyl phosphine and calibration compound (3 μl; hexadecane or undecane) were added and the corresponding alcohols were analyzed by GC. This represented the initial ratio of the hydroperoxides. To the remaining two fractions of hydroperoxides in hexane dry thionin exchanged MY was added. One of them was irradiated ($\lambda > 420$ nm; CS #3-73) under positive pressure of oxygen and the other was kept in dark. Following this treatment the two hexane–zeolite slurries were filtered and the zeolite residues were extracted with acetonitrile twice. The hexane supernatant from the two extractions was analyzed for unreacted olefin and any other products. None were present in the hexane layer. The hydroperoxides present in acetonitrile extracts were converted to the alcohols by adding triphenyl phosphine and analyzed by GC using 2 μl of calibration compound. A comparison of the amounts of alcohols present before after gave an indication regarding the thermal and photo stabilities of hydroperoxides within thionin exchanged MY zeolites.

4.10. Theoretical calculations

Computational studies of the binding of alkali metal ions to 5-phenyl-2-methyl-2-pentene and 4-phenyl-2-methyl-2-butene were carried out using Titan program version 1.0.5 (Schrodinger Inc., Portland, OR) at the HF, density functional theory (B3LYP) levels. The polarized 6-31G* basis set was used for C, H, Li, and Na. For the heavier metal ions K, Rb, Cs pseudo-potential basis sets (core potentials) LACVP* were used.

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