A DFT Study on the Interaction of Li^+ and Na^+ with Alkyl-Substituted Ethenes

George E. Froudakis[a] and Manolis Stratakis*[a]

Keywords: Density functional calculations / Alkali metals / Pi interactions / Zeolites

The interaction of Li^+ and Na^+ with several alkyl-substituted ethenes was calculated by the DFT method. Two trends were found. The first is that, for the majority of alkenes, the cations do not bind on top of the double bond, but close to it, either towards the more- or the less-substituted side of the alkene. This type of interaction is found even with highly symmetrical alkenes such as tetramethylethene. The second trend is that there is a relatively strong interaction between both cations and the alkyl chains of the double bond at the homoallylic position. These calculations were correlated to regioselectivity results in the dye-sensitized photooxygenation of alkenes within alkali-metal exchanged zeolite Y.

Introduction

Computational and experimental studies on cation-π interactions have attracted significant attention recently, primarily due to their significance in biological systems.[1] They have also been proposed to play a significant role in intrazeolite reactions.[2] Zeolites are crystalline aluminosilicates whose primary structure is formed by edge-sharing SiO_4^{4-} and AlO_4^{5-} tetrahedra.[3] Uniform channels and cavities of molecular dimensions are repeated along the structure of the zeolite lattices. Due to the lower valence of the aluminum relative to silicon, an excess negative charge (one per Al atom) is balanced by alkali metal cations, mainly Na^+. The cations are placed in the interior of the cavities and can easily be exchanged.

The product distribution of organic reactions within alkali metal-exchanged zeolites is often different from reactions in homogeneous media, due to the so called "shape selectivity".[4] Furthermore, complexation of the alkali metal cations to the guest organic molecules (either reactants or products) inside the zeolite cages has been proposed to affect either the equilibrium of the reaction or the stability of the product-forming transition states. For example, the photosensitized isomerization of *trans*- to *cis*-1,2-diphenylcyclopropane within zeolite Y was postulated to proceed via the interaction of the cation with the π-system of the aryls.[5] Small cations such as Li^+ interact more efficiently with the *cis*-isomer, and at equilibrium the *cis*-1,2-diphenylcyclopropane prevails (91%); with larger cations, which interact less efficiently, the *cis*/*trans* ratio at equilibrium is lower (e.g. 65:35 for the Cs^+). Also, the stereoselective hydration of alkenes by traces of H_2O present within the cages of zeolite Li-Y[6] has been attributed to cation-π interactions.

Recently, we[7] and others[8,9] have examined the regioselectivity, stereoselectivity and diastereoselectivity in the singlet-oxygen ene reaction of trisubstituted alkenes within dye-supported zeolite Na-Y, and found remarkable differences in the distribution of the products compared to the reaction in solution. The proposed intrazeolite models consider that interaction of the alkali metal cation with the olefin π-bond is likely to affect the stability of the transition states of the ene hydroperoxidation reaction. Furthermore, complexation of the Na^+ to alkenylarenes was postulated recently to alter the chemoselectivity in their intrazeolite photooxygenation reaction.[10]

Theoretical calculations on the interaction of simple alkenes with alkali metal cations are very limited. Only the complexation of Na^+ to ethene,[11] propene[12] and isobutylene[12] has been reported so far. The vast majority of the literature studies on cation-π interactions deal with arenes. Alkali metal cations have been known to bind strongly on the π-face of aromatics. Surprisingly, the Na^+-benzene binding enthalpy is roughly equivalent to the binding enthalpy of Na^+ to H_2O.[1a,11c] Since this interaction is of great biological significance, several experimental and computational studies have been reported,[13] which mainly study the complexation of alkali metal cations or the ammonium ion with the aromatic moieties of amino acid side chains, such as benzene (in Phe), phenol (in Tyr), indole (in Trp) and imidazole (in His).

As part of our interest in the role of cation-π interactions in the product distribution of thermal and photochemical

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[a] Department of Chemistry, University of Crete,
71409 Iraklion, Greece
Fax: (internat.) +30-2810/393-601
E-mail: stratakis@chemistry.uoc.gr

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reactions within alkali metal-exchanged zeolite Y, we report in this paper a DFT study on the interaction of lithium and sodium cations with several alkyl-substituted ethenes.

Results

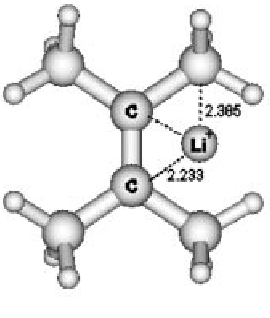
The theoretical treatment of the neutral and the lithium- or sodium-bound molecules involved Density Functional Theory (DFT) with the three-parameter hybrid functional of Becke and the Lee−Yang−Parr correlation functional (B3LYP). The level of the calculations used herein was B3LYP/6-31G*.[14]

The results obtained in the present work will be discussed individually and by comparison of the lithium and sodium geometries of two classes of alkenes. Those possessing only methyl or hydrogen substituents on the double bond (tetramethylethene, trimethylethene, *cis*-2-butene, *trans*-2-butene and isobutylene), and those possessing at least one alkyl group other than a methyl (*cis*-3-hexene and 2-methyl-2-hexene).

Methyl-Substituted Ethenes

Tetramethylethene

For the lithium cation binding to tetramethylethene two local minima were found at the B3LYP/6-31G* level of theory. A C_{2v} structure, where the cation is on top of the double bond (**1a**), and a C_s structure where Li^+ lies towards the *cis*-methyl groups (**1b**). For **1b**, the dihedral angle between the plane of the p-orbitals and the plane formed by the Li^+ and the olefinic carbons is 32°. Also, **1b** is more stable by 1 kcal/mol. For **1a** (see Supporting Information), the distance between Li and the olefinic carbons is 2.276 Å; for **1b** (Figure 1), the same distance is 2.233 Å, and the distance between Li and the nearest allylic carbons is 2.385 Å. Mulliken population analysis shows that almost half of the positive charge of the cation is transferred to the alkene for both structures **1a** and **1b**.



1b

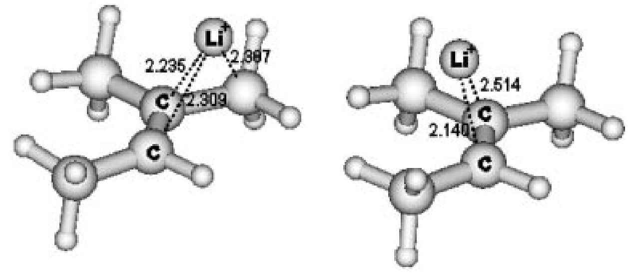
Figure 1. Local minimum structure **1b** of Li^+ binding to tetramethylethene (at the B3LYP/6-31G* level)

By replacing Li^+ with Na^+, two similar binding sites were found (**1c** and **1d**), which are isoenergetic (their relative energy difference is 0.1 kcal/mol). For **1d**, where Na^+ lies towards the *cis*-methyls, the dihedral angle is 23°, which indicates that Na^+ prefers to be closer to the double bond than the cation in **1b**. The Na−sp^2-carbon distances are longer by approximately 0.3 Å than the corresponding Li−sp^2-carbon distances. In addition, Na^+ transfers only 30% of its positive charge to the alkene.

These results were also tested at the MP2/6-31G* level of theory. For both cations minima with geometric and energetic characteristics similar to the DFT method were found. More specifically, for the Li^+ interaction with tetramethylethene, structures **1a** and **1b** differ in energy by 1 kcal/mol (exactly as at the B3LYP/6-31G* level), the cation−carbon distances increase by only 0.03 Å, whereas the cation-π bond dihedral angle is 38°.

Trimethylethene

Interaction of Li^+ with trimethylethene gives the two local isoenergetic minima **2a** and **2b** in which the cation lies either towards the less- or the more-substituted side of the alkene, but not on top of the carbon−carbon double bond (Figure 2). For **2a**, the cation is placed on the less-substituted side of the alkene forming a dihedral angle of 26° with respect to the plane of the π bond. The Li distances with the less- and the more-substituted sp^2-carbons are 2.309 and 2.235 Å, respectively. Also, the distance between Li and the allylic carbon on the less-substituted side of the alkene is 2.387 Å.



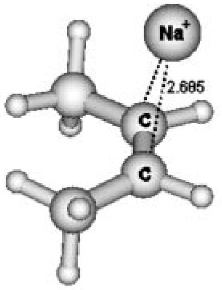
2a **2b**

Figure 2. Local minima structures **2a** and **2b**, calculated at the B3LYP/6-31G* level, of Li^+ binding to trimethylethene

For **2b**, the cation is placed on the more-substituted side of the alkene, with a dihedral angle of 18°. The Li distances to the less- and the more-substituted sp^2-carbons are 2.140 and 2.514 Å. Contrary to these, for the Na^+ binding to trimethylethene only one local minimum was found (**2c**), in which the cation sits close to the less-substituted carbon of the double bond, and slightly out of the plane of the π-bond, towards the less-substituted side of the alkene (dihedral angle of 8°). The Na distances from the less- and the more-substituted sp^2-carbons are 2.570 and 2.747 Å (see Supporting Information). These results were also tested with the MP2 method and found to be in agreement with the DFT method. For this reason, comparison of these two methods was limited to trimethyl- and tetramethylethene.

cis-2-Butene

For the interaction of Li^+ and Na^+ with *cis*-2-butene only one local minimum was found in each case, with the cation sitting slightly towards the non-substituted side of the alkene, forming dihedral angles of 7° (**3a**) and 6° (**3b**), respectively, with respect to the plane of the p-orbitals (Figure 3). The *sp²* carbon−Li distance in **3a** is 2.231 Å, whereas the *sp²* carbon−Na distance in **3b** is 2.685 Å.

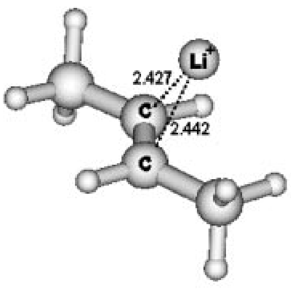


3b

Figure 3. Local minimum structure **3b** of Na^+ binding to *cis*-2-butene (at the B3LYP/6-31G* level)

trans-2-Butene

Complexation of Li^+ to *trans*-2-butene affords the two almost isoenergetic minima **4a** and **4b**. In **4a** (see Supporting Information), Li^+ sits on top of the double bond forming a C_2 structure with an olefinic carbon−Li distance of 2.312 Å. In **4b** (Figure 4), the cation lies on either side of the alkene forming a dihedral angle of 17° with respect to the π-plane. For this structure, the cation is slightly closer to one olefinic carbon than to the other. The distances of Li to the olefinic carbons are 2.427 and 2.442 Å, and the distance of Li to the closest allylic carbon is 2.427 Å. Vibrational frequency analysis of the C_2 structure **4a** revealed a true local minimum and not a transition state. The lowest frequency of **4a** is 13 cm^{-1} with an IR intensity of 54 km/mol, which indicates movement of the cation from **4a** to **4b** and vice versa. In contrast to the Li^+ results, for the Na^+ interaction with *trans*-2-butene, only the C_2 minimum **4c** exists. The Na−olefinic carbon distance was found to be 2.660 Å.



4b

Figure 4. Local minimum structure **4b** of Li^+ binding to *trans*-2-butene (at the B3LYP/6-31G* level)

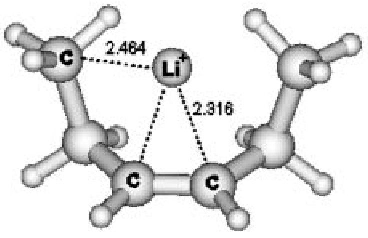
Isobutylene

The Na^+ interaction with isobutylene (2-methylpropene) has been calculated recently by McMahon and Ohanessian using the MP2/6-31G* method.[12] It was reported that the cation sits on top of the double bond and is displaced towards the less-substituted carbon at a distance of 2.582 Å. For comparison, we calculated the Li^+ and Na^+ interaction with isobutylene using the B3LYP/6-31G* method. The Na^+ ion was found to be at almost the same position, and its distance from the less-substituted olefinic carbon was 2.520 Å, in agreement with the results from the MP2/6-31G* method. The Li^+−isobutylene complex has a very similar minimum structure, with a Li distance from the secondary olefinic carbon of 2.161 Å.

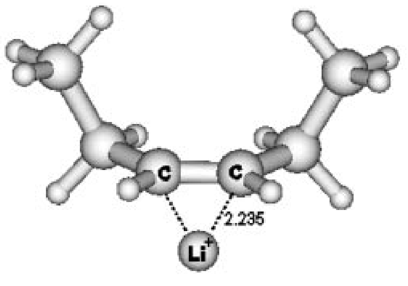
Alkyl-Substituted Ethenes

cis-3-Hexene

The interaction of Li^+ with *cis*-3-hexene affords two local minima (Figure 5). In the first (**5a**), the alkyl groups loop to interact through their homoallylic carbons with the cat-



5a



5b

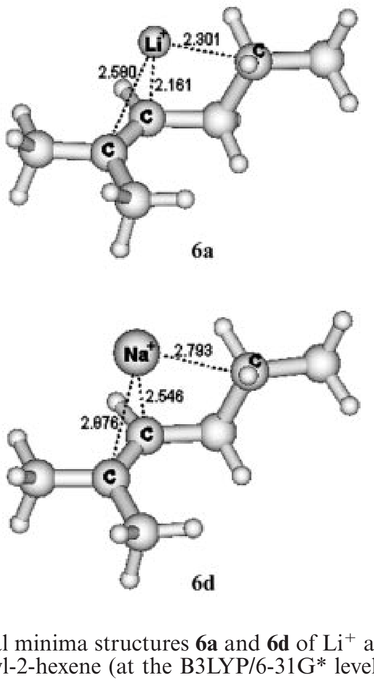
Figure 5. Local minima structures **5a** and **5b** of Li^+ binding to *cis*-3-hexene (at the B3LYP/6-31G* level)

ion. The cation is placed in the middle of the C−C double bond and slightly towards the more-substituted side of the alkene, forming a dihedral angle of 11° with respect to the plane of the π-bond. The distance between Li$^+$ and the olefinic carbons (2.316 Å), is similar to the distance to the homoallylic carbons (2.464 Å). In addition, Li$^+$ transfers 60% of its positive charge to the alkene. In the second minimum (**5b**), the alkyl groups are directed away from the cation to the opposite plane of the double bond. In this case, the cation is also placed in the middle of the C−C double bond and towards the more-substituted side of the alkene, forming a much larger dihedral angle of 32°. The olefinic carbon−Li distance is 2.235 Å. Surprisingly, structure **5a** is more stable than **5b** by 3.0 kcal/mol.

Similar results were found for the Na$^+$ interaction with *cis*-3-hexene. The two minima in which the cation either interacts with the alkyl groups (**5c**), or resides on the opposite side (**5d**), differ by 2.0 kcal/mol, with **5c** being more stable. In contrast to the Li$^+$ complexes, for both structures (**5c** and **5d**) the Na$^+$ is placed towards the less-substituted side of the alkene with dihedral angles of 3° and 8° respectively. The C−Na distances are 2.681 and 3.097 Å from the olefinic and homoallylic positions in **5c**, respectively, and 2.649 Å from the olefinic position in **5d**.

2-Methyl-2-hexene

For the Li$^+$ interaction with 2-methyl-2-hexene, three local minima **6a**−**6c** were found. In the more stable complex **6a** (Figure 6), the cation sits on top of the secondary olefinic carbon and slightly directed towards the more-substituted side of the alkene, forming a dihedral angle of 5° with respect to the π-plane. The homoallylic carbon of the *n*-propyl chain is oriented towards the cation, in agreement with the more stable structure **5a** of the Li$^+$ interaction with *cis*-3-hexene.



6a

6d

Figure 6. Local minima structures **6a** and **6d** of Li$^+$ and Na$^+$ binding to 2-methyl-2-hexene (at the B3LYP/6-31G* level)

The distances of Li to the less-substituted olefinic carbon and to the homoallylic carbon of the alkyl chain are 2.161 and 2.301 Å, respectively, while the distance from the more-substituted olefinic carbon is 2.580 Å. For structures **6b** and **6c** (see Supporting Information), the cation and the alkyl chain have opposite orientations. In **6b**, the cation sits towards the more-substituted side of the double bond forming a dihedral angle of 32° with respect to the plane of the p-orbitals. The distances of Li to the tertiary and the quaternary olefinic carbons are 2.155 and 2.381 Å respectively. In **6c**, Li$^+$ resides on the less-substituted side forming a dihedral angle of 25°. The distances of Li to the tertiary and the quaternary olefinic carbons are 2.288 and 2.235 Å. The structures **6b** and **6c** are less stable than **6a** by 3.0 and 4.0 kcal/mol, respectively. The relative stability of **6a** compared to **6b** is due to the lack of interaction of the cation with the homoallylic position of the alkyl chain, as found for **5b** and **5a**.

For the Na$^+$ interaction with 2-methyl-2-hexene, two local minima **6d** and **6e** were found. The position of the cation and the direction of the alkyl chain in the more stable complex **6d** (Figure 6) are similar to **6a**. The only difference is that the Na$^+$ is directed slightly towards the less-substituted side of the alkene at a dihedral angle of 3° with respect to the π-system. The distances of Na to the tertiary olefinic carbon and to the homoallylic carbon of the alkyl chain are 2.546 and 2.793 Å, respectively, while the distance from the quaternary olefinic carbon is 2.876 Å. In contrast to the Li$^+$ complexes **6b** and **6c**, for the case of Na$^+$ only one minimum (**6e**) with similar geometry was found (see Supporting Information), in which the cation is directed towards the more-substituted side of the alkene forming a dihedral angle of 8°. The distances of Na to the tertiary and the quaternary olefinic carbons are 2.507 and 2.839 Å, respectively. The structure **6e** is less stable than **6d** by 2.0 kcal/mol.

Discussion

Two major trends can be recognized from the interaction of the cations with the alkenes presented herein. The complexation of Li$^+$ and Na$^+$ with the π-system does not occur on top of the double bond, but either towards the more- or the less-substituted side of the alkene. A typical example is trimethylethene (Figure 2). Even for the highly symmetrical tetramethylethene, the structures in which binding of the cations occurs towards the *cis*-methyls (**1b** and **1d**) are isoenergetic (for Na$^+$) or even more stable (for Li$^+$) than the structure where the cations bind on top and in the middle of the double bond (Figure 1). Li$^+$ interacts more strongly with the π-system than Na$^+$. However, sodium prefers to bind closely to the plane of the p-orbitals of the alkene, and with non-symmetrically substituted ethenes slightly towards the less-hindered side of the double bond.

To explain the "out-of-π-plane" binding trend, we must take into account two major parameters: (i) polarization of the double bond by the cation, and (ii) steric effects. Interaction of the symmetrical tetramethylethene with the cation generates a partial positive charge on the olefinic carbons. Due to this electron depletion, the electron density between the C_α and $C_{sp}{}^2$ bonds increases as a result of hyperconjugation. Therefore, the cation shifts from the plane of the π-system toward the allylic carbons. In the case of the nonsymmetrically substituted trimethylethene, polarization of the double bond by the cation occurs in such a way that the more-substituted olefinic carbon bears a partial positive charge, and the cation is found closer to the less-substituted olefinic carbon. Due to hyperconjugation, the two geminal carbon atoms attract the cation either towards the more- or the less-substituted side of the alkene. For the case of the Li^+ binding, when the cation resides in the more-substituted side of the alkene (structure **2b**), its position is very close to the olefinic π-plane for steric reasons. For structure **2a**, however, where the cation is placed on the more-substituted side, this steric hindrance is smaller and the cation is found further from the π-plane than in **2b** (dihedral angle of 28° in **2a**, versus 18° in **2b**). If we replace Li^+ with Na^+, the steric hindrance for binding towards the more-substituted side of the alkene is higher, and only structure **2c** is found as a local minimum, in which the cation is directed towards the less-substituted side of the alkene.

The second trend is that with ethenes possessing an alkyl chain other than a methyl group, a relatively strong interaction of the cations with the homoallylic position of the chain occurs. This is evident in *cis*-3-hexene (Figure 5), where both ethyl groups loop to interact with the cation (complexes **5a** and **5c**). The structures where the two alkyls are oriented in the opposite direction relative to the cation are less stable by 2−3 kcal/mol. This observation is also supported by the examination of the local minima structures of Li^+ and Na^+ complexation to 2-methyl-2-hexene (Figure 6), where, again, the *n*-propyl chain interacts with the cation through its homoallylic carbon (**6a** and **6d**). Agostic interactions of Li^+ with an alkyl chain have been observed in some crystal structures of organolithium compounds,[15] and could be attributable to polarization effects. Alkanes are known to be substantially more polarizable than arenes.[16] Due to this polarization, alkyl chains could also bind to a cation. For example, the binding energy of Na^+ with cyclohexane[17] is quite remarkable (exothermic by 8.4 kcal/mol). Such alkyl-cation attractive interactions might be the driving force for the Li^+ to be placed on the less-substituted side of the double bond in *cis*-2-butene (structure **3a**) and on the more-substituted side in the case of the higher analogue *cis*-3-hexene (structure **5a**). Also, in the direct comparison of the Li^+ binding to trimethylethene and 2-methyl-2-hexene, structure **6a**, where the cation resides towards the more-substituted side of the double bond in 2-methyl-2-hexene, is far more stable than structure **6c**, where the cation resides towards the less-substituted side. For the case of *cis*-3-hexene, however, the analogous structures **2a** and **2b** are isoenergetic.

In the light of these calculations, we would like to discuss the experimental results[7a,8,9] in the regioselectivity of singlet-oxygen ($^1O_2$) ene reactions with alkenes adsorbed onto dye-supported zeolite Na-Y. It has been postulated that conformational effects and cation-π interactions within the supercages of zeolite Na-Y may control the reactivity of the allylic hydrogen atoms for abstraction in the intermediate perepoxide. Complexation of a trisubstituted alkene to the cation *does not occur on top* of the π-system, but either towards the less- or the more-substituted side. We propose that formation of the intermediate perepoxide, with orientation towards the less-substituted side of the trisubstituted alkene, may be facilitated by the out-of-π-plane position of the cation. The driving force is the electrostatic interaction between the negatively charged oxygen atom and the cation (Figure 7). The perepoxide oriented on the less-substituted side of the alkenes leads to allylic hydrogen atom abstraction at the *twin*[18] position. In the absence of the cation, oxygen preferentially forms the intermediate perepoxide pointing towards the more-substituted side of the alkene (cis effect selectivity),[19] a phenomenon that has been debated for several years and has been attributed to an entropy-controlled process. For example, in a series of *gem*-dimethyl-trisubstituted alkenes (Figure 7), although the *twin* methyl group is approximately 5−10% reactive if photooxygenation occurs in solution, within zeolite its reactivity increases to 30−65% depending on the substituents at the *lone* position.[7a,9b]

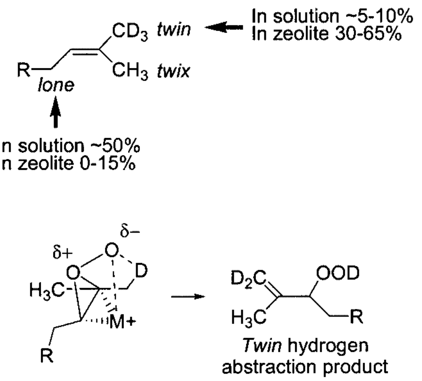


Figure 7. Regioselectivity trends in the photooxygenation of trisubstituted alkenes

The tendency of the cations to interact with the homoallylic carbon atoms of the alkyl chains can also explain the low, or even lack of, reactivity of the methene hydrogen atoms at the *lone* position of trisubstituted alkenes (Figure 8). According to the models postulated so far,[8c] upon interaction of a *gem*-dimethyl-trisubstituted alkene such as **1** with the cation, the alkyl group (R) adopts a conformation away from the cation (structure **1a**). Thus, the allylic methene hydrogens cannot interact with $^1O_2$ and are unreactive. Taking into account the present calculations we propose that interaction of **1** with Na^+ within the cages of Na-Y places the R group towards the cation (structure **1b**) and singlet oxygen attacks from the opposite olefinic plane with respect to the cation. Although the allylic methene hydrogens should now be reactive, they have an inappropriate conformation for abstraction since they cannot adopt a perpendicular orientation with respect to the plane of the double bond. Therefore, they are less reactive or even unreactive.[19] The proposed interaction of **1** with Na^+ within Na-Y (structure **1b**) resembles the situation where R = Ph (**2**). For **2**, a strong interaction between the cation and the aryl ring is expected to place the benzylic hydrogens (structure **2a**) at an unreactive conformation,[7a] similar to **1b**.

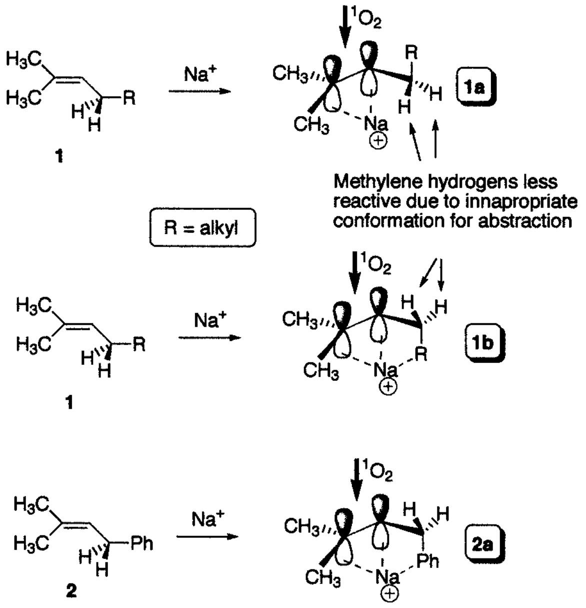


Figure 8. Possible interaction of alkenes **1** and **2** with Na^+ within the cages of zeolite Na-Y

In conclusion, based on theoretical calculations we have presented evidence that cation-π interactions and their subsequent conformational changes on the alkyl-substituted ethenes can be correlated to the product distribution in their intrazeolite photooxygenation reaction with olefins.

Supporting Information Available

Structures **1a**, **2c**, **4a**, **6b**, **6c** and **6e** and a table with the Mulliken charges for Li^+ and Na^+ of all structures. Detailed information about the calculated structures **1a−6e** are available from the authors upon request.

Acknowledgments

This work was supported in part by the Greek Secretariat of Research and Technology.

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[1] [1a] J. C. Ma, D. A. Dougherty, *Chem. Rev.* **1997**, *97*, 1303−1324. [1b] K. S. Kim, P. Tarakeshwar, J. Y. Lee, *Chem. Rev.* **2000**, *100*, 4145−4186. [1c] G. W. Gokel, L. J. Barbour, R. Ferdani, J. Hu, *Acc. Chem. Res.* **2002**, *35*, 878−886.

[2] For some recent selected examples see: [2a] D. H. Barich, T. Xu, J. Zhang, J. F. Haw, *Angew. Chem. Int. Ed.* **1998**, *37*, 2530−2531. [2b] S. Senger, L. Radom, *J. Am. Chem. Soc.* **2000**, *122*, 2613−2620. [2c] A. Pöppl, T. Rudolf, P. Manikandan, D. Goldfarb, *J. Am. Chem. Soc.* **2000**, *122*, 10194−10200. [2d] I. Milas, M. A. C. Nascimento, *Chem. Phys. Lett.* **2001**, *338*, 67−73.

[3] *Introduction to Zeolite Science and Practice* (Eds.: H. van Bekkum, E. M. Flaningen, J. C. Jansen), Elsevier: Amsterdam, 1991.

[4] [4a] S. E. Sen, S. M. Smith, K. A. Sullivan, *Tetrahedron* **1999**, *55*, 12657−12698. [4b] N. J. Turro, *Acc. Chem. Res.* **2000**, *33*, 637−646.

[5] P. Lakshminarasimhan, R. B. Sunoj, J. Chandrasekhar, V. Ramamurthy, *J. Am. Chem. Soc.* **2000**, *122*, 4815−4816.

[6] K. Pitchumani, V. Ramamurthy, *Tetrahedron Lett.* **1996**, *37*, 5297−5300.

[7] [7a] M. Stratakis, G. Froudakis, *Org. Lett.* **2000**, *2*, 1369−1372. [7b] M. Stratakis, G. Kosmas, *Tetrahedron Lett.* **2001**, *42*, 6007−6009. [7c] M. Stratakis, R. Nencka, C. Rabalakos, W. Adam, O. Krebs, *J. Org. Chem.* **2002**, *67*, 8758−8763.

[8] [8a] X. Li, V. Ramamurthy, *J. Am. Chem. Soc.* **1996**, *118*, 10666−10667. [8b] R. J. Robins, V. Ramamurthy, *Chem. Commun.* **1997**, 1071−1072. [8c] V. Ramamurthy, P. Lakshminarasimhan, C. P. Grey, L. Johnston, *Chem. Commun.* **1998**, 2411−2424. [8d] J. Shailaja, J. Sivaguru, R. J. Robbins, V. Ramamurthy, R. B. Sunoj, J. Chandrasekhar, *Tetrahedron* **2000**, *56*, 6927−6943.

[9] [9a] E. L. Clennan, J. P. Sram, *Tetrahedron Lett.* **1999**, *40*, 5275−5278. [9b] E. L. Clennan, J. P. Sram, *Tetrahedron* **2000**, *56*, 6945−6950.

[10] M. Stratakis, C. Rabalakos, *Tetrahedron Lett.* **2001**, *42*, 4545−4547.

[11] [11a] C. A. Deakyne, M. Meot-Ner, *J. Am. Chem. Soc.* **1985**, *107*, 474−479. [11b] S. Hoyau, K. Norrman, T. B. McMahon, G. Ohanessian, *J. Am. Chem. Soc.* **1999**, *121*, 8864−8875. [11c] D. Feller, *Chem. Phys. Lett.* **2000**, *322*, 543−548.

[12] T. B. McMahon, G. Ohanessian, *Chem. Eur. J.* **2000**, *6*, 2931−2941.

[13] For some recent selected examples see: [13a] S. L. De Wall, E. S. Meadows, L. J. Barbour, G. W. Gokel, *J. Am. Chem. Soc.* **1999**, *121*, 5613−5614. [13b] H. Minoux, C. Chipot, *J. Am. Chem. Soc.* **1999**, *121*, 10366−10372. [13c] S. Bartoli, S. Roelens, *J. Am. Chem. Soc.* **1999**, *121*, 11908−11909. [13d] J. P. Gallivan, D. A. Dougherty, *J. Am. Chem. Soc.* **2000**, *122*, 870−874. [13e] F. M. Siu, N. L. Ma, C. W. Tsang, *J. Am. Chem. Soc.* **2001**, *123*, 3397−3398. [13f] A. Gapeev, R. C. Dundar, *J. Am. Chem. Soc.* **2001**, *123*, 8360−8365. [13g] J. Hu, L. J. Barbour, G. W. Gokel, *Chem. Commun.* **2001**, 1858−1859.

[14] Gaussian 94, Revision D.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, R. Replogle, R. Gomperts, R. L. Martin, D. L. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Inc. Pittsburgh PA, 1995.

[15] W. N. Setzer, P. von R. Schleyer, *Adv. Organomet. Chem.* **1985**, *24*, 353−451.

[16] I. E. Graven, M. R. Hesling, D. R. Laver, P. B. Lukins, G. L. D. Ritchie, J. Vrbancich, *J. Phys. Chem.* **1989**, *93*, 627−631.

[17] S. Mecozzi, A. P. West, D. A. Dougherty, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 10566−10571.

[18] For the terminology *lone, twin* and *twix* see: W. Adam, N. Bottke, O. Krebs, *J. Am. Chem. Soc.* **2000**, *122*, 6791−6792.

[19] M. Stratakis, M. Orfanopoulos, *Tetrahedron* **2000**, *56*, 1595−1615.

Received June 19, 2002
[O02330]