the primary step of eq 12. For the adsorbed phase, the secondary product C_2H_4 along with CO is observed.[77] Acetylene photochemistry by 185 nm produces the radicals H• and C_2H• in the gas phase and a number of secondary products.[76] The adsorbed-phase reaction 13 is by contrast remarkably clean, with hydrogen exchange among isotopomers the only evidence for chemistry.[78] Finally, 185-nm gas-phase photochemistry of SO_2 produces SO and O and secondary reactions generate SO_3.[76] However no reaction for this system occurs in the adsorbed phase.[79] It is likely that the arrangements of the excited adsorbed species play a crucial role in the resulting photochemistry.[19] While the mechanisms of adsorbed-phase photochemistry on dielectric substrates have been explored for LiF(100),[19,20] we view the understanding of simple adsorbed-phase reactions like those in eqs 12–14 to be essentially lacking.

Finally, we turn our attention to the most poorly understood (but likely most important) energy processes at salt surfaces. Here the surfaces are on particulates thrown into the atmosphere by the world's oceans. The salt particulates are freed of halides by reaction with sulfur and nitrogen oxides from anthropogenic and natural sources.[80–82] While these chemical exchange processes have been reproduced in the laboratory for gas-phase reactions with both liquid[82] and solid surfaces,[83] the mechanisms for the reactions have not been established. We believe the spectroscopic techniques described in this Account may help elucidate these mechanisms.

Registry No. NaCl, 7647-14-5.

(76) Okabe, H. *Photochemistry of Small Molecules*; Wiley: New York, 1978.
(77) Berg, O.; Ewing, G. E. *J. Phys. Chem.* 1991, 95, 2908.
(78) Dunn, K. Private communication.
(79) Berg, O. Private communication.
(80) Hitchcock, D. R.; Spiller, L. L.; Wilson, W. E. *Atmos. Environ.* 1980, 14, 165.
(81) Junge, C. E. *Tellus* 1956, 8, 127.
(82) Robbins, R.; Cadle, R.; Eckhardt, D. *J. Meteorol.* 1959, 16, 53. Cadle, R.; Robbins, R. *Discuss. Faraday Soc.* 1960, 30, 155.
(83) Finlayson-Pitts, B. J.; Livingston, F.; Besko, H. *Nature* 1990, 343, 622.

Photochemical and Photophysical Studies of Organic Molecules Included within Zeolites[†]

V. Ramamurthy,* D. F. Eaton, and J. V Caspar

Central Research and Development, Experimental Station, The Du Pont Company, Wilmington, Delaware 19880-0328

Introduction

Being inspired by and having realized the complexity of natural systems, chemists have utilized a number of organized/confined media to study the photochemical and photophysical behavior of guest molecules. Examples of organized media in which the guest molecules' behavior has been investigated include molecular crystals, inclusion complexes (both in the solid and solution states), liquid crystals, micelles and related assemblies, monolayers, LB films, surfaces, and more recently natural systems such as DNA.[1] The studies carried out thus far come under the following categories: (a) influence of media on the photochemistry and photophysics of molecules; (b) photochemistry and photophysics as a tool to understand the media; (c) influence of photochemistry and photophysics on the media; and (d) studies directed toward applications— devices, solar energy, biological implications. In this Account an overview of the activities in our laboratory,

V. Ramamurthy, after obtaining training in photochemistry under the direction of R. S. H. Liu (University of Hawaii, Ph.D., 1974), P. de Mayo (University of Western Ontario, postdoctoral research, 1974–1975), and N. J. Turro (Columbia University, postdoctoral research, 1975–1978), joined the faculty of the Department of Organic Chemistry, Indian Institute of Science, Bangalore, India, where he remained until 1987. In 1987 he joined Du Pont Central Research and Development, Wilmington, DE, as a member of the research staff where he continues his interest in the area of organic photochemistry.

David F. Eaton is Research Manager, Materials Science, within Du Pont Central Research and Development with responsibility for research programs in photoscience, organic and inorganic nonlinear optics, and thin film physics. His education was obtained at Wesleyan University (A.B., 1968) and Caltech (Ph.D., Organic Chemistry, 1972). He has worked in several areas of photochemistry and photoimaging during his career with Du Pont.

J. V Caspar received his B.S. (1978) degree from the Massachusetts Institute of Technology. After completing his Ph.D. (1982) at the University of North Carolina at Chapel Hill under the direction of T. J. Meyer, he spent a year as a Postdoctoral Fellow with H. B. Gray at the California Institute of Technology. He joined the Central Research and Development Department at DuPont as a member of the research staff in 1983. His interests continue to revolve around diverse areas of photochemistry, photophysics, and spectroscopy.

[†]Contribution No. 6177.
(1) Fox, M. A., Ed. *Organic Phototransformation in Non-homogeneous Media*; American Chemical Society: Washington, D.C., 1985. Thomas, J. K. *Chemistry of Excitation at the Interfaces*; American Chemical Society: Washington, D.C., 1984. Ramamurthy, V., Scheffer, J. R., Turro, N. J., Eds. *Organic Chemistry in Anisotropic Media*. Tetrahedron Symposia in Print 29. *Tetrahedron* 1987, 43, 1197–1746. Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987. Matsuura, T., Anpo, M., Eds. *Photochemistry on Solid Surfaces*; Elsevier: Amsterdam, 1989. Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: New York, 1991. Schneider, H. J., Durr, H., Eds. *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; VCH: Weinheim, 1991. Honda, K., Ed. *Photochemical Processes in Organized Molecular Systems*; North-Holland: Amsterdam, 1991. Ramamurthy, V., Ed. *Photochemistry in Organized and Constrained Media*; VCH: New York, 1991.

Table I
Dependence of Physical Parameters of M Y Zeolites on the Cation

cation (M^+)	ionic radius of the cation (Å)	electrostatic field (V/Å) within the cage	electrostatic potential (e/r) of the cation	spin–orbit coupling	vacant space within the supercage (Å^3)	
					Y zeolite	X zeolite
Li	0.76	2.1	1.67		834	873
Na	1.02	1.3	1.05	27	827	852
K	1.38	1.0	0.75	87	807	800
Rb	1.52	0.8	0.67	360	796	770
Cs	1.67	0.6	0.59	840	781	732

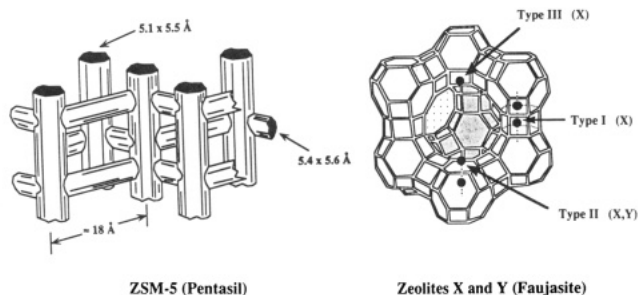Structures of Zeolites Used in this Work

Figure 1. Structures of zeolites ZSM-5 and faujasites (X and Y). The positions of cations in X and Y zeolites are shown as types I, II, and III. Type II and III cations are accessible to organic molecules included within supercages.

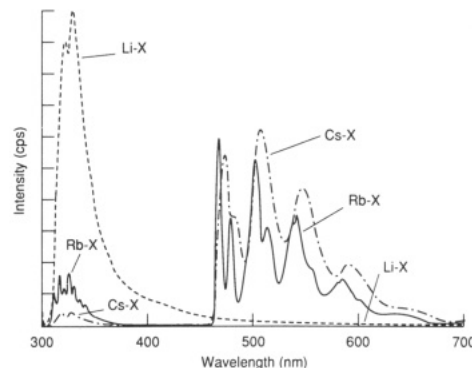Cation Dependent Emission from NAPHTHALENE included in the Supercages of Faujasites

Figure 2. Emission spectra at 77 K of naphthalene included in Li X, Rb X, and Cs X (excitation λ 285 nm). Note that the ratio of phosphorescence to fluorescence changes with the cation, but the ratio change is independent of the excitation wavelength.

utilizing zeolite as a medium for photochemical and photophysical studies, is presented.[2] We highlight how one can utilize a zeolite matrix to control the photophysical and photochemical behavior of guest molecules included within it.

Zeolites may be regarded as open structures of silica in which aluminum has been substituted in a well-defined fraction of the tetrahedral sites.[3] The frameworks thus obtained contain pores, channels, and cages of different dimensions and shapes. The substitution of trivalent aluminum ions for a fraction of the tetravalent silicon ions at lattice positions results in a network that bears a net negative charge which is compensated by positively charged counterions. The topological structure of X- and Y-type zeolites consists of an interconnected three-dimensional network of relatively large spherical cavities, termed supercages (diameter of about 13 Å; Figure 1). Each supercage is connected tetrahedrally to four other supercages through 8-Å windows or pores. Charge-compensating cations are exchangeable, and such an exchange brings along with it a variation in a number of physical characteristics such as electrostatic potential and electric field within the cage, the spin–orbit coupling parameter, and the vacant space available for the guest within the supercage (Table I). Among the medium-pore-sized zeolites, perhaps the most studied are the pentasil zeolites, ZSM-5 and ZSM-11 (Figure 1). The pentasils are composed of two intersecting channel systems. For ZSM-5, one system consists of straight channels with a free diameter of

about 5.4–5.6 Å and the other consists of sinusoidal channels with a free diameter of about 5.1–5.5 Å. For ZSM-11, both are straight channels with dimensions of about 5.3–5.4 Å. The volume at the intersections of these channels is estimated to be 370 Å^3 for a free diameter of about 8.9 Å. Other zeolites of interest for photochemical studies include the LZ-L, mordenite, offretite, omega, and beta.

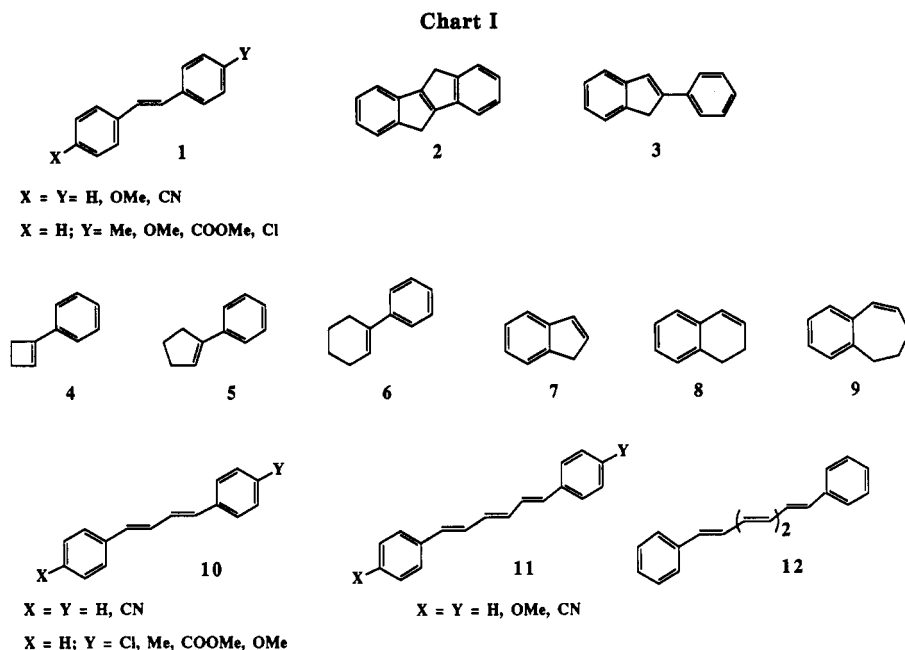## Cation-Dependent Photobehavior of Organic Guests Included with Faujasites

Heavy-Atom Cation Effect. *Enhanced Phosphorescence from Aromatics and Olefins.* In this section we illustrate how a change in the alkali cation present within supercages of faujasites alters the effective spin–orbit coupling available for a zeolite-included guest molecule. By utilizing this technique we have been able to observe phosphorescence in systems for which previous attempts have yielded only negative results. This cation-enhanced triplet generation can also be used to control the photoproduct distribution obtained during the dimerization of acenaphthylene.

As shown in Figure 2, the emission spectrum of naphthalene is profoundly affected by inclusion in faujasites.[4] For low-mass cations such as Li$^+$ and Na$^+$, the emission spectra show the typical naphthalene blue fluorescence. However, as the mass of the cation increases (e.g., from Rb$^+$ to Cs$^+$ to Tl$^+$), there is a dramatic decrease in fluorescence intensity with a concomitant increase in the intensity of phosphorescence.

(2) For leading references, see: Garcia-Garibay, M. A.; Zhang, Z.; Turro, N. J. *J. Am. Chem. Soc.* **1991**, *113*, 6212. Yoon, K. B.; Kochi, J. K. *J. Phys. Chem.* **1991**, *95*, 3780. Iu, K. K.; Thomas, J. K. *J. Phys. Chem.* **1991**, *95*, 506. Johnston, L. J.; Scaiano, J. C.; Shi, J. L.; Siebrand, W.; Zerbetto, F. *J. Phys. Chem.* **1991**, *95*, 10018. Krueger, J. S.; Lai, C.; Li, Z.; Mayer, J. E.; Mallouk, T. In *Inclusion Phenomena and Molecular Recognition*; Atwood, J., Ed.; Plenum Press: New York, 1990; p 365.

(3) Breck, D. W. *Zeolite Molecular Sieves: Structure, Chemistry, and Use*; John Wiley and Sons: New York, 1974. Dyer, A. *An Introduction to Zeolite Molecular Sieves*; John Wiley and Sons: Bath, U.K., 1988. van Bekkum, H., Flanigen, E. M., Jansen, J. C., Eds. *Introduction to Zeolite Science and Practice*; Elsevier: Amsterdam, 1991.

(4) Ramamurthy, V.; Caspar, J. V; Corbin, D. R.; Eaton, D. F. *J. Photochem. Photobiol. A* **1989**, *50*, 157. Caspar, J. V; Ramamurthy, V.; Corbin, D. R. *Coord. Chem. Rev.* **1990**, *97*, 225. Phosphorescence, although not to the same extent as by heavy cations, can also be enhanced from a number of aromatics included in light-atom cation zeolites by the use of zenon gas and alkali halides as inert filters. Ramamurthy, V.; Sanderson, D. R. Unpublished results.

Chart I

X = Y= H, OMe, CN

X = H; Y= Me, OMe, COOMe, Cl

X = Y = H, CN

X = H; Y = Cl, Me, COOMe, OMe

X = Y = H, OMe, CN

Both the singlet and triplet excited-state lifetimes (τ_T and τ_S) of naphthalene are cation dependent, with both decreasing as the cation mass increases. These effects have been established to be due to the heavy cation effect[5a] by the following observations: (a) a log–log plot of τ_T^{-1} vs ξ^2 is linear with a maximum predicted slope of unity; (b) a linear relationship between singlet and triplet decay rates with cation variation is observed; and (c) consistent with the smaller energy gap between the S_1 and T_1 as compared to the T_1 and S_0 states, the singlet decay (via intersystem crossing to T_1) is influenced more by the cation than is the triplet decay. The magnitude of the heavy-atom effect we observe in zeolites is significantly larger than that observed for the 1,5-naphtho-22-crown-6 exchanged with heavy-atom cations where the cation is rigidly held over the naphthalene π-face.[5b] In fact the zeolite samples show heavy-atom effects nearly as large as for a series of 1-halonaphthalenes where the perturbers are covalently attached to the chromophore.[5c] By utilizing optically detected magnetic resonance (ODMR) in zero applied magnetic field, we were able to deduce a model of the geometry of the cation–aromatic (naphthalene) interaction within the supercages of faujasites.[6] The triplet-sublevel-specific dynamics for adsorbed naphthalene shows a distinct increase in relative radiative character and total rate constant of the out-of-plane x-sublevel (perpendicular to molecular plane) with increasing mass of the cation perturber. This is consistent with the naphthalene being adsorbed through its π-cloud at a cation site.

Enhanced phosphorescence is observed for a wide range of different organic guests when included in Tl^+-exchanged faujasites.[7] The only set of examples of guests for which phosphorescence is not observed are fused aromatics which are too large in diameter to fit
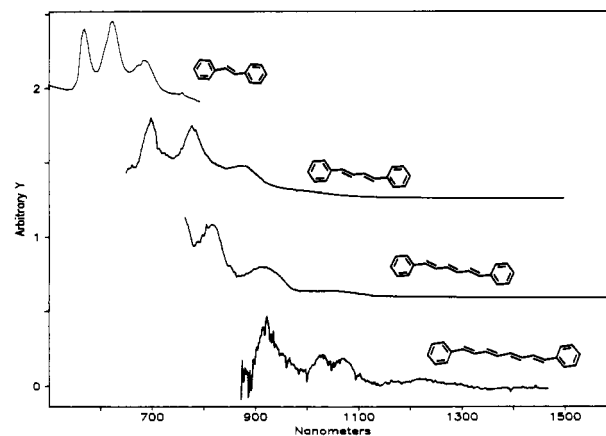
(5) (a) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1969. (b) Larson, J. M.; Sousa, L. R. *J. Am. Chem. Soc.* **1978**, *100*, 1942. (c) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905.
(6) Ramamurthy, V.; Caspar, J. V; Corbin, D. R.; Schlyer, B. D.; Maki, A. H. *J. Phys. Chem.* **1990**, *94*, 3391.
(7) Ramamurthy, V.; Caspar, J. V; Eaton, D. F.; Kuo, E. V.; Corbin, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 3882.

Figure 3. Phosphorescence spectra at 77 K of α,ω-diphenyl polyenes included in Tl X. Excitation wavelengths: stilbene, 295 nm; diphenylbutadiene, 340 nm; diphenylhexatriene, 350 nm; diphenyloctatetraene, 375 nm.

through the 8-Å windows of the X- and Y-type zeolites (e.g., coronene and triphenylene). This phenomenon is not restricted to faujasites alone. Enhanced phosphorescence is observed for guest molecules within heavy-atom cation exchanged ZSM-5, L, M-5, Ω-5, and β.

It is easy to appreciate the potential of the unusual environment of the zeolite when one realizes that even olefins, systems that under normal conditions do not show phosphorescence, emit from their triplet states when included in Tl^+-exchanged faujasite and pentasil zeolites. Upon excitation, *trans*-stilbene and related model compounds **2** and **3**, a number of para-substituted *trans*-stilbenes **1**, several 1-phenylcycloalkenes (**4–6**), and phenylalkenes (**7–9**) (Chart I) included in Tl X and in Tl ZSM-5 emit phosphorescence and fluorescence both at room temperature and at 77 K (Figure 3).[7,8] An even more striking example is provided by α,ω-diphenyl polyenes (**10–12**), which phosphoresce upon inclusion in Tl^+-exchanged zeolites (Figure 3).[6,7] To our knowledge no authentic phos-
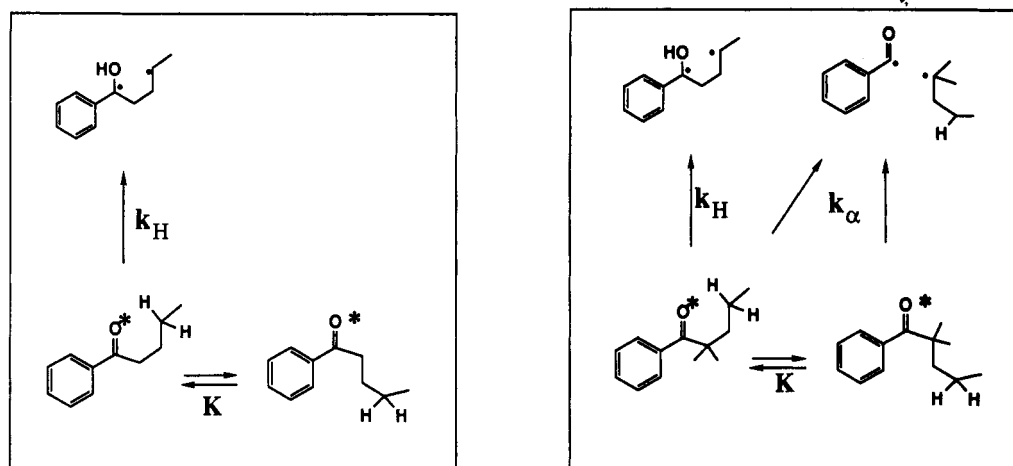
(8) Ramamurthy, V.; Caspar, J. V; Corbin, D. R. *Tetrahedron Lett.* **1990**, *31*, 1097.

Chart II

13   14   15   16   17

R = Alkyl   18

19 and 20

19 a X = CH₂   n = 4   20 a X = CO; n = 7
    b X = CH₂CH₂   n = 4   b X = CO; n = 8
    c X = CH₂   n = 5   c X = CO; n = 9
    d X = CH₂CH₂   n = 5
    e X = CH₂CH₂   n = 6

Scheme I

cis

trans

- Excited singlet (S₁) gives essentially *cis* dimer (t/c ~ 0.03)

- Excited Triplet (T₁) gives *trans* and *cis* dimers (t/c ~1.7); slightly solvent polarity dependent

- Poor intersystem crossing from S₁ to T₁ in the absence of external perturbations

phorescence spectra from α,ω-diphenyl polyenes and cyclic and acyclic phenylalkenes have been previously reported, although phosphorescence from several *trans*-stilbenes has been recorded at 77 K in organic glasses containing ethyl iodide as the heavy-atom perturber.[9]

Heavy-Atom Cation Influence on Photoreactions. On the basis of the above discussion on enhanced triplet formation in the presence of a heavy-atom cation, one should be able to utilize alkali cations to control the extent of the singlet and triplet reactivities of guest molecules included within zeolites. We have utilized the photobehavior of acenaphthylene as an example to illustrate this strategy. Irradiation of acenaphthylene in solution yields both the cis and the trans dimers; the singlet gives predominantly the cis dimer, whereas the triplet gives both the cis and trans dimers in comparable amounts (Scheme I).[10] Photolyses of dry solid inclusion complexes of acenaphthylene in various cation-exchanged (Li, Na, K, and Rb) Y zeolites gave the cis and trans dimers, the ratio of which strongly depended upon the cation.[11] The cis to trans dimer ratio, relative efficiency of dimerization, relative triplet yields, and triplet lifetimes of acenaphthylene are dependent on the cation. High triplet yield and high yield of the triplet-derived trans dimer are indeed obtained in K Y and Rb Y, as one would expect on the basis of heavy-atom cation effect.

Light-Atom Cation Effect. While the heavy-atom cations influence the behavior of guests through high

spin–orbit coupling parameters, the light-atom cations, as presented in this section, modify the behavior of guests through their high charge density/electrostatic potential (Table I). Two of the features that depend directly on the charge density/electrostatic potential of the cation are the micropolarity of the supercage and the binding strength between the cation and the guest molecule.

In this context, the following observations made with the photophysical probes pyrene, pyrenecarbaldehyde, and *p*-(dimethylamino)benzonitrile are worth noting:[12] (a) the supercage is highly polar when the cation is Li or Na, and (b) the polarity of the cage decreases with an increase in cation size (Li > Na > K > Rb > Cs). By utilizing the reported correlation of solvent parameter $E_T(30)$ for *p*-(dimethylamino)benzonitrile,[13] the supercages of Li X and Na X are qualitatively estimated to have polarities similar to that of a methanol–water (1:1) mixture, while those of Rb X and Cs X are estimated to have polarities close to that of propanol.

The importance of light-atom cations in binding aromatic guest molecules within supercages is brought out by the ²H NMR studies on phenanthrene.[14] The strength of the binding interaction between the cation and the guest molecule, as estimated from the NMR data, is directly dependent on the charge density/electrostatic potential of the cation. The higher the charge density, the stronger the binding (ΔH of binding: Na⁺, 14.9; K⁺, 11.0; Cs⁺, 7.9 kcal mol⁻¹). IR and thermogravimetric data reveal a similar trend for aryl alkyl ketones included in supercages.[15] The carbonyl stretching frequency of valerophenone shows a pronounced cation dependence: Na X, 1651; Cs X, 1675 and neat 1687 cm⁻¹. The temperatures of desorption of the related octanophenone adsorbed over M⁺ Y zeolites as measured by thermogravimetric analyses also depend on the cation: Li Y, 407; K Y, 391; Cs Y, 341 °C.

A clear illustration of the light-atom cation influence on photophysical properties of guest molecules is seen in the diffuse reflectance spectra of aromatics (e.g., pyrene, benzene, and anthracene)[16] and in the phos-

(9) Saltiel, J.; Khalil, G. E.; Schanze, K. *Chem. Phys. Lett.* 1980, *70*, 233. Gorner, H. *J. Phys. Chem.* 1989, *93*, 1826.

(10) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum Press: New York, 1976; pp 435–443.

(11) Ramamurthy, V.; Corbin, D. R.; Kumar, C. V.; Turro, N. J. *Tetrahedron Lett.* 1990, *31*, 47.

(12) Ramamurthy, V.; Sanderson, D. R.; Eaton, D. F. *Photochem. Photobiol.*, in press. Ramamurthy, V. In *Proceedings of the Ninth International Zeolite Conference*; von Ballmoos, R., Higgins, J. B., Treacy, M. M. J., Eds.; Butterworths: Stoneham, MA, in press.

(13) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: New York, 1988.

(14) Hepp, M.; Ramamurthy, V.; Corbin, D. R.; Dybowski, C. *J. Phys. Chem.* 1992, *96*, 2629.

(15) Ramamurthy, V.; Corbin, D. R.; Eaton, D. F. *J. Org. Chem.* 1990, *55*, 5269.

Scheme II

Scheme III

phorescence emission spectra of aryl alkyl ketones (e.g., acetophenone, valerophenone, and octanophenone)[17] in X zeolites. In aromatics the lowest energy symmetry-forbidden electronic absorption band gains intensity with light cations. In the case of aryl alkyl ketones, phosphorescence emission spectra suggest that the nature of the lowest triplet is inverted from an nπ^* to a $\pi\pi^*$ state by the light cation.[18]

Dramatic variations in product distribution, dependent on the cation, have been obtained for a large number of carbonyl systems (13–20) poised for both Norrish type I and type II processes (Chart II).[17,19] This has been interpreted to be a reflection of the light-atom cation effect as illustrated in Scheme II with valerophenone and α,α-dimethylvalerophenone as examples.[17] Interaction between the light-atom cation and the carbonyl group would be expected to favor conformations not suitable for the type II process. Such

a reduction in the type II favorable conformer population should result in a decrease in the rate of hydrogen abstraction and in a reduction of the triplet lifetime.[20] Indeed, the latter has been observed (triplet lifetime of valerophenone in solution, <5 ns; in Li X, 4–5 μs; Na X, 0.8 μs; Cs X, <0.2 μs).[17] The above model predicts that in systems such as α,α-dimethylvalerophenone, capable of both type I and type II processes, type I products will be obtained in enhanced yields. Results obtained with a large number of acyclic and cyclic ketones (Chart II) follow this prediction.[19] With ketones 13–18, which undergo the type I reaction in competition with the type II process in solution, the type I product, benzaldehyde, is obtained in enhanced yield in X and Y zeolites. Impressive results are obtained with macrocyclic ketones 19 and 20, which in solution do not undergo type I cleavage. In these cases, the yield of Norrish type I product increased from 0% in isotropic media to as high as 60% within zeolites. Although Norrish type I products were obtained in every cation-exchanged X and Y zeolite, the yield was higher when Li or Na was the cation.

Cation Size Effect. *Supercage Free Volume (Reaction Cavity Size) Control by the Choice of Cation.* The free volume available for an organic guest molecule within the supercages of faujasites depends on the number and nature of the cation (Table I). Turro and

(16) Ramamurthy, V. Unpublished results. Ramamurthy, V. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; p 429. Ramamurthy, V. In *Inclusion Phenomena and Molecular Recognition*; Atwood, J., Ed.; Plenum Press: New York, 1990; p 351.

(17) Ramamurthy, V.; Corbin, D. R.; Eaton, D. F. *J. Chem. Soc., Chem. Commun.* 1989, 1213. Ramamurthy, V.; Corbin, D. R.; Johnston, L. J. *J. Am. Chem. Soc.* 1992, *114*, 3870.

(18) Baum, E. J.; Wan, J. K. S.; Pitts, J. N. *J. Am. Chem. Soc.* 1966, *88*, 2652. Kearns, D. R.; Case, W. *J. Am. Chem. Soc.* 1966, *88*, 5087. Lamola, A. A. *J. Chem. Phys.* 1967, *47*, 4810.

(19) Corbin, D. R.; Eaton, D. F.; Ramamurthy, V. *J. Org. Chem.* 1988, *53*, 5384. Ramamurthy, V.; Corbin, D. R.; Turro, N. J.; Sato, Y. *Tetrahedron Lett.* 1989, *30*, 5829. Ramamurthy, V.; Lei, X. G.; Turro, N. J.; Lewis, T. J.; Scheffer, J. R. *Tetrahedron Lett.* 1991, *32*, 7675.

(20) Alexander, E. C.; Uliana, J. A. *J. Am. Chem. Soc.* 1974, *96*, 5644. Wagner, P. J. *Acc. Chem. Res.* 1983, *16*, 461. Wagner, P. J.; Park, B. S. *Org. Photochem.* 1991, *11*, 227.

Scheme IV

Figure 4. Excitation (above) and diffuse reflectance (below) spectra of pyrene within Rb Y zeolite. Note that the excitation spectra of the monomer and excimer differ and that the correspondence between the excitation spectra of the monomer and diffuse reflectance spectrum is excellent.
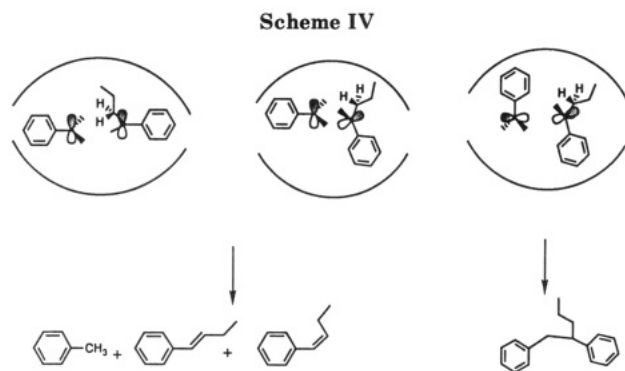
co-workers have exploited this feature in their studies on dibenzyl ketones.[21] One example provided below from our own studies[22,23] highlights the importance of the size of the cation on the product distribution.

Photolysis of α-alkylbenzyl benzyl ketones **21** in solution yields a number of products, among which diphenylalkanes AA, AB, and BB, resulting from the coupling of the two benzylic radicals (Scheme III) and obtained in a statistical ratio of 1:2:1, are important to this discussion.[24] In general, two radical species can terminate by either a coupling or a disproportionation process. Within the supercages of X and Y zeolites, two benzylic radicals react by *both* coupling and disproportionation processes, the latter yielding the olefins.[15,22] This is clearly different from what happens in solution. The ability of the disproportionation reaction, an unobserved process in solution, to become the major process within a supercage is attributed to the differences in motions executed by the reactant fragments during these two processes (Scheme IV). A relatively larger overall motion would be required to bring the two benzylic radical fragments together for head-to-head coupling than that required to move an alkyl group of one of the benzylic radical fragments so that one of its methylene hydrogens is in a suitable position for abstraction by the other benzylic carbon radical. Consistent with the model that the radical pair would prefer the pathway of "least volume and motion" when the free space around it is small, the yield of the disproportionation products increased with the decrease in the size of the reaction cavity, i.e., with the increase in the size of the cation.

Site Inhomogeneity and Multiple Occupancy. The discussions above did not address a basic question: "Should the zeolite be considered a microheterogeneous or a homogeneous medium?" Unlike silica and other related surfaces,[25] the internal structures of zeolites are highly homogeneous and possess well-defined uniform cages/cavities/channels. Studies by us,[7,26] Scaiano,

Johnston and co-workers,[27] and Thomas and co-workers[28] have shown that the distribution of organic molecules within zeolites is not uniform. A few of our observations pertinent to this aspect are highlighted below.

Phosphorescence spectra of *trans*-stilbene included in Tl X are excitation wavelength dependent.[7,8] This dependence is attributed to the presence of various noninterconverting (within the triplet lifetime) rotational conformers (phenyl ring rotated with respect to the double bond) of *trans*-stilbene within the supercage. This is unlike *trans*-stilbene dissolved in an organic solvent where a single minimum-energy conformation is favored. Such a wavelength-dependent phosphorescence has been observed with other olefins such as phenylindene **2**, 1,2-dinaphthylethylene, and 1,4-diphenylbutadiene **10** (Chart I) included in Tl X.

In X and Y zeolite matrixes, the excitation spectra for the monomer and the excimer emissions of pyrene and pyrenecarbaldehyde differ significantly (Figure 4), implying that there are pyrene/pyrenecarbaldehyde molecules under at least two different environments within the cages of faujasites.[12,26] Such a phenomenon is the result of the occupancy difference within cages—the guest molecules are not uniformly distributed within the cages: cages of both single and double occupancies are present. While monomer emission comes from molecules present in both types of cages, the excimeric emission probably originates from molecules present only in doubly occupied cages (the rise time for excimer emission is less than 1 ns).[28] Naphthalene triplets and excited singlets of a few aromatics in M X (M = K, Rb, and Cs) zeolites show multiexponential decay at temperatures above 150 K.[4] The above studies indicate that one should consider the zeolite–guest system as "microheterogeneous" and that one should not treat all guest molecules to be identical within zeolites.

(21) Turro, N. J.; Wan, P. *J. Am. Chem. Soc.* **1985**, *107*, 678. Turro, N. J.; Cheng, C. C.; Lei, X. G.; Flanigen, E. M. *J. Am. Chem. Soc.* **1985**, *107*, 3740. Turro, N. J.; Lei, X. G.; Cheng, C. C.; Corbin, D. R.; Abrams, L. *J. Am. Chem. Soc.* **1985**, *107*, 5824. Turro, N. J.; Zhang, Z. *Tetrahedron Lett.* **1989**, *30*, 3761.

(22) Ramamurthy, V.; Corbin, D. R.; Eaton, D. F.; Turro, N. J. *Tetrahedron Lett.* **1989**, *30*, 5833.

(23) Corbin, D. R.; Eaton, D. F.; Ramamurthy, V. *J. Am. Chem. Soc.* **1988**, *110*, 4848.

(24) Nageshwer Rao, B.; Syamala, M. S.; Turro, N. J.; Ramamurthy, V. *J. Org. Chem.* **1987**, *52*, 5517.

(25) Turro, N. J. *Tetrahedron* **1987**, *43*, 1589. Johnston, L. J. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; p 359.

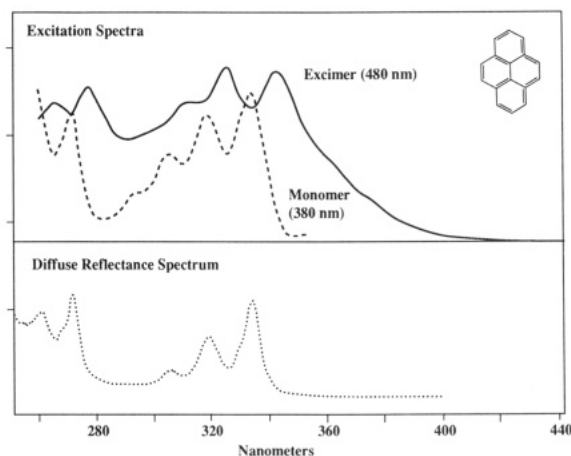(26) Ramamurthy, V.; Caspar, J. V *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 211.

(27) Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1985**, *63*, 1308. Wilkinson, F.; Willsher, C. J.; Casal, H.; Johnston, L.; Scaiano, J. C. *Can. J. Chem.* **1986**, *64*, 539. Kelly, G.; Willsher, C. J.; Wilkinson, F.; Netto-Ferreira, J. C.; Olea, A.; Weir, D.; Johnston, L. J.; Scaiano, J. C. *Can. J. Chem.* **1990**, *68*, 812.

(28) Liu, X.; Liu, K.-K.; Thomas, J. K. *J. Phys. Chem.* **1989**, *93*, 4120. Liu, K.-K.; Thomas, J. K. *Langmuir* **1990**, *6*, 471. Suib, S. L.; Kostapapas, A. *J. Am. Chem. Soc.* **1984**, *106*, 7705.

Scheme V

22   R' = Phenyl and R = Alkyl
23   R = R' = alkyl

Cyclization Products
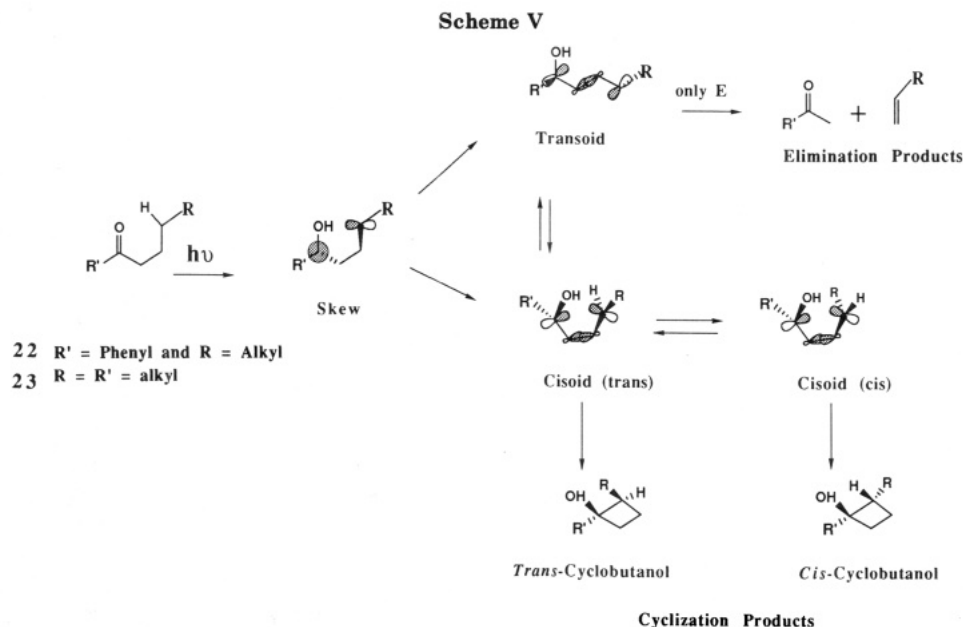
Cavity Size Control by the Choice of Zeolite

Results discussed in the preceding section suggest that the size of the reaction cavity and the free volume within play an important role in controlling the reaction course. Are these conclusions general and applicable to other organized media? We believe that they are. Differences in product selectivity obtained for a particular reaction within various organized media can be attributed to the size, shape, and nature (stiff or flexible) of the reaction cavity available for the reactant molecules.[29,30] The degree of tolerance of the "reaction cavity" to the distortions that accompany a reaction is expected to play an important role in the extent of selectivity obtained. To explore this concept, we investigated the photobehavior of a few ketones and olefins in two zeolites having distinctly different size and shape—faujasites and pentasils.[31,32]

Photolysis of aryl alkyl ketones 22 such as valerophenone, octanophenone, and other higher analogs included in pentasil zeolites (ZSM-5 and ZSM-11) gave via the Norrish type II γ-hydrogen abstraction process (Scheme V) *only* elimination products. In contrast, both cyclization and elimination products are obtained in faujasites and in isotropic solution media.[17,21] The preference for the elimination processes in pentasils has been rationalized on the basis that the relatively large motions required for the conversion of the primary 1,4-diradical in skew conformations to cyclobutanols, either directly or via the cisoid diradicals, are not tolerated by the narrow channels of pentasils (Scheme V). Results obtained with alkanones 23 of carbon numbers C_{10}–C_{18} support this contention.[31] In the case of alkanones where the bulky phenyl group in aryl alkyl ketone is replaced by an *n*-alkyl chain (C_1–C_4), both elimination (olefin and alkanone of shorter chain length) and cyclization products (*cis*- and *trans*-cyclobutanols) are obtained in both faujasites and pentasils.

(29) Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386.
(30) Ramamurthy, V.; Weiss, R. G.; Hammond, G. S. *Adv. Photochem.*, in press.
(31) Ramamurthy, V.; Sanderson, D. R. *Tetrahedron Lett.* **1992**, *33*, 2757. Ramamurthy, V.; Sanderson, D. R. Unpublished results.
(32) Ramamurthy, V.; Caspar, J. V; Corbin, D. R.; Eaton, D. F.; Kauffman, J. S.; Dybowski, C. *J. Photochem. Photobiol. A* **1990**, *51*, 259.
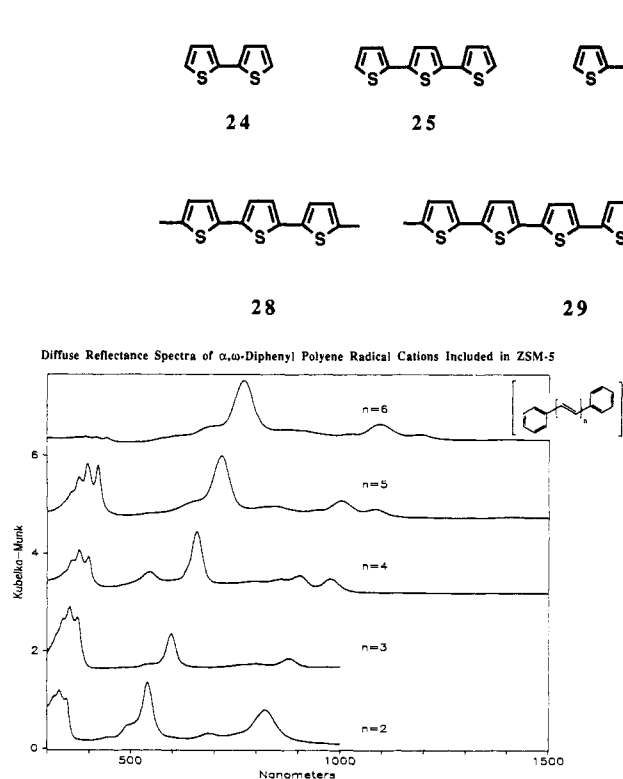
The thesis that the size matching between the host and the guest is essential for achieving maximum selectivity is supported by a comparison of the selectivity seen between the *cis*- and the *trans*-cyclobutanols in the channels of pentasils.[31] Both *trans*- and *cis*-cyclobutanols are obtained from a number of alkanones 23 (C_6–C_{18} ketones) when they are irradiated in hexane, Na X, and Na Y, with the ratio differing slightly among the three media. However, in pentasils *trans*-cyclobutanol was preferentially obtained in the case of 4-alkanones (4-nonanone to 4-octadecanone). Such a preference for the *trans*-cyclobutanol in the channels of ZSM-5 and ZSM-11 is believed to result from the differences in size and shape of the two cyclobutanol isomers and their diradical precursors. Between the *trans*- and the *cis*-cyclobutanols and their precursor diradicals, the cis isomer and its precursor 1,4-diradical possess shape and size which are relatively large (bulky) to fit into the channels of ZSM-5. On the basis of the above argument, one would expect the alkanones, in which the *trans*- and the *cis*-cyclobutanols have closely similar shapes and sizes, to yield *cis*-cyclobutanol along with the trans isomer. This is certainly the case. Alkanones such as 2-hexanone, heptanones (2- and 3-), and octanones (2-, 3-, and 4-) give both *trans*- and *cis*-cyclobutanols.

Generation, Reactivity, and Photophysics of Reactive Intermediates within Zeolites

The above discussion suggests that one can intuitively predict the behavior of zeolite-included guests following certain basic rules. This is clearly not totally true. Lack of understanding still underlies this field. We were pleasantly surprised to encounter a simple strategy by which radical ions of organic molecules could be generated and stabilized within zeolites. Although the observations made to date relate directly to radical ions, potential clearly exists to extend this technique to other reactive intermediates.

Generation of *α,ω*-Diphenyl Polyene Radical Cations. When activated Na ZSM-5 (Si/Al = 22) in 2,2,4-trimethylpentane was stirred with *α,ω*-diphenyl polyenes (*trans*-stilbene, diphenylbutadiene (*n* = 2), diphenylhexatriene (*n* = 3), diphenyloctatetraene (*n* =

Chart III

24   25   26   27

28   29   30

Figure 5. Room-temperature diffuse reflectance spectra of the radical cations of α,ω-diphenyl polyenes generated and stabilized within Na ZSM-5.
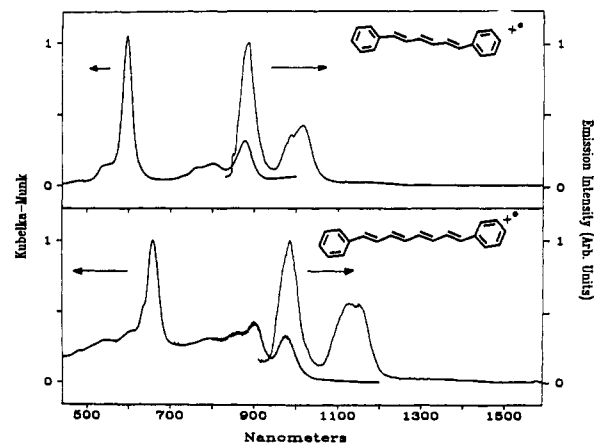

Figure 6. Emission (77 K) and diffuse reflectance (room temperature) spectra of diphenylhexatriene•+ (above) and diphenyloctatetraene•+ (below) included in Na ZSM-5.

4), diphenyldecapentaene ($n = 5$), and diphenyldodecahexaene ($n = 6$)) (Figure 5), the initially white zeolite and colorless to pale-yellow olefins were transformed into highly-colored solid complexes within a few minutes.[33] Diffuse reflectance and ESR results favor the conclusion that the colored species formed upon inclusion of α,ω-diphenyl polyenes in Na ZSM-5 are radical cations (Figure 5). The colored α,ω-diphenyl polyene radical cations generated in the channels of Na ZSM-5 were found to be unusually stable; even after several weeks of storage at ambient temperature in air, the colors persisted and the peak positions of the diffuse reflectance spectra were unchanged. This is to be contrasted with their short lifetimes in solution (microseconds) and in solid matrices (seconds). Although the absolute amount of included guest that can be oxidized is estimated to be small, this is more than sufficient to carry out spectroscopic studies.

Reactivity of Radical Cations within Zeolites—Formation of the Cation Radical and Dication of Oligothiophenes. When bithiophene **24**, terthiophene **25**, or quaterthiophene **26** (Chart III) was included into activated ZSM-5 or Na β, highly-colored radical cations of these species were formed immediately.[34] A most interesting aspect of this study relates to the reactivity of these radical cations in the channels of ZSM-5. On standing at room temperature or with mild heating (60–140 °C), new bands appear at longer wavelengths in the diffuse reflectance spectrum. These bands are due not to decomposition of the cation radical, but rather to further oligomerization. By careful analysis

of the diffuse reflectance spectra at various temperatures and those of model compounds (**27–30**, Chart III), we were able to assign the transitions to the neutrals, monocations, and dications of thiophene oligomers. The peak positions for the neutral oligomers, cations (polarons), and dications (bipolarons) all vary in a systematic manner with inverse oligomer chain length. A detailed analysis of these dependences provides useful predictions of the properties of bulk doped polythiophene. If thiophene oligomers are to be considered as models for doped polythiophenes, cation radicals of α,ω-diphenyl polyenes should serve as models for polyacetylenes. Indeed a linear relationship between the electronic transitions of the α,ω-diphenyl polyene radical cation and the chain length is observed.[35] To our knowledge this is the first study in which the evolution of the electronic structure of doped polythiophene and polyacetylene from monomer to polymer has been successfully carried out for chain lengths between two and nine, and this is made possible by the unique features of the zeolite medium.

Photophysical Studies of Radical Cations Included in Zeolites. Our technique of generating and stabilizing radical cations within the channels of zeolites has enabled us to investigate the photophysical properties of the cation radicals of diphenylhexatriene and diphenyloctatetraene and the dications of thiophene oligomers included in Na ZSM-5.[34] The emission spectra of the cation radicals of diphenylhexatriene and diphenyloctatetraene are provided in Figure 6. The unconventional technique that we discovered for radical ions could be extended to other reactive intermediates such as radicals, diradicals, radical ions, carbonium ions,

(33) Ramamurthy, V.; Caspar, J. V; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 594.

(34) Caspar, J. V; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600.

(35) Ramamurthy, V. *Chimia*, in press. Ramamurthy, V.; Caspar, J. V. Unpublished results.

carbanions, carbenes, and nitrenes.

Concluding Remarks

This Account has highlighted ways in which the inclusion of organic molecules within zeolites can alter the basic photochemical and photophysical properties of guest molecules. One might predict that in the coming years photochemistry will be a tool that will make a significant contribution toward a better understanding of the physical characteristics of zeolites—location, aggregation, mobility, and diffusion of guests within zeolites. The host–guest complex strategy allows one to control the size of the reaction cavity. Relative sizes of the guest and the free space around it are important factors to be considered when choosing a host system. With the proper choice of a guest and a host, one can control the relative sizes of the reaction cavity and the free space around the guest, and thus one can have a handle on the photobehavior of the included guest. In this context, zeolites offer several advantages over organic hosts: (a) zeolites with a number of sizes and shapes are commercially available, and therefore one has a choice;[36] (b) zeolites do not absorb light in the

region where most organic molecules do; (c) generally, they do not undergo reaction with the guest molecules under nonforcing conditions; and (d) the internal properties of zeolites can also be fine tuned by variation of the silicon to aluminum ratio, by co-inclusion of solvents[37] or other adsorbents, and by the variation of cations. This mix of advantageous properties will prove valuable in future studies and applications.

(36) Zeolites X, Y, L, M-5, Ω-5, and silicalite are available from Molecular Sieve Department (UOP) of Union Carbide, and pentasils (ZSM-5) can be obtained from Conteka B. V., Sweden. Pentasils may also be prepared by the literature procedure: Rollman, L. S.; Volyocsik, E. K. In *Inorganic Syntheses*; Wiley: New York, 1983; pp 61–68. Zeolite-β is prepared by following the literature procedure. Zeolites were activated by heating them in an aerated furnace at 500 °C for about 12 h.
(37) Ramamurthy, V.; Corbin, D. R.; Turro, N. J.; Zhang, Z.; Garcia-Garibay, M. A. *J. Org. Chem.* **1991**, *56*, 255.

Nucleoside Phosphate Sugars: Syntheses on Practical Scales for Use as Reagents in the Enzymatic Preparation of Oligosaccharides and Glycoconjugates

Jürgen E. Heidlas, Kevin W. Williams, and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

For many years, the carbohydrates present in living organisms have been identified primarily with passive roles: compounds used for energy storage, as structural units of cells, and for solubilizing and sorting components of glycoproteins. Recent advances in glycobiology and carbohydrate biochemistry have caused a fundamental reexamination of the importance of carbohydrates in biology. It is now evident that the oligosaccharide residues of glycoconjugates (glycoproteins, glycolipids, and glycophospholipids) serve as recognition sites for a variety of important intra- and intermolecular

communication events.[1–3] These structures function, inter alia, as specific binding sites for various bacteria, viruses, and soluble toxins.[3–7] Cell-surface glycoconjugates help to regulate the growth and differentiation of cells, and they play a role in organogenesis.[8] The cell-surface lectins of mammalian cell adhesion (LEC-CAMs or selectins)[9–13] may be crucial mediators

Jürgen E. Heidlas studied food chemistry at the Julius-Maximilians-University, Würzburg, Germany. He received his Ph.D. from the Department of Food and Biotechnology of the Technical University of Berlin (with Roland Tressl) in 1990, working on the enzymatic formation of chiral hydroxy compounds. During 1990–1991, he was a postdoctoral fellow at Harvard University with Professor G. M. Whitesides. His major scientific interest is the application of enzymes to biotechnological processes.

Kevin W. Williams received his B.A. in chemistry at Lincoln University in Pennsylvania. He received his Ph.D. from the University of Pittsburgh, Department of Chemistry (with Julius Rebek, Jr.) in 1990. During 1991–1992 he was an NSF postdoctoral fellow at Harvard University with G. M. Whitesides. His major scientific interest is in the area of medicinal chemistry with an emphasis on rational drug design.

George M. Whitesides received his B.A. from Harvard University and his Ph.D. (with J. D. Roberts) from the California Institute of Technology in 1964. He worked at MIT for almost 20 years and is now a member of the Department of Chemistry at Harvard University. His research interests include materials science, surface chemistry, rational drug design, carbohydrate biochemistry, and molecular recognition.

(1) Sharon, N. *Complex Carbohydrates*; Addison-Wesley: Reading, MA, 1975.
(2) Horowitz, M. I., Pigman, W., Eds. *The Glycoconjugates*; Academic: New York, 1977, 1978; Vols. I and II.
(3) Horowitz, M. I., Ed. *The Glycoconjugates*; Academic: New York, 1982; Vols. III and IV.
(4) Schauer, R. *Adv. Carbohydr. Chem. Biochem.* **1982**, *40*, 131–234.
(5) Liener, I. E., Goldstein, I. J., Eds. *The Lectins: Properties, Functions and Applications in Biology and Medicine*; Academic: New York, 1986.
(6) Paulson, J. C. In *The Receptors*; Conn, P. M., Ed.; Academic: New York, 1985; Vol. 2, pp 131–219.
(7) Sairam, M. R. In *The Receptors*; Conn, P. M., Ed.; Academic: New York, 1985; Vol. 2, pp 307–340.
(8) Rademacher, T. W.; Parekh, R. B.; Dewek, R. A. *Annu. Rev. Biochem.* **1988**, *57*, 785–838.
(9) Bevilacqua, M. P.; Stenglein, S.; Gimbrone, M. A., Jr.; Seed, B. *Science* **1989**, *243*, 1160–1165.
(10) Brandley, B. K.; Swieder, S. J.; Robbins, P. W. *Cell* **1990**, *63*, 861–863.
(11) Larsen, E.; Palabrica, T.; Sajer, S.; Gilbert, G. E.; Wagner, D. D.; Furie, B. C.; Furie, B. *Cell* **1990**, *63*, 467–474.
(12) Moore, K. L.; Varki, A.; McEver, R. P. *Cell Biol.* **1991**, *112*, 491–500.