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CATION –GUEST INTERACTION WITHIN ZEOLITES: LI$^+$ EXCHANGED ZEOLITES ARE UNIQUE

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Lithium cations present in the supercages of zeolite X and Y activate guest molecules through electrostatic interaction with the π-cloud. Such an interaction may have consequences on the reactivity–photochemical and thermal–of the guest organic molecule.

Recent reports by Jiao and Schleyer predict that light ions such as Li$^+$ can accelerate rearrangement reactions of certain olefins.[1,2] Supercages of zeolites (Figure 1) offer an unique environment to explore such a possibility.[3] Electrostatic interaction between light alkali ions and aromatic and olefinic systems has been known for quite some time in the gas phase.[4] Presence of such a type of interaction between aromatic molecules and alkali ions within zeolite supercages has been inferred from neutron diffraction and NMR studies.[5,6] In this report, preliminary results of our attempts to explore the consequence of such interaction on chemical reactivity of zeolite included organic molecules are presented.

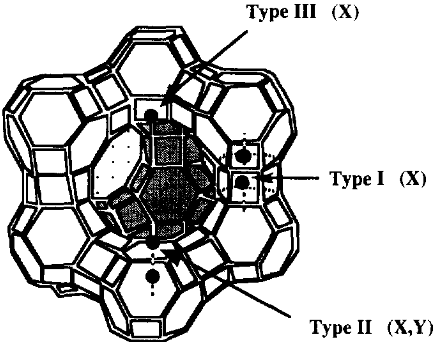
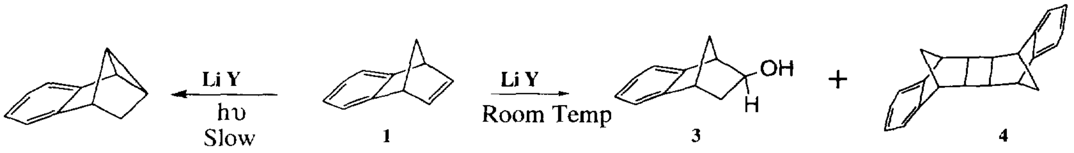


Figure 1: Circles indicated by arrows represent cations.

Our initial encounter with the activation (inactivation?) of π-systems with Li$^+$ ion occurred during a search for methods to place zeolite included benzonorbornadiene (**1**) and dibenzobarrelene (**2**) in their triplet excited states. While as expected,[7] heavy cations such as Cs$^+$ and Tl$^+$ ions enhanced formation of the triplets of **1** and **2**, to our surprise photochemical reactivity of **1** and **2** when included within either Li Y or Li X was considerably reduced.[8] Further probing, as described below, led us to believe that this is the result of electrostatic interaction between Li$^+$ ion and **1** and **2**. To our surprise, under certain conditions spontaneous thermal reaction occurred when **1** is included within either Li X or Li Y.



Scheme 1

The experimental procedure consisted of stirring known amounts of benzonorbornadiene **1** or dibenzobarrelene **2** and activated Li Y or Li X in dry hexane. The solution was stirred for several hours at room temperature and filtered and washed with hexane. The combined washings showed neither the presence of **1** (or **2**) nor any other products. However, extraction of the zeolite with methylene chloride and GC analyses of the extract (in the case of **1**) showed that the zeolite not only contained unreacted **1** (<10%) but also two other products whose ratio varied depending on the condition of inclusion (Scheme 1).[9] In the case of **1**, depending on the extent of water content within the zeolite and on the loading level, exo-benzonorborneol **3** and the dimer **4** were formed (Scheme 1). When the zeolite was very dry and the loading level was less than one molecule per 16 cages, stirring in hexane did not lead to any products. However, at such low loading levels, wet conditions favored quantitative formation of **3**. At high loading levels (more than two molecules per supercage) under dry conditions, the dimer **4** was the exclusive product. Formation of these occurred spontaneously upon stirring of **1** in hexane with activated Li X or Li Y. As shown in Figure 2, the relative distribution of **3** and **4** can be controlled by the loading level of **1** in partially wet Li X or Li Y.

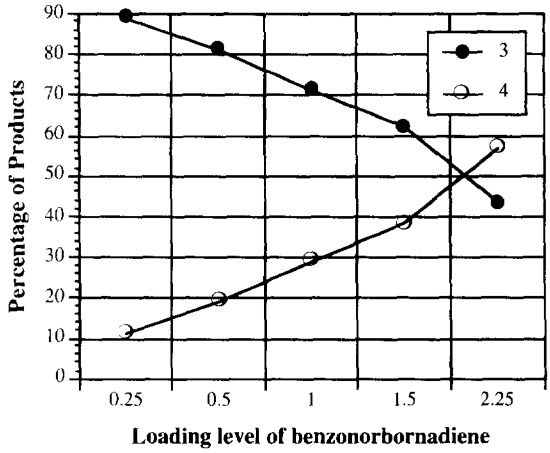
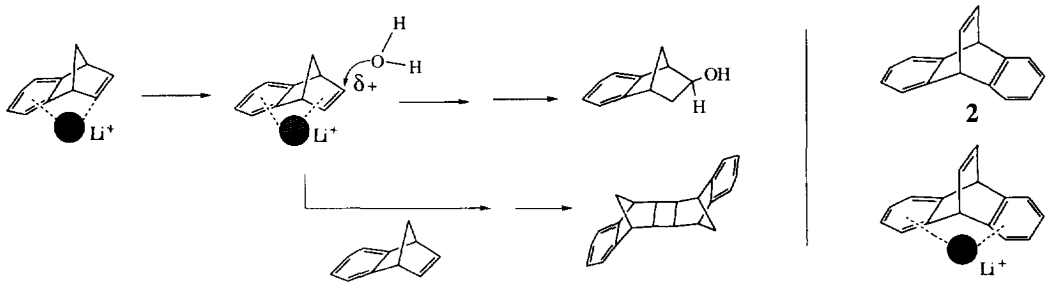


Figure 2: Dependence of product distribution on the loading level of **1** within Li Y.

No products resulting from spontaneous thermal reaction were obtained upon inclusion of **1** in K^+, Rb^+ and Cs^+ exchanged X and Y zeolites. However, small amounts of **3** and **4** were obtained in Na Y and Na X. On the other hand, under no conditions, **2** gave any products upon inclusion within Li X or Li Y. This was surprising since its photoreactivity, like that of **1**, slowed upon inclusion in Li X or Li Y.

Formation of **3** and **4**, does not arise via radical cation since radical cation of **1**, generated within very dry Ca Y, gave products of hydrogen abstraction from solvent hexane. No such products are formed under the conditions described above. Further, radical cation of **2** gives several products which are not formed within Li X or Li Y.[10] Results presented here can not be interpreted in terms of cation formation through the action of Brϕnsted acid sites present within zeolites.[11] The two systems investigated here are stable to acids such as HCl.

Reactivity of **1** and inertness of **2** within Li^+ exchanged zeolite can be understood on the basis of electrostatic interaction between the light cation Li^+ and the π-structure as illustrated in Scheme 2. According to this model, activation (polarization) of the double bond in **1** leads to attack by nucleophile such as water and the parent olefin. Inertness of the double bond in **2** towards the above reactants can be understood on the basis that Li^+ ion binds in this case in such a way that the interaction occurs with the two aromatic rings. Under such conditions, the double bond remains unactivated. This model is consistent with the reported binding energies of Li^+ in the vapor phase: binding energy of Li^+ ion to benzene is much higher (37 kcal/mole) than to simple olefins (~28 kcal/mole).[4] We are in the process of extending this study to benzobarrelene and barrelene to test the above hypothesis.



Scheme 2

We have shown above that Li^+ exchanged zeolites are unique and can be used to activate generally less active olefins. While this may be valuable under certain conditions, this can generate problems during photochemical studies. Results presented here point out that it is important to probe the characteristics of zeolites before they are used as molecular reaction vessels. We are extending our studies to other systems and reactions to exploit the use of "naked' Li^+ to lower the transition state of various processes. Attempts are underway to provide spectroscopic evidence for the presence of electrostatic interaction between Li^+ and **1** and **2**.[12]

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