Chiral Photochemistry within Zeolites

Abraham Joy and V. Ramamurthy*[a]

Dedicated to John R. Scheffer on the occasion of his 60th birthday

Abstract: Chiral induction of chemical reactions continues to be one of the main concerns of chemists. While basic rules of chiral induction of thermal reactions have been reasonably established, the same is not true of photochemical reactions. Short excited state lifetime and low activation energies for reactions in the excited state(s) leave very little room for manipulating the diastereomeric transition states. Yet impressive chiral induction of photochemical reactions in the solid state has been achieved. On the other hand, chiral induction of photoreactions of organic molecules in solution continues to be inefficient at ambient conditions. We are exploring the possibility of employing zeolites as a media for achieving chiral induction during photoreactions. The motivating force for such an attempt is the fact that chiral chemistry in the solid state is not completely general due to the fact that not all molecules crystallize. To achieve chiral induction one needs a chiral perturber. Zeolites are not chiral and therefore the perturber is added to the medium. Thus the medium for a photoreaction is a chirally modified zeolite. Of the several reactions investigated, results on photoelectrocylization of tropolone alkyl ethers are discussed at length. The confined space offered by the zeolite supercage forces a reactant and the chiral inductor to interact intimately to yield enantiomerically enriched product. Due to the transitory nature of the reaction cavity in solution such close interactions are less likely in isotropic solvent media. The examples discussed herein show negligible chiral induction in solution, whereas in a zeolite one obtains induction as high as 90%.

Keywords: chiral induction · photochemistry · tropolones · type II reaction · zeolites

Introduction

The efforts of chemists during the past few decades have advanced the field of thermal asymmetric synthesis to a great extent.[1] Complex molecules can now be synthesized as single enantiomers. Unfortunately, asymmetric photochemical reactions have not enjoyed the same level of success.[2] In the past, chiral solvents, circularly polarized light, and chiral sensitizers have been utilized to conduct enantioselective photoreactions. The highest chiral induction achieved by any of these approaches at ambient temperature and pressure has been about 30% (2–10% *ee* is common in photochemical reactions under the above conditions).[2, 3] A chiral auxiliaries approach, a popular method in solution thermal chemistry, has also been used with success in photochemistry by Scharf and coworkers.[2d] Of the various approaches, crystalline state and solid host–guest assemblies have provided the most encouraging results.[4] Two approaches have been used to achieve chiral induction in the crystalline state. In one, by a group at the Weizmann Institute, the achiral reactant is crystallized into a chiral space group.[4b] The limited chances of such crystallization of organic molecules renders this approach less general. In the second approach, developed by Scheffer et al., an ionic chiral auxiliary is used to effect a chiral environment.[5] This limits the approach to molecules with carboxylic acid groups that form crystallizable salts with chiral amines or vice versa. Yet another highly successful approach developed by Toda has made use of organic hosts that contain chiral centers (e.g., deoxycholic acid, cyclodextrin, 1,6-bis-(o-chlorophenyl)-1,6-diphenyl-2,4-diyne-1,6-diol,).[6] The success of this approach is limited to guests that can form solid solutions with the host without disturbing the host's macrostructure. The reactivity of molecules in the crystalline state and in solid host–guest assemblies is controlled by the details of molecular packing. Currently, molecular packing and consequently the chemical reactivity in the crystalline state, cannot be reliably predicted.[7] Therefore even after successfully crystallizing a molecule in a chiral space group or complexing a molecule with a chiral host or a chiral auxiliary, there is no guarantee that the guest will react in the crystalline state. Hence even though crystalline and host–guest assemblies have been very useful in conducting enantioselective photoreactions, their general applicability thus far has been limited.

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[a] Prof. Dr. V. Ramamurthy, A. Joy
Department of Chemistry
Tulane University
New Orleans, LA 70118 (USA)
Fax: (+1)504-865-5596
E-mail: murthy@mailhost.tcs.tulane.edu

We believe that zeolites offer a solution to the above limitations. For example, guest molecules present within zeolites possess greater freedom than in crystals/solid host–guest assemblies and less freedom than in isotropic solvents. This permits molecules within zeolites to react more freely than in crystals/solid host–guest assemblies and more selectively than in solutions. Zeolites, unlike organic host systems, can include a large number of molecules, with the only limitation being that the dimensions of the guest be less than the pore dimensions of the zeolite. A variety of molecules can therefore be included within a zeolite and induced to react. A major deficiency is that the zeolite is not chiral. In order to be a useful chiral medium this serious limitation has to be overcome and our approach in this context has been to chirally modify the zeolite.

Discussion

What is a zeolite?

Zeolites are crystalline aluminosilicates with open framework structures made up of the primary building blocks $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra that are linked by all their corners to form channels and cages of discrete size with no two aluminum atoms sharing the same oxygen.[8] Due to the difference in charge between the $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, the net framework charge of an aluminum-containing zeolite is negative and hence must be balanced by a cation, typically an alkali or alkaline earth metal cation. The adsorbed molecules are located in the cavities of the zeolites, and access to these cavities is through a pore or window whose size can be the same or smaller than the cavities. The dimension of this pore determines the size of the molecule that can be adsorbed into these structures. We have utilized X and Y zeolites as media for our chiral studies and the structure of these are mentioned below. Faujasite zeolites X and Y are large-pore zeolites with the unit cell compositions $M_{86}(AlO_2)_{86}(SiO_2)_{106}\cdot 264\,H_2O$ and $M_{56}(AlO_2)_{56}(SiO_2)_{136}\cdot 253\,H_2O$, respectively, where M is the charge-compensating cation. These cations occupy three different positions within the zeolites X and Y (Figure 1). Of the three types of cation locations only types II and III are located within the supercage where an organic molecule is expected to reside. Due to the hygroscopic nature of the cations zeolites tend to adsorb considerable amounts of water. These water molecules can be desorbed through activation at high temperatures creating space for organic guest molecules to be included. The free volume available for the adsorbed molecule within the supercage depends on the number and nature of the cation (for example, it varies from 873 Å^3 in Na X to 732 Å^3 in Cs X).

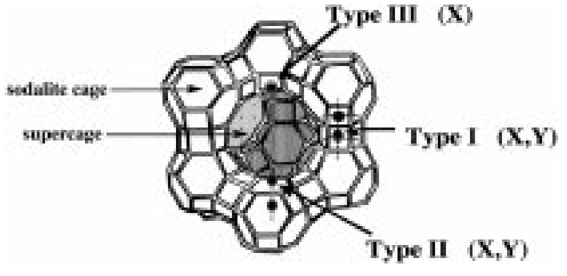

Figure 1. The basic structural unit (supercage) of X and Y zeolites. Cation locations within a supercage are shown in dark spheres. The supercage is connected to adjacent four supercgaes through the 8 Å windows.

A chiral zeolite

An ideal approach to achieving chiral induction in a constrained medium such as a zeolite would be to make use of a chiral medium. To our knowledge no zeolite that can accommodate organic molecules currently exists in a stable chiral form.[9, 10] Though zeolite beta and titanosilicate ETS-10 have unstable chiral polymorphs, no pure enantiomorphous forms have been isolated. Although many other zeolites can, theoretically, exist in chiral forms (e.g., ZSM-5 and ZSM-11) none has been isolated in such a state. In the absence of readily available chiral zeolites, we are left with the choice of creating an asymmetric environment within zeolites by the adsorption of chiral organic molecules. We have achieved this through two approaches: a) by including an optically pure organic molecule as an adsorbent within a zeolite and b) by exchanging the inorganic cations present in zeolites with chiral ammonium ions. The third approach currently being investigated is to covalently link chiral organic molecules through free silanol groups present on the surfaces of a zeolite.

The chiral inductor that is used to modify the zeolite interior will determine the magnitude of the enantioselectivity of the photoproduct. The suitability of a chiral inductor for a particular study depends on its inertness under the given photochemical condition, its shape, size (in relation to that of the reactant molecule and the free volume of the zeolite cavity) and the nature of the interaction(s) that will develop between the chiral agent and the reactant molecule/transition state/reactive intermediate. One should recognize that no single chiral agent might be ideal for two different reactions or structurally differing substrates undergoing the same reaction. These are inherent problems of chiral chemistry. Lack of sufficient examples in the literature necessitates a certain amount of empiricism at this stage. Thus pursuit of a path of 'rational combinatorial approach' until ground rules are established is a wise choice.

Intrazeolite adsorption and light transmission

In spite of the fact that zeolites are one of the most widely used catalysts, studies with zeolites often raise questions. An often asked question is how can one be sure that the reaction occurs within a zeolite and not on the surface. Guest molecules are usually loaded into the zeolite by stirring a solution of the guest in hexane with an activated zeolite (e.g., Na Y). If the guest is colored the color transfer from hexane to the zeolite is hard to miss. Analysis (GC or HPLC) of the hexane layer at this stage often confirms the absence of the guest molecules in the hexane solution. Since much more than a monolayer of external surface coverage of guest molecules is possible, the molecules must be present in multilayers on the

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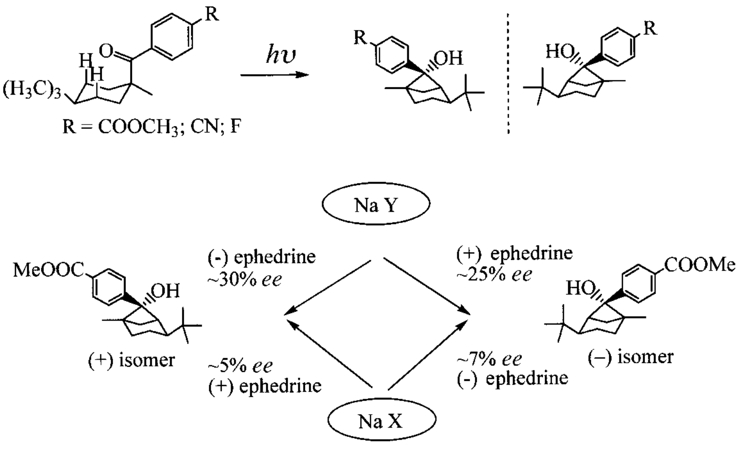
external surface or be included on the internal surfaces of a zeolite. The forces involved in the two scenarios differ. Stronger interaction between cations and guest molecules is expected within a zeolite whereas only intermolecular interactions between guest molecules are expected to prevail on the outside. Molecules adsorbed on the outside surface can hence be washed off with excess hexane, whereas the guest molecules residing inside require extraction with polar solvents.

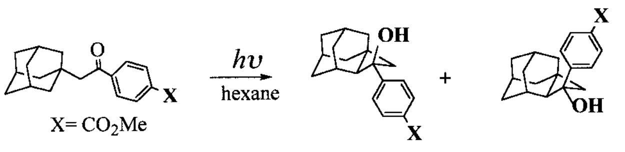
Another question that is raised is: How can light reach a molecule adsorbed within a zeolite? Zeolites are made up of an Al-O-Si framework and, like glass and quartz, are transparent to UV/Vis radiation, but due to their size, scatter light. While scattering is an inconvenience it is not expected to influence the absorption characteristics of a zeolite. Another concern is how can one be sure that all reactant molecules will be in a cage that contains a chiral inductor. One should recognize that to ensure high enantioselectivity it is important that every supercage be chirally modified. In the absence of any current techniques by which this can be achieved, our approach has been to use the chiral inductor in excess so that all cavities will be filled with one or more chiral inductors. Many cages containing more than one chiral inductor by this process will not be able to accommodate a reactant molecule. This approach, though admittedly it does not utilize all the cages of a zeolite, ensures that a reactant molecule when present within a cage will most often be in the company of a chiral inductor. Another approach of ensuring that the chiral inductor and the reactant stay together is to link the reactant and the chiral inductor through a methylene chain (chiral auxiliary). Examples of both approaches are presented below.

A noncovalent chiral induction strategy

In the context of chiral induction in photochemical reactions, we have examined photoelectrocyclization (see Scheme 5), the Norrish–Yang reaction (Schemes 1 and 2), the Schenk-ene reaction (Scheme 3), and the Zimmerman di-π-methane rearrangement within zeolites (Scheme 4), and the choice has been dictated by ease of synthesis of reactants, feasibility of separation of chiral products, and amenability of the reaction for spectroscopic investigations.[11] The photoreactions per se are not of paramount importance, but the information they provide will help to establish the concept and generate a model for future experiments. Most encouraging results have been obtained with electrocyclization of tropolone alkyl ethers (Scheme 5). Results on tropolone alkyl ethers are briefly discussed below. Based on results thus far obtained we have developed a model that establishes that chiral chemistry within a zeolite follows a predictable pattern and provides an insight into our current approach towards chiral chemistry within a zeolite.

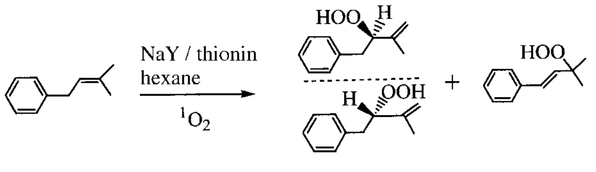


Scheme 1. Results on the enantioselective Norrish–Yang photocylization of *trans*-4-*tert*-butyl-1-methylcyclohexyl aryl ketone. Note that the same isomer of the chiral inductor favors opposite isomers within Na Y and Na X.



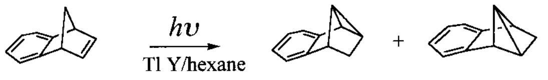
hexane	0.4 (*ee*: 0)	1(*ee*: 0)
Na Y	1 (*ee*: 0)	1 (*ee*: 0)
Na Y/(–) ephedrine	0.7 (*ee*: 35%)	1 (*ee*: 3%)

Scheme 2. Results on enantioselective Norrish–Yang photoreaction of 1-adamantyl-*p*-carbomethoxyacetophenone (X = $COOCH_3$). Note that the chiral induction on the two isomers vary. In one case 35% *ee* and in the other 3% *ee* is obtianed.



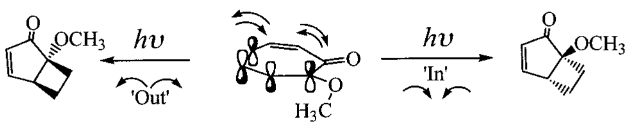
no chiral inductor	0 - 0.05 % *ee*
ephidrene hydrochloride	15.5 % *ee*

Scheme 3. Results on the enantioselective photooxidation of an olefin. Products were analyzed by converting the hydroperoxides to alcohol by treatment with triphenylphosphine.



Tl Y	*ee* ~0
Tl Y / ephedrine·HCl	*ee* ~15%

Scheme 4. Results on the enantioselective photoreaction (Zimmerman di-π-methane reaction) of benzonorbornadiene. The reaction originates from the triplet state. The cation Tl^+ helps to generate the triplet state of the reactant.



Scheme 5. Photoelectrocyclization (4e) of tropolone methyl ether: 'in' and 'out' cyclizations give opposite stereoisomers.

Upon excitation tropolone alkyl ethers undergo 4p electron disrotatory ring closure to yield racemic products; depending on the mode of disrotation opposite enantiomers are obtained (Scheme 5).[12] Enantiomerically pure products can be obtained by controlling the mode of ring closure. One obvious approach is to adsorb tropolone alkyl ethers on a surface that is likely to restrict one of the two modes of rotation. For example tropolone alkyl ether is expected to experience different extents of steric interaction with the surface when it rotates inwards or outwards. Since tropolone alkyl ether is not expected to show a preference for adsorption from one enantiotopic face over the other (Figure 2) adsorption on a surface by itself is not expected to influence enantioselectivity. To achieve chiral induction preferential adsorption from one enatiotopic face of the tropolone alkyl ether may be brought about by chirally modifying the surface. In Figure 2 a cartoon representation of how a chiral inductor present on a surface may control the mode of adsorption by tropolone methyl ether is provided. A surface that can hold the chiral inductor firmly in place is required to achieve the desired goal. Surfaces such as silica and alumina, which do not contain cations, are expected to be less effective in this regard. Cations in zeolites are expected to strongly interact with chiral inductors and thus present them in certain geometries to the reactant molecule. Based on this rationale we examined the photochemistry of tropolone alkyl ethers within chirally modified zeolites. The enantiomeric excesses (*ee*) obtained with tropolone alkyl ethers are dependent on the chiral agent (Scheme 6), the alkoxy substituent (Scheme 7), the water content within the supercage (Scheme 8), the nature and number of cations (Scheme 8), and the temperature. The results obtained with tropolone alkyl ethers clearly illustrate the complexities of chiral induction within a zeolite and point out the parameters that need to be optimized to obtain high *ee* values. The high *ee* value of 69% obtained with tropolone ethyl phenyl ether is most encouraging (Scheme 8).[13]

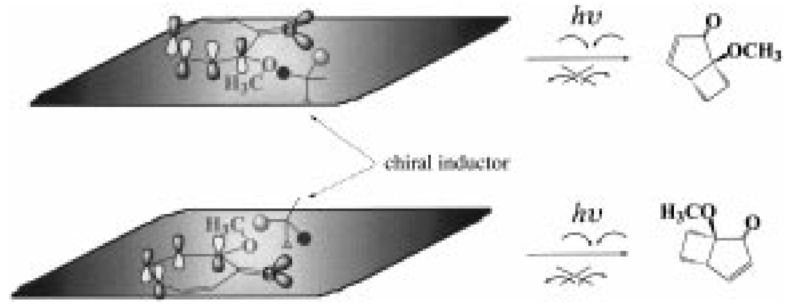
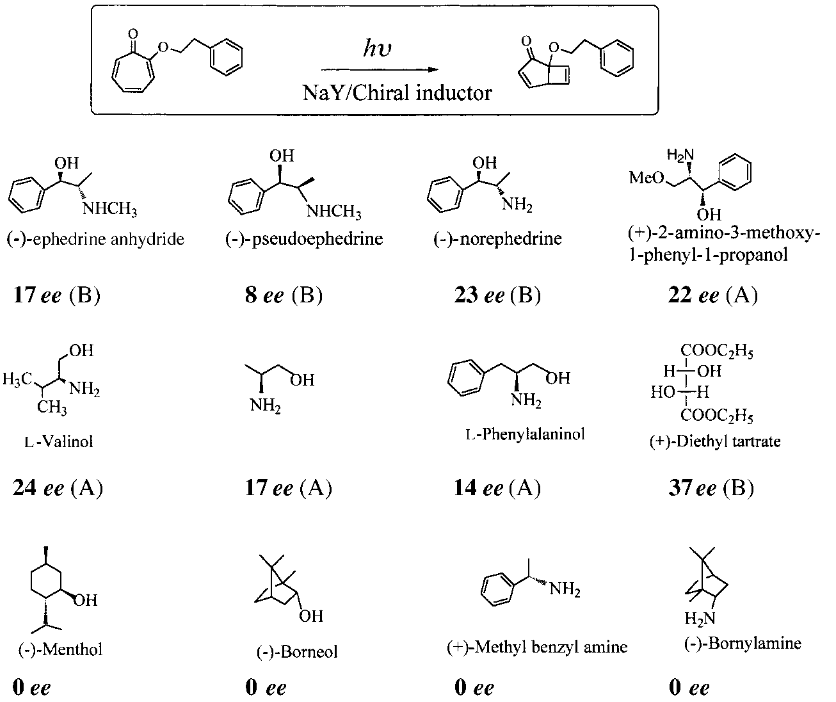
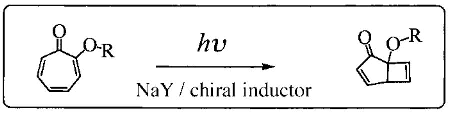


Figure 2. Adsorption of tropolone alkyl ether (TAE) on a surface: Chiral inductor may control the enantiotopic face by which TAE adsorbs. In the absence of a chiral inductor TAE will show no preference for adsorption from either enantiotopic face. Note that the same chiral inductor interacts differently when the TAE adsorbs through different enantiotopic faces.



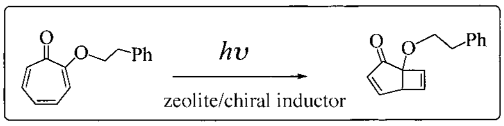
Scheme 6. Results of studies on the photocyclization of tropolone ethylphenyl ether within chirally modified Na Y zeolite: dependence of *ee* value on the chiral inductor. Note that the isomer which elutes first on the HPLC column is arbitrarily labeled as A. Only the chiral inductors with two susbtituents yield any *ee*.

Based on the observation that the best *ee* is obtained with bifunctional chiral agents (ephedrine, pseudoephedrine, norephedrine, and valinol; see Scheme 6) we tentatively conclude that a multi point interaction between the reactant molecule, the chiral inductor, and the zeolite interior is necessary to induce preferential adsorption of tropolone alkyl ether from a single enantiotopic face. The recognition points in these cases are most likely the hydroxy, amino, and aryl groups of the inductor, the cations of the zeolite and the carbonyl and methoxy groups of tropolone alkyl ether. The overall arrangement (Figure 3; generated by CACHE program)[14] shows hydrogen bonding between the chiral inductor and tropolone methyl ether as well as electrostatic interaction between the cation on the zeolite and the phenyl group of the chiral inductor. This view reveals that one of the faces of tropolone methyl ether is fairly open, while the other is encumbered by the zeolite surface. Such an arrangement would only favor one of the two modes of disrotatory



	Chiral inductor	%ee	Chiral inductor	%ee
R = CH_3	ephedrine	17	norephedrine	35
R = CH_2CH_3	ephedrine	8	norephedrine	11
R = $CH(CH_3)_2$	ephedrine	0	norephedrine	6

Scheme 7. Results of studies on the photocyclization of tropolone alkyl ether within Na Y zeolite: the *ee* value is dependent on the alkoxy substituent. Note that the isomer which elutes first on the HPLC is arbitrarily labeled as A. With increasing bulkiness of the substituent the *ee* value decreases.



Chiral inductor	Enantiomeric excess (%) "wet"	Enantiomeric excess (%) "dry"
Na Y/ (+) ephedrine	17 (A)	69 (B)
Na Y/(−) pseudoephedrine	8 (B)	20 (A)
Na Y/(−) norephedrine	23 (B)	38 (A)
Na X/ (+) ephedrine	9 (B)	
Li Y/ (+) ephedrine		22 (B)
KY/ (+) ephedrine		11 (B)
Rb Y/ (+) ephedrine		2 (B)

Scheme 8. Results of studies on the photocyclization of tropolone alkyl ether within zeolites. Note that the isomer which elutes first on the HPLC column is arbitrarily labeled as A. The nature of the favored enantiomer is reversed between wet and dry zeolites and between Na Y and Na X. The extent of *ee* depends on water content (wet and dry), the nature of the cation (Li, Na, K, Rb Y), and the number of cations (Na Y vs. Na X).

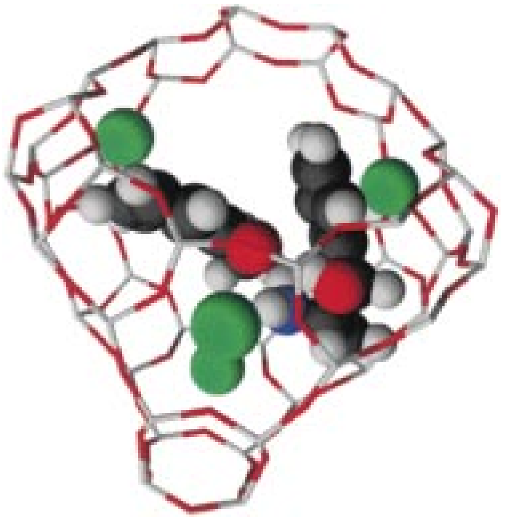


Figure 3. A CACHE representation of tropolone methyl ether and norephedrine included within a supercage. Hydrogen bonding between the chiral inductor and the tropolone methyl ether are preserved within a zeolite. The model should be considered as very approximate; the structure was not optimized within the cage. The cations (large spheres) hold the tropolone alkyl ether and the chiral inductor onto the zeolite surface.

cyclization. Since 100% enantioselectivity is not observed it is obvious that not all molecules are present in this idealized arrangement.

The dependence of chiral induction (% *ee*) on the nature and number of cations (Scheme 8) suggests a crucial role of the cation present in the supercages in the chiral induction process. This is further strengthened by the results observed with wet and dry zeolites. The presence of water decreases chiral selectivity (Scheme 8). Water molecules that are expected to hydrate the cation will make the latter less effective in holding the tropolone alkyl ether on the zeolite surface. They also disrupt the close interaction between the reactant and the chiral inductor. A simple cartoon representation for the influence of water is presented in Figure 4.

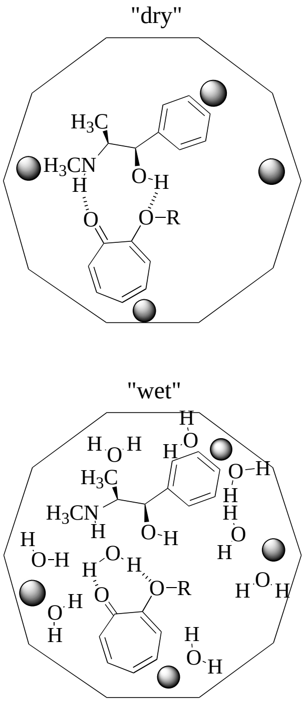


Figure 4. A cartoon representation of tropolone methyl ether and norephedrine included within a supercage under wet and dry conditions. The model helps to rationalize the difference in *ee* obtained under the two conditions. Dark circles represent the cations. Hydrogen bonding between the chiral inductor and interaction between the cation and tropolone methyl ether are disturbed by water molecules.

Admittedly the model discussed above is restricted to a single system. Further, the visualization is based on a system that contains two functional groups (carbonyl and alkoxy) that can interact with a chiral inductor through hydrogen bonds. The model thus will not hold well when the reactant contains a single chromophore or groups that cannot interact through hydrogen bonds. At present we do not have enough information to build a comprehensive model that would be applicable to all systems. Based on the preliminary data we conclude that our ability to control the geometry of adsorption of a reactant within a cavity of a zeolite will play an important role in achieving high *ee* values during a photochemical reaction. Therefore the choice of the chiral inductor and the conditions of the reaction may prove to be the deciding factors in achieving high enantioselectivity.

In addition to the enantiomeric excess of the product, the nature of the enantiomer being enhanced is also of great concern. All our systems are well behaved in the sense that, as expected, the optical antipode of the chiral inductor always gives the opposite enantiomer of the product.[11] This is consistent with the expectations. However, the water molecules unexpectedly switch the isomer being enhanced (compare wet vs. dry in Scheme 8). For example, in the case of tropolone ethyl phenyl ether, (−)-ephedrine favored the A enantiomer within 'wet' Na Y and the B enantiomer within 'dry' Na Y.[1] Also the number of cations makes a difference. For example, in the case of tropolone ethyl phenyl ether (−)-norephedrine favored the A enantiomer in Na Y and the B enantiomer in Na X, that is, depending on the number of cations present within a supercage the different enantiomers are favored by the same chiral agent. Even more puzzling is the fact that as discussed in the following section the nature of the cation itself can alter the isomer being enhanced by the same chiral inductor. A good understanding of these observations is essential to establish the ground rules for chiral induction within a zeolite.

Chiral auxiliary approach: A chiral amplification approach

Photochemical reactions conducted in solution invariably give low *ee* (≈2–10%).[2, 3] On the other hand, in the crystalline state examples with very high *ee* (>95%) are not uncommon.[4–6] Unfortunately, the *ee* value with most of our examples in zeolites tends to fall within these extremes. The absence of racemic products has, however, been very encouraging. While the asymmetric induction obtained within zeolites thus far is not comparable to the >90% *ee* generated by thermal reactions, we wish to point out that the pioneering attempts on enantioselective reaction with a soluble catalyst published in 1966 produced <10% *ee*.[16] Efforts by a number of groups during the last three decades have dramatically improved this number to >99%. Similarly, the first report of asymmetric induction in the crystalline state by Penzien and Schmidt in 1969 presented only 6% *ee*.[17] It has taken about 25 years to improve this number to >90% *ee*. The field of zeolite-based chiral photochemistry is just evolving and in its infancy—we would like to believe!

In the examples discussed above we have used a chiral inductor to induce chirality on the product of a reaction. In the absence of any specific interaction between a chiral inductor and a reactant we have been unable to force every reactant molecule close to a chiral agent. This is one of the main reasons for poor enantioselectivity. The 69% *ee* obtained in the case of tropolone ethyl phenyl ether/ephedrine/Na Y (dry) despite this limitation is remarkable. In an effort to reduce this limitation and to maintain closeness between the chiral center and the reaction site we have begun investigating examples where the chiral inductor is covalently linked to the tropolone system (Figure 5). Although in the long run the 'noncovalent chiral inductor' chiral strategy will prove to be more useful, versatile, and simple, we have turned our attention to the chiral auxiliary methodology. We envisioned that a confined space offered by a zeolite would augment the influence of a chiral auxiliary. It is gratifying to observe that this is indeed the case.

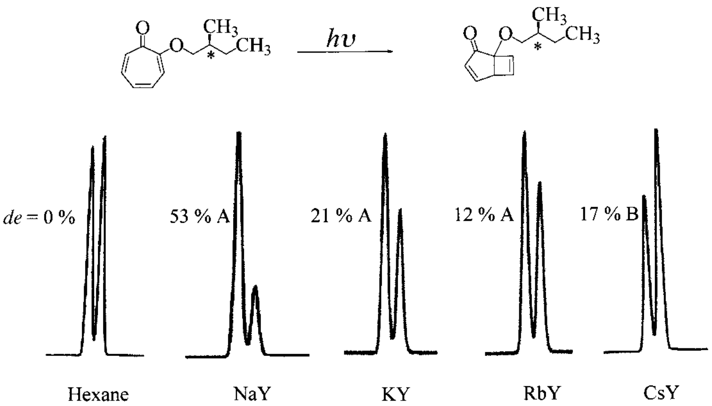


Figure 5. Results of studies on the photocyclization of (S)-tropolone 2-methyl butyl ether within various cation-exchanged Y zeolites. The HPLC traces clearly illustrate the dependence of *de* on the cation. Note the isomer B increases with the increasing size (and decreasing charge density) of the cation. The diastereomeric excess (%) and the isomer enhanced are shown on the HPLC traces.

Irradiation of the (*S*)-tropolone 2-methyl butyl ether shown in Figure 5 in solution yields a 1:1 mixture of diastereomeric products. Clearly, in solution the presence of the chiral auxiliary in proximity to the reactive center has no influence on the product stereochemistry. On the other hand, the same molecule when irradiated within Na Y gave the product in about 53% diastereomeric excess (Figure 5). The smaller and controlled space provided by the zeolite supercage apparently has forced the chiral center to establish communication with the reaction site. Considering that the chiral center has only alkyl groups (unlike the chiral inductors discussed in the previous section, Scheme 6) one would not expect any special interactions to develop between the chiral auxiliary and the

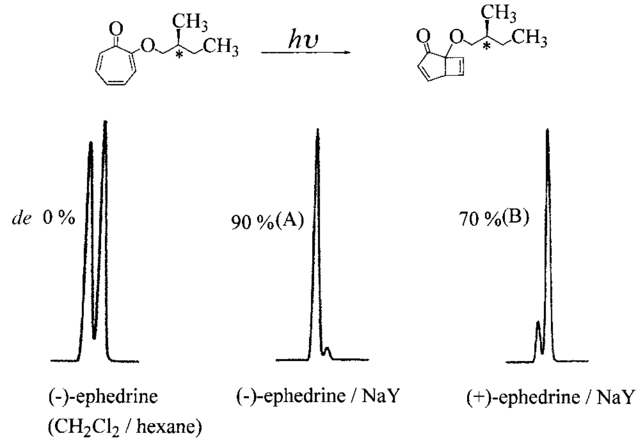


Figure 6. Results of studies on the photocyclization of (S)-tropolone 2-methyl butyl ether within chirally modified Na Y zeolite. The diastereomeric excess (%) and the isomer enhanced are shown on the HPLC traces. The non-identical reversal of the product enantiomer by the antipodes of the chiral inductor ephedrine is due to the fact that not all molecules are in proximity to a chiral inductor. Chiral induction also occurs due to the chiral auxiliary present in the molecule.

reaction centers within a zeolite. It is the small 'reaction cavity' that has enforced a certain amount of discipline on the reacting molecule. As shown in Figure 5, the cation plays a very important role. As the cation size increases (or the binding ability decreases) the extent of diastereoselectivity decreases. By the time one reaches Cs$^+$ the isomer that is enhanced is switched from A to B. This is the first clear indication that the cation controls the extent and the nature of selectivity.

The most exciting result was obtained when (S)-tropolone 2-methyl butyl ether was irradiated within an ephedrine-included Na Y (Figure 6). In the absence of ephedrine, diastereomer A is obtained in 53 % diastereomeric excess. When ($-$)-ephedrine was used as the chiral inductor the same isomer was enhanced to the extent of 90 %. On the other hand, (+)-ephedrine favors the B diastereomer to the tune of 70 % diastereomeric excess. These observations are truly remarkable. High *de* values has been achieved through the use of two chiral inducers and a confined space. The importance of this result becomes more apparent when one recognizes that irradiation in solution of the same compound in presence of ephedrine gave a 1:1 diastereomeric mixture (Figure 6). Zeolite is essential to achieve the high *de*. The exact mechanism operative is still unclear. Research along these lines is underway in our laboratory.

Future

Our goals in the area of zeolite-based chiral chemistry are a) to establish that a zeolite, when properly prepared/functionalized can serve as a matrix for conducting enantioselective reactions (both photo and thermal), and b) to discover the underlying factors that control the asymmetric induction within zeolites and thus develop a 'model' that will help us predict and plan asymmetric photoreactions within zeolites. Our long-range objective is to prepare reusable zeolite-based materials for asymmetric catalysis of photochemical processes. Chirally modified zeolites cast into zeolite membranes, zeolite thin films, zeolite silica sol–gel suspensions, and zeolite polymer composites could prove to be very valuable catalysts. First, however, we must establish the feasibility of employing zeolite matrices for noncatalytic asymmetric induction. Thus far our efforts have been in this direction.

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