

PHOTOCHEMISTRY OF ORGANIC MOLECULES IN MICROSCOPIC REACTORS

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ABSTRACT

The photochemistry of dibenzyl ketone and its derivatives has been employed to investigate the ability of zeolite molecular sieves to modify and to control the reaction channels available to organic molecules adsorbed on the internal and external zeolite surfaces. It is found that the observed photochemistry is very sensitive to the size/shape characteristics of the substrate ketones and of the pores and internal void space of the zeolites. Although unprecedented reactions of ketones have been found to be induced by absorption of the ketones on the zeolite surfaces, the reactions are consistent with expectations based on the topological structure of the zeolite surfaces and on the mechanism of ketone photolysis in homogeneous solution.

Zeolite Molecular Sieves. Designer Microscopic Reactors

Zeolites (from the Greek words *zeo*, "to boil" and *lithos* "stone")¹ are synthetic or natural minerals that often expel water so violently when heated that they appear to boil.² Classical zeolites are crystalline aluminosilicates whose internal porous structure contain channels and/or cages filled with exchangeable cations and which may also be filled with adsorbed water. The framework composition of zeolites consists of cations, aluminum, silicon, and oxygen. The framework constitution of zeolites consists of tetrahedral Al atoms and tetrahedral Si atoms linked by the sharing of O atoms (Figure 1). The porous structure of zeo-

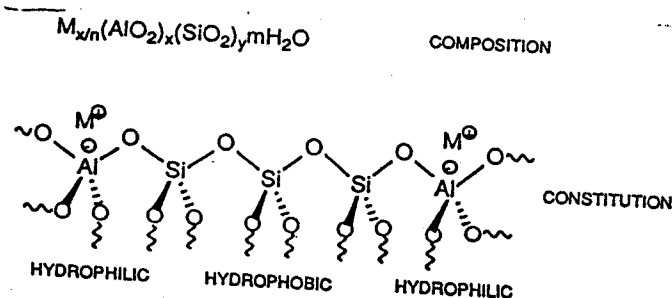


Figure 1. Composition and constitution of a classical aluminosilicate zeolite framework. The subscript x refers to the number of Al atoms (negative charges) in the framework; the subscript y refers to the number of Si atoms in the framework; and the subscript n refers to the charge of cation M.

lites results from the framework configuration, i.e., the three-dimensional geometric network of AlO_4 and SiO_4 tetrahedra. The zeolite frameworks which are obtained from natural or synthetic preparations contain pores, channels, cages, and interconnected voids. These void spaces and the internal zeolite surface occur in periodic fashion because of the crystalline nature of the framework. The combination of the topology of the internal void space and the chemical characteristics of the internal framework structure provide chemists with "designer microscopic reactors" in which chemical reactions can be performed. It can be imagined that the size and shape of these microscopic reactors, in conjunction with the peculiarities of molecular diffusion in periodically repeating void spaces will result in unusual characteristics of chemical reactions which are performed on molecules adsorbed on zeolites. Indeed, the ability of zeolites to selectively adsorb molecules based on size/shape selectivity rules has led to their designation as "molecular sieves". As a result of this "sieving" characteristic, the usual domination of substrate molecular structure in determining the course of chemical reactions might be replaced in certain circumstances by a domination of environmental structure in determining the course of chemical reactions for reactions conducted on

lines in the figure represent an oxygen bridge. The cubooctahedron is termed the sodalite unit and deserves as the building blocks for the faujasite zeolites. NaX corresponds to the faujasite type with a Si/Al of ca. 1.5, i.e., NaX is a strongly hydrophilic zeolite.

For the chemist, the important topological characteristics (size/shape characteristics of the internal void space) of NaX are the relatively large cavities (roughly spherical "supercages" of ca. 13Å diameter) which are connected by pores (roughly circular "windows" of ca. 8Å diameter). These "supercages" and "windows" constitute the internal surface of NaX zeolites and may be represented topologically as a sequence of periodic "supercages" and "windows" extending in three dimensions. Figure 3 shows a simple representation of a two dimensional slice of the NaX internal surface. It is important for the chemist to remember that NaX is "loaded" with Na⁺ ions which are not shown explicitly and that individual particles of NaX possess an external surface on which pores exist that provide access to the internal surface only to molecules whose size and shape are such as to allow them to pass readily through these entries to the internal surface. only to molecules whose size and shape are such as to

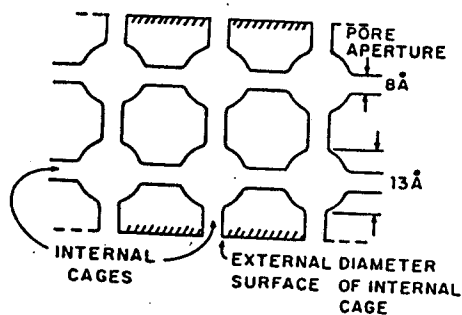


Figure 3. Simple topological representations of the X (top) and ZSM (bottom) classes of zeolites. The representation shows a two dimensional slice of the solid.

allow them to pass readily through these entries to the internal surface.

The framework of the ZSM class involves a pentasil (Figure 2) rather than a sodalite building block. These building blocks link together to form chains or sheets which generate a void space topology which consists of long tubular channels of diameter of ca. 6Å and lengths of ca. 50Å. These channels intersect to produce a void network resembling a plumbing pipe network (Figure 4).

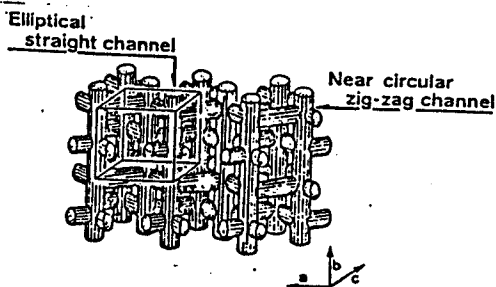


Figure 4. Schematic representation of the void space of the ZSM class of zeolites. Note that there exist two types of channels: the "zig-zag" and linear types. The latter are slightly larger in diameter than the former.

In the systems to be discussed in this report the ratio of the internal surface area to the external surface area will be very large (>1000). As a result this large excess of internal surface relative to external surface will provide a very simple driving force for occupancy of the internal surface for any adsorbed molecules that have the size/shape characteristics which allow entry to the internal surface.

Selection of Substrate Structure and Reaction Systems Based on Zeolite Characteristics.

Consideration of the topological features of the zeolite structures shown in Figure 3 provides a powerful driving force to imagine reactions and substrates both to check the validity of the simple representation of zeolite internal framework, and to engineer unusual chemical sequences. The key issues we shall consider are those related to size/shape and diffusion/

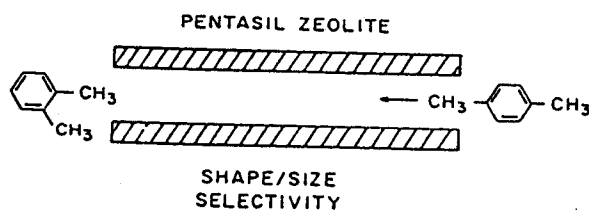
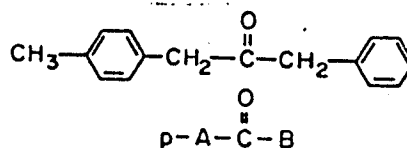
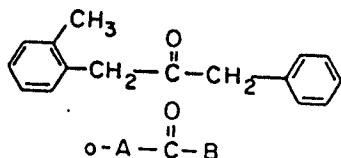


Figure 6. Schematic representation of the shape/size selectivity of pentasil zeolites. The size/shape of p-xylene allows it to be readily adsorbed on the internal zeolite framework, whereas the size/shape of o-xylene prevents it from being readily adsorbed on the internal zeolite framework.

which its long axis lies along the long axis of the ZSM channel, and thereby achieve an effective kinetic diameter (in this orientation) that is equal to that of benzene. The experimental manifestation of these ideas is the observation that ZSM zeolites serve as chromatographic material to quantitatively separate o-xylene from p-xylene (the former is not adsorbed, and the latter is strongly adsorbed)². This striking size/shape selectivity led us to consider DBK derivatives that might display differing photochemical reactions on zeolites as a result of factors which resemble those that allow the separation of o-xylene from p-xylene. Our approach was to investigate the photochemistry of the o-methyl DBK (o-ACOB) and the p-methyl DBK (p-ACOB) adsorbed on ZSM zeolites.



Conceptual and Experimental Strategies for Investigation of Size/Shape Selectivity of Photochemical Reactions of DBK's Adsorbed on ZSM Zeolites.

The conceptual framework for the investigation of DBK photochemistry on ZSM zeolites involves the production of a geminate triplet radical pair by photolysis of ketones adsorbed on the ZSM surface. From the working mechanism of DBK photochemistry it is expected that the competition between diffusional separation and radical pair reactions will then determine the observed products. From the results of o-xylene and p-xylene adsorption on ZSM zeolites it is expected that o-ACOB will be adsorbed mainly on the external surface of ZSM zeolites, whereas p-ACOB will be adsorbed mainly on the internal surface of ZSM zeolites (Figure 7).

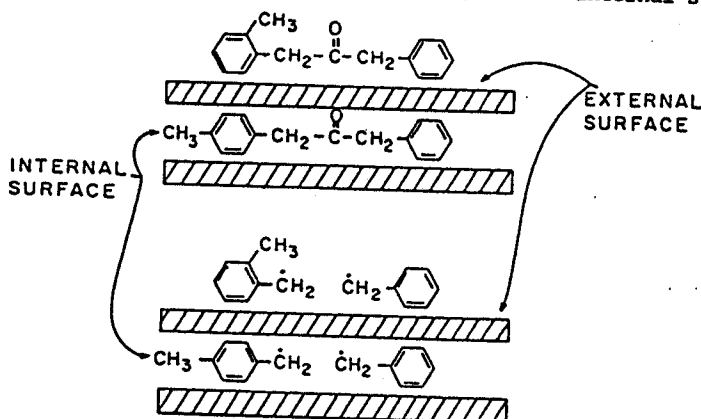
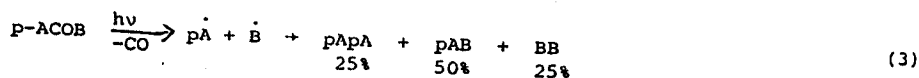
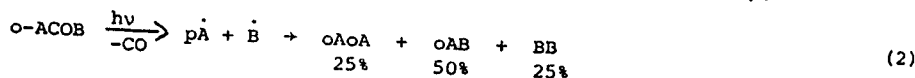


Figure 7. Schematic representation of the adsorption of o-ACOB (on the external surface) and of p-ACOB (on the internal surface) of ZSM zeolites. Photolysis produces oA and B radicals on the external surface, and produces pA and B radicals on the internal surface.

If what happens next is determined by diffusion on the ZSM surface, the reaction pathways available to the radical pairs produced from o-ACOB and p-ACOB might differ substantially. The experimental strategy is simply to measure product structures and infer how the "reaction channels" are related to the zeolite channels!

The photolysis of o-ACOB and p-ACOB in homogeneous solution leads to similar results: the three coupling products of benzyl radicals are formed (eqns. 2 and 3):



oAOA and BB as major products. Two simple tests of the mechanism are possible: a temperature test and a scavenging test.

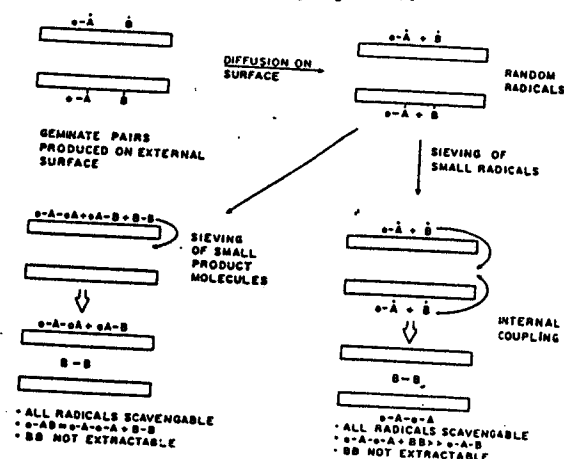


Figure 9. Proposed mechanism for the negative cage effect observed for the photolysis of o-ACOB on ZSM zeolites. See text for discussion

As the temperature of photolysis is lowered, the major products from photolysis of o-ACOB change from oAOA + BB to a mixture containing ever increasing amounts of oAB. At about -20°C oAB² (oAOA+BB) so that the cage effect has "risen" from ca. -100% to ca. 0%. A further decrease in temperature causes the yield of oAB to continue to increase until at -78°C , oAB is the major product, i.e., the cage effect is ca. +100%! The temperature effect is consistent with a relatively high activation energy for sieving of B radicals from the external to the internal surface. This causes radical coupling to occur mainly on the external surface as the temperature is decreased to -20°C . At this temperature random radical coupling occurs on the external surface. Below this temperature, diffusional separation of geminate pairs on the external surface slows down and geminate coupling becomes increasingly efficient until at -78°C only geminate coupling occurs.

The addition of free radical scavengers that are too large to enter the internal surface to the o-ACOB reaction system results in complete scrambling of the oA and B radicals (Figure 10).

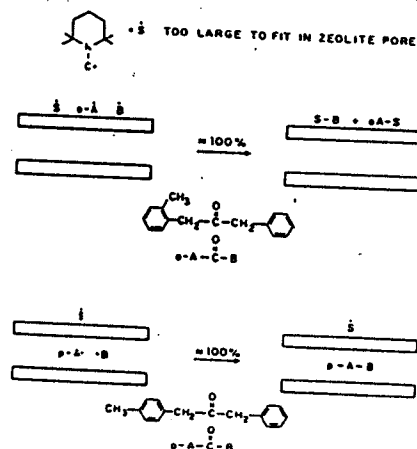


Figure 10. Radical scavenging of o-ACOB and p-ACOB. The free radical S is too large to enter the internal ZSM surface. Co-adsorption of this scavenger does not result in radical trapping in the case of p-ACOB, but results in nearly quantitative trapping in the case of o-ACOB.

Importantly, addition of the same scavenger to the p-ACOB reaction system results in negligible scavenging of pA and B radicals.

Thus, the photolysis of o-ACOB and p-ACOB on ZSM zeolites allows a striking confirmation of the remarkable size/shape characteristics of zeolite molecule sieves in controlling chemical reactions of molecules adsorbed on the zeolite surface. The ability to control chemical reactivity via dynamics of molecular diffusion through channel systems of zeolites has been termed "molecular traffic control" of chemical reactions.¹³

Size and Shape Characteristics of X Zeolites. A Remarkable Effect of Additives.

The 8 Å diameter of the windows of X zeolites that leads to the supercages is large enough to allow ready diffusion of DBK molecules into the supercages. The diffusional characteristics of organic molecules adsorbed on NaX have been extensively studied because of the importance of this zeolite and of related zeolites as catalytic materials.¹⁴ In general, the diffusion of adsorbed molecules becomes impeded as more molecules are added to the surface, i.e., as the surface coverage is increased.¹⁵ This result is attributed to the increasing interference to diffusion of molecules due to the occupancy of the windows leading to the

is consistent with experiment.

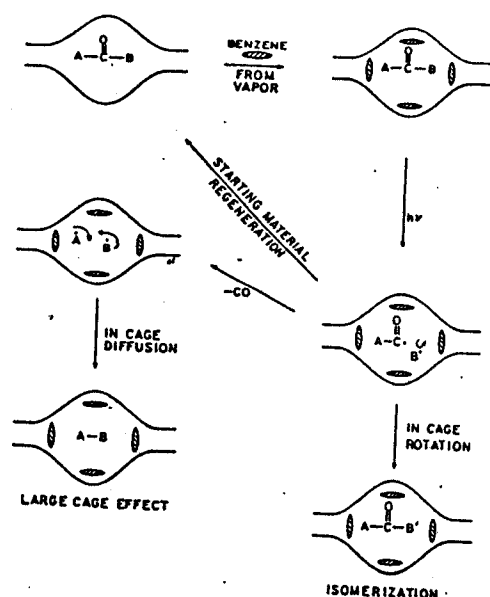


Figure 12. Schematic mechanism for the photolysis of DBK and substituted DBK's at low coverage on NaX. Diffusional separation is inhibited because of the congestion imposed by benzene coadsorbed in the supercages. See text for discussion.

Mechanism of Photolysis of Isomerization of DBK Adsorbed on NaX.

A proposed mechanism for formation of the isomeric DBK's is shown in Figure 13. The primary geminate triplet radical pair is compelled by congestion within the supercage to undergo self-reaction rather than diffusion and decarbonylation. Radical coupling may occur to regenerate DBK itself. Since this would regenerate the starting material, it would not be observed in normal product analysis. However, ^{13}C enrichment studies would provide information on this point. Coupling of the acyl radical to the benzene ring of the benzyl radical would lead to an isomeric ketone as shown in Figure 13. An intermediate expected, but not yet isolated, is the species produced by this first addition step (Figure 13). The isolated products are produced by a hydrogen transfer which achieves aromatization and produces the observed products.

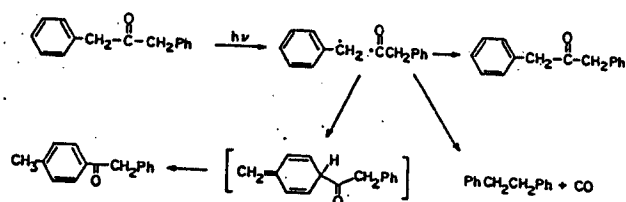


Figure 13. Proposed mechanism for formation of isomeric ketones from photolysis of DBK on NaX.

It is interesting to speculate whether the photoisomerization could be achieved twice by a two photon process. If this occurred, DBK would be turned "inside out" and would produce a benzophenone product. Indeed, it was found that the photolysis of DBI on NaY, a zeolite which possesses the same internal surface topology as NaX, but which possesses a higher Si/Al ratio, produces a benzophenone as the major product.¹⁶

Photolysis of Large Ring Cyclophanes Adsorbed on NaX Zeolites. Encarceration of Products by Ship in Bottle and Reptation Mechanisms.

The photolysis of small ring 2-phenyl cyclophanes has been shown to result in the formation of enals as the major products (Figure 14).¹⁸ No evidence for coupling of the primary radical pair to produce an isomeric ketone has been reported. If such a coupling occurred analogous to the photoisomerization of DBK observed on NaX, a cyclophane product would be produced (C_n , Figure 14). The size and shape of a cyclophane structure is quite distinct from that of the precursor cycloanone. In fact, from molecular models it is expected that for 12 carbon cyclophanes the product, cyclophane, if formed in a supercage, could not exit because its size exceeds that of the window to allow exit from the supercage. These considerations suggested to us a "ship in bottle" strategy for encarceration of product molecules in a supercage as a result of change in the size/shape characteristics which result upon going from the starting material to the product. If it is true that the adsorbed starting cycloanone has a smaller size than the cyclophane, and if the cyclophane is produced in a supercage, then the product of a photochemical reaction would be encarcerated within the zeolite internal surface.

for the execution of photochemistry, and on the other hand takes advantage of the information concerning the structures of novel environments to develop new photoreactions. The next step in the process is to let an interaction between the photochemistry and the novel environment provide new insights to each system. The basic idea was to produce a geminate triplet radical pair or biradical from a substrate adsorbed on a zeolite surface. Simple product analyses allow the determination of geminate radical pair combination efficiency (i.e., the extent of the cage effect) and the ability of the zeolite surface to control reaction channels available to the primary geminate radical pair and subsequent radical pairs (i.e., the extent of formation and structure of isomeric ketones). The results allow conclusions to be made concerning the size/shape selectivity features of zeolite molecular sieves on photochemical reactions. This information should also be useful in adding to our knowledge of the mechanism of catalytic processes which occur on zeolites, since diffusion and size/shape selectivity are hallmark features of these catalytic materials.²⁰

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