Increasing the Heavy Atom Effect of Xenon by Adsorption to Zeolites: Photolysis of 2,3-Diazabicyclo[2.2.2]oct-2-ene

Mark A. Anderson and Charles B. Grissom*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received May 8, 1996⊗

Abstract: The distribution of products in the photolysis of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) is determined by the electronic spin state of the cyclohexane-1,4-diyl intermediate. Triplet cyclohexane-1,4-diyl yields 1,5-hexadiene (HD) while singlet cyclohexane-1,4-diyl produces bicyclo[2.2.0]hexane (BCH) as the stable product. Intersystem crossing (ISC) between the two diyls is enhanced by an external heavy atom effect. Direct photolysis (366 nm) of DBO in NaY zeolite containing adsorbed xenon yields a product ratio of 75:25 in favor of the triplet product, HD. This is a 24% increase in triplet product from direct photolysis in *n*-octane. The dramatic enhancement of ISC may be caused by polarization of the Xe atom in the faujasite cage, thereby allowing it to reach its full potential as a heavy atom perturbant. The 3:1 product ratio derives from complete equilibration of the three triplet electron spin states and the singlet spin state either in the short-lived diazenyl diradical or on a *high-energy* surface of the 1,4-cyclohexanediyl in which the singlet and triplet states are degenerate. The same 75:25 product ratio is achieved (without Xe adsorbed to the zeolite) when the Na^+ cation of the zeolite is exchanged with Cs^+ cation. This is not surprising since Xe and Cs^+ are isoelectronic and therefore should share similar spin−orbit coupling characteristics. Also reported are the product ratios when photolysis of DBO is carried out in zeolites containing other monovalent cations (Li^+, Na^+, K^+, Rb^+).

Introduction

Heavy atom (HA) solvents are commonly used in photochemistry to enhance intersystem crossing (ISC) in the excited state and in reactive radical pairs.[1] An increase in ISC can alter fluorescence or phosphorescence quantum yields, or change the distribution of stable products that arise from singlet and triplet precursors.[2] Intermolecular HA-induced ISC arises via spin−orbit coupling (SOC) interactions, with the magnitude of SOC increasing as the nuclear charge increases and the outer valence shell begins to fill.[1d] Bromine-containing and iodine-containing hydrocarbon solvents offer some of the most convenient and widely-used perturbants, but they have an undesirable reactivity toward many free radical species.[3] Xenon offers the possibility of even higher SOC with no reactivity toward radical abstraction, but with a filled valence shell, its ability to promote ISC is minimal in a nonpolarizing environment.

Zeolites offer an attractive alternative to solution chemistry when looking for heavy atom effects in the photochemistry of organic compounds. The faujasite class of zeolites contains cations that may be exchanged for heavy cations (i.e. Rb^+, Cs^+, Tl^+) that can increase the rate of intersystem crossing between singlet and triplet electron spin multiplicities. In general, the faujasite cage itself is non-reactive in organic systems and allows products to be removed by extraction with organic solvents, or by dissolution of the matrix by acid. The faujasites also offer the ability to adsorb other molecules in close proximity and, in the case of the Xe atom, slightly polarize the filled valence electron shell.[4]

The faujasite framework is comprised of a three-dimensional network of oxygen-sharing AlO_4^- and SiO_4 tetrahedra that form small and relatively spherical structures known as sodalite cages. The sodalite cage has an opening that is too small to allow the entrance of most organic molecules. Multiple sodalite cages are joined together to form and surround even larger void spaces in the faujasites to form supercages. Each supercage is ≈13 Å across and has a volume of ≈800 Å^3. The supercage has four "windows", each ≈7.5 Å in diameter, to allow guest molecules access to the interior. Each negatively charged AlO_4^- is countered by a cation (M^+),[4] and the overall formula for the faujasites is $M^+(AlO_3)^-(SiO_3)_n$. The cations occupy three separate sites of the faujasites (I, II, III). Two of these sites (II, III) allow interaction between the cation and adsorbed organic molecules. The final site for the cation (I) is located inside a sodalite cage and is thus precluded from interaction with a guest molecule.[5]

The arrangement of the supercage results in an electrostatic gradient within the supercage such that the overall polarity of the supercage decreases with increasing cation size ($Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$). Previous studies have shown that the photochemistry of a guest molecule can be altered by the heavy atom influence of the cation through the spin-orbit coupling parameter (with Rb^+ and Cs+), or the light atom effect (Li^+ and Na^+) that affects the guest by high charge density. Lastly, the photochemistry may be changed simply by the steric factors associated with the supercage.[5] For this investigation, the NaY zeolite was chosen for study.

---

* Author to whom correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1996.

[1] (a) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Engelwood Cliffs, 1969. (b) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummings: Menlo Park, 1978. (c) Koziar, J. C.; Cowan, D. O. *Acc. Chem. Res.* **1978**, *11*, 334. (d) Khudyakov, I. V.; Serebrennikov, Y. A.; Turro, N. J. *Chem. Rev.* **1993**, *93*, 537.

[2] (a) Horrocks, A. R.; Wilkinson, F. *Proc. R. Soc.*, Ser. A **1968**, *306*, 257. (b) Robinson, G. W. *J. Mol. Spectrosc.* **1961**, *6*, 58. (c) Burton, C. S.; Noyes, W. A., Jr. *J. Chem. Phys.* **1968**, *49*, 1705.

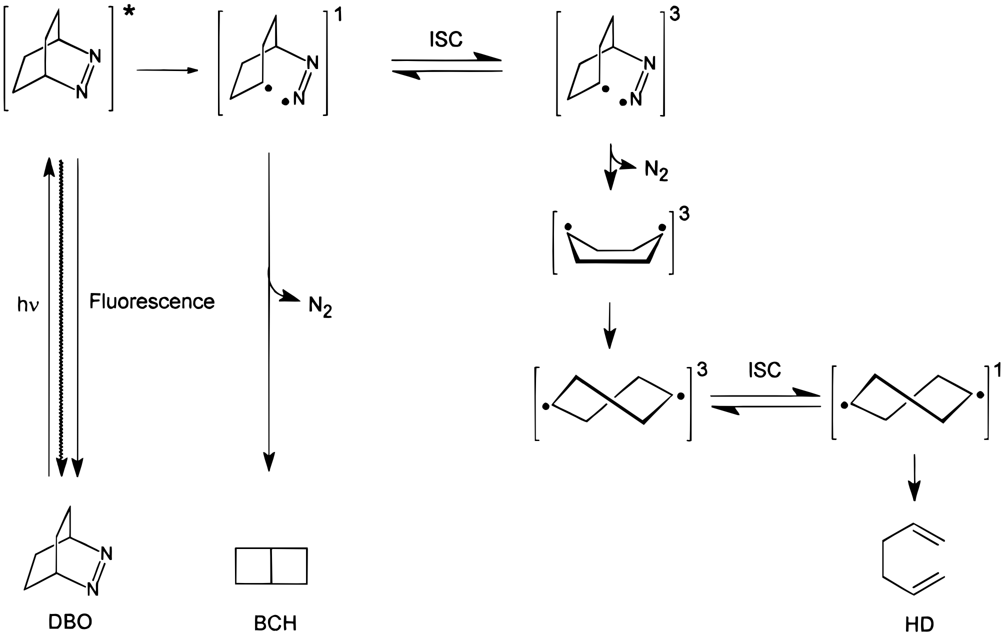
[3] SOC constants: Br, 2460 cm^{-1}, I, 5069 cm^{-1}. Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker Inc.: New York, 1993; p 339.

[4] (a) Cheung, T. T. P.; Fu, C. M.; Wharry, S. *J. Phys. Chem.* **1988**, *92*, 5170. (b) Ito, T.; Fraissard, J. *J. Chem. Phys.* **1982**, *76*, 5225. (c) Ito, T.; Fraissard, J. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 451.

[5] (a) Ramamurthy, V.; Eaton, D. F.; Caspar, J. V. *Acc. Chem. Res.* **1992**, *25*, 299. (b) Borecka, B.; Gunmundsdottir, A. D.; Olorsson, G.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1994**, *116*, 10322. (c) Ramamurthy, V. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; p 429.

S0002-7863(96)01546-6 CCC: $12.00

Scheme 1



DBO Photolysis. In this study we have chosen 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) as a reporter molecule for ISC through SOC. DBO undergoes deazatization following direct irradiation of the N═N chromophore, or singlet sensitization to yield 1,5-hexadiene (HD) and bicyclo[2.2.0]hexane (BCH) with a product ratio of 51:49 in *n*-octane.[6] ISC is possible at two points. The first is the diazenyl diradical formed when the first C−N bond is broken. Rapid ISC here would yield a 1:3 ratio of singlet:triplet cyclohexane-1,4-diyl after deazatization. Rapid ISC may also occur *as the activated cyclohexane-1,4-diyl forms* to determine the stable product outcome at a point when the energy difference between the singlet and triplet spin states is small.[6] Further ISC does not occur in the short-lived 1,4-cyclohexanediyl boat intermediate because of the large ΔE_{st} (Scheme 1). The ratio of hexadiene: bicyclohexane can be increased to a limiting value of ≈75:25 HD:BCH by increasing amounts of bromooctane or iodooctane cosolvent.[6] This feature makes the photolysis of DBO a convenient and sensitive probe of SOC-induced ISC in reactive diradicals.

Xenon Heavy Atom Effects. The noble gases, Xe in particular, have been used extensively to enhance ISC rates. Carroll and Quina used Xe as a HA fluorescence quencher in the determination of ISC quantum yields in benzene derivatives.[7] At the same time, Macbeath and Unger showed experimentally that Xe promoted ISC in the photolysis of monofluorobenzene, as indicated by a decrease in the fluorescence quantum yield and by an increase in the rate of *cis*-2-butene photoisomerization.[8] More recently, Morgan and Pimentel used steady-state and time-resolved emission spectroscopy to show that Xe produced an increase in the phosphorescence quantum yield and a concomitant decrease in the fluorescence quantum yield of (dimethylamino)benzonitrile in cryogenic Xe matrices. This was attributed to an increase in the $T_1 \rightarrow S_0$ and $S_1 \rightleftharpoons T_1$ rates via HA-induced SOC.[9] Other examples of Xe-induced ISC in anthracenes and β,γ-unsaturated ketones are known.[10]

Results and Discussion

Xenon Heavy Atom Effect in Solution. Photolysis of DBO was carried out in solution (0.03 M DBO/*n*-octane) as a function of increasing Xe pressure. The sample was degassed by a series of 5 freeze−pump−thaw cycles prior to admission of Xe at a final pressure of 5−120 psi, with 120 psi corresponding to a Xe concentration of 1.3 M in *n*-octane at 25 °C.[11] Photolysis was carried out at 366 nm as previously described.[6] Only a 3% increase in the amount of triplet derived product, from 51:49 to 54:46 HD:BCH, was observed. By comparison, a 1.1 M iodooctane solution increases the triplet product by ≈10%.[6]

Xenon Heavy Atom Effect in Zeolites. Xenon exhibits a much larger HA effect when bound in the zeolite cage with DBO. The extent of photolysis was typically 1−2% in the zeolite and GC analysis was used to determine the ratio of products. This procedure was repeated with the other noble gases, He and Ar, as controls for which no HA-induced SOC is expected. [It should be noted that, in all cases, the zeolite samples were handled in a dry N_2 atmosphere or under vacuum. In high amounts, water can displace the guest molecule from the supercage. In smaller amounts it may collect around the openings of the supercage and hinder loading of DBO, or extraction of the product.[5c,12]]

The DBO/Xe/NaY adsorbate exhibited a dramatic increase in the amount of triplet product to ≈75:25 HD:BCH upon photolysis throughout the range of 5−120 psi Xe (Figure 1). The 3:1 ratio of triplet:singlet products is consistent with complete equilibration of the three triplet states and the singlet state if the $\Delta E_{ST} = 0$. This equilibrium is reached at relatively low pressures of Xe because of specific adsorption in the faujasite cage and localization of DBO in close proximity to Xe. Other studies using Xe to enhance ISC have shown that

---

[6] Anderson, M. A.; Grissom, C. B. *J. Am. Chem. Soc.* **1995**, *17*, 5041.

[7] (a) Carroll, F. A.; Quina, F. H. *J. Am. Chem. Soc.* **1972**, *94*, 6246. (b) Carroll, F. A.; Quina, F. H. *J. Am. Chem. Soc.* **1976**, *98*, 1.

[8] MacBeath, M. E.; Unger, I. *Can. J. Chem.* **1971**, *49*, 594.

[9] Morgan, M. A.; Pimentel, G. C. *J. Phys. Chem.* **1989**, *93*, 3056.

[10] (a) Tanaka, F.; Hirayama, S.; Shobatake, K. *Chem. Phys. Lett.* **1992**, *195*, 243. (b) Calcaterra, L. T.; Schuster, D. I. *J. Am. Chem. Soc.* **1981**, *103*, 2460.

[11] *Solubility Data Series Vol. 2 Krypton, Xenon and Radon-Gas Solubilities*; Clever, H. L., Ed.; Pergamon Press: New York, 1979; p 159.

[12] Turro, N. J.; Cheng, C.; Abrams, L.; Corbin, D. R. *J. Am. Chem. Soc.* **1987**, *109*, 2449.

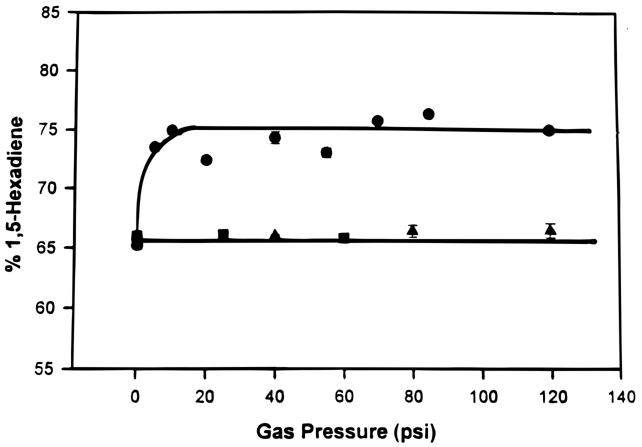


Figure 1. Percent 1,5-hexadiene produced in the direct photolysis (366 nm) at 25 °C of DBO in NaY zeolite as a function of xenon (●), argon (■), and helium (▲) gas pressures.

the first Xe molecule provides most of the enhanced ISC effect. Additional Xe atoms have a smaller or an inconsequential added effect.[13]

The effect of Xe is to increase ISC in the diazenyl diradical or after the second C−N bond cleavage has occurred as the cyclohexane-1,4-diyl is forming on an activated (high energy) surface. On this high-energy surface the energies of the singlet and triplet states are degenerate. There is no effect of Xe on the $^1(n\rightarrow\pi^*)$ and $^3(n\rightarrow\pi^*)$ transition in DBO before bond cleavage, as indicated by the unaltered fluorescence lifetime and emission spectrum of DBO and the DBO/zeolite adsorbate in the presence and absence of Xe (see supporting information). Phosphorescence has never been observed in DBO.[14]

The value of SOC for ground-state noble gases is quite small, as only a trivial amount of polarization exists in the filled (closed-shell) valence octet. Spin−orbit coupling values for the excited state are reported to be as follows: He, 0.7 cm^{-1}; Ne, 520 cm^{-1}; Ar, 940, cm^{-1}; Kr, 3480 cm^{-1}; and Xe, 6080 cm^{-1}.[3] These should be regarded as being close to maximum values that will only be realized in a high-energy environment. If the SOC of Xe were as high as 6080 cm^{-1}, then a Xe concentration of 1.3 M should have produced more than a 3% increase in triplet product, by comparison to the 10% increase in triplet product realized with 20% iodooctane (1.1 M) solution. We believe adsorption of the Xe atom in the electrostatic environment of the zeolite cavity polarizes the Xe atom and increases its ability to induce SOC. Although this polarization may be small in NaY,[4a] this slight polarization may be sufficient to induce a high level of SOC. This polarization will decrease the energy gap between the ground state and the lowest excited state and thereby increase SOC.[1] Alternatively, a van der Waal's complex of Xe with DBO during photolysis may be sufficient to induce SOC.

Effects of Heavy Atom Cations in the Faujasite Cage. A large volume of work detailing the enhancement of ISC rates by heavy atom cations in zeolites is available.[5,15] In elegant work, Ramamurthy et al. have shown that heavy atom cations have been used to record phosphorescence from polyenes for which phosphorescence had never been observed previously.[15a] Furthermore, when faujasites are exchanged with heavy cations (e.g. Rb$^+$, Cs$^+$, and Tl$^+$), the normal fluorescence emission spectrum of excited naphthalene can be replaced with a low-energy emission band ascribed to phosphorescence. This effect has been seen with several other organic guests.[15a,c] Another excellent example is the observation of phosphorescence at 298 K from *trans*-stilbenes in Tl$^+$-containing faujasites. This is significant in that only weak phosphorescence from stilbenes has been recorded at 77 K in an organic glass containing ethyl iodide as the heavy atom perturbant.[16] These effects are attributed to the enhanced intersystem crossing efficiency of the heavy cation zeolites along with their ability to encapsulate the guest and keep it close to the cation. In this study, we have photolyzed DBO in light and heavy cation exchanged Y zeolites to compare with the effects induced by Xe.

Table 1. Diene and Bicyclohexane Production in the Direct Photolysis of DBO as a Function of Faujasite Y Cation

zeolite	% 1,5-hexadiene	% bicyclo[2.2.0]hexane
LiY	62.6 ± 0.8	38.4 ± 0.8
NaY	64.8 ± 0.5	35.2 ± 0.5
KY	65.6 ± 0.8	34.4 ± 0.8
RbY	72.5 ± 0.5	27.5 ± 0.5
CsY	74.8 ± 0.9	25.2 ± 0.9
NaA	65.7 ± 0.7	34.3 ± 0.7

Table 2. Estimated Spin−Orbit Coupling Constants for Metal Cations and the Isoelectronic Noble Gas Atoms

cation (isoelectronic noble gas)	electronic configuration	spin−orbit coupling constants (ζ/cm^{-1})[a]
Li$^+$ (He)	1s^2	0.7
Na$^+$ (Ne)	He 2s^2 2p^6	520
K$^+$ (Ar)	Ne 3s^2 3p^6	940
Rb$^+$ (Kr)	Ar 4s^2 4p^6	3480
Cs$^+$ (Xe)	Kr 5s^2 5p^6	6080

[a] Reference 3. The ζ/cm^{-1} values were estimated by finding ζ_p for an excited sp^n configuration. A p-electron was promoted to form the excited configuration.

The results for Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ exchanged zeolites are shown in Table 1. Two trends are readily apparent. First, the heavy atom cations, Rb$^+$ and Cs$^+$, show an increase in the percentage of diene. The amount of diene formed when Cs$^+$ is included in the zeolite matrix is the same as that produced when Xe is adsorbed in the zeolite. The percentage of diene remains at ≈75% when the DBO/CsY adsorbate is flushed with Xe and photolyzed. This observation suggests that ISC has produced an equilibrium between singlet and triplet spin states and that Cs$^+$ and adsorbed Xe have roughly the same effect on the rate of ISC. This is not surprising, since these species are isoelectronic and should have similar SOC parameters.

SOC Constant for Cs$^+$. The SOC constant that is often reported for Cs$^+$ is 840 cm^{-1}, but this is derived for the first excited electronic state, and not for Cs$^+$.[3,5a] If this value were correct, Cs$^+$ would have only a minimal ability to induce SOC. The electronic states for Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ compare more closely with the noble gases He, Ne, Ar, Kr, and Xe and should have similar SOC constants. In fact, since the metal cations contain an additional proton in the nucleus, their respective SOC constants may be slightly greater than the corresponding noble gases. The contrasting values are given in Table 2.

It has been suggested that the electron cloud of the AlO$_4^-$ moiety, which forms part of the faujasite wall, is highly extended

---

(13) Kim, T.; Choi, Y. S.; Yoshihara, K. *Chem. Phys. Lett.* **1995**, *247*, 541.

(14) (a) Engel, P. S.; Steel, C. *Acc. Chem. Res.* **1973**, *6*, 275. (b) Clark, W. D. K.; Steel, C. *J. Am. Chem. Soc.* **1971**, *93*, 6347. (c) Engel, P. S.; Nalepa, C. J. *Pure Appl. Chem.* **1980**, *52*, 2621.

(15) (a) Ramamurthy, V.; Caspar, J. V.; Eaton, D. F.; Kuo, E. W.; Corbin, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 3882. (b) Ramamurthy, V.; Corbin, D. R.; Kumar, C. V.; Turro, N. J. *Tetrahedron Lett.* **1990**, *31*, 47. (c) Ramamurthy, V.; Caspar, J. V.; Corbin, D. R.; Eaton, D. F. *J. Photochem. Photobiol A* **1989**, *50*, 157.

(16) (a) Saliel, J.; Khalil, G. E.; Schange, K. *Chem. Phys. Lett.* **1980**, *70*, 233. (b) Garner. H. *J. Phys. Chem.* **1989**, *93*, 1826.

spatially and may tend to completely shield the cationic charge. However, it was pointed out in the same work that the larger cations (>Na^+) protrude beyond the electronic cloud of AlO_4^-. In this case, the nature of the species will clearly be cationic.[4a] To consider these cations to have the low SOC value of the excited ground state atom seems unreasonable.

The second trend from Table 1 is the increased fraction in diene production relative to photolysis of DBO in *n*-octane. The increase in HD:BCH product ratio from 50:50 to 65:35 in the light cation exchanged zeolites at first seemed to suggest that the micropolarity of the cage is increasing the rate of ISC. Zeolites containing light cations have a greater electrostatic field within the cage ($Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$) and are known to produce changes in the photophysics of organic molecules.[5a] It is possible that the electrostatic field within the cage may be polarizing the DBO molecule (most likely after at least one C−N bond has broken) thereby leading to an increased rate of ISC.

To evaluate this possibility, DBO was photolyzed while adsorbed to the *surface* of NaA zeolite. NaA has much smaller openings to the cage system (≈2 Å) thereby excluding most organic molecules from the supercage. No difference in product yield was observed in the photolysis in the supercage and on the surface. DBO was adsorbed onto celite as a further investigation of surface photolysis. The HD:BCH product ratio was within 1% of the NaA results. These results suggest that the electrostatic field inside the supercage is not responsible for the increase in diene production in the Li^+, Na^+, and K^+ Y faujasites.

The surface photolysis results also seem to minimize the importance of the "lebensraum", or void space effect, on the product distribution. Turro and co-workers have shown the effect of varying the supercage size on product ratios in the photolysis of dibenzyl ketone (DBK).[17] DBK photolysis in homogeneous solution yields diphenylethane (DPE) as the only isolated product. When the DBK is introduced inside MY zeolites, the yield of DPE decreases and the appearance of two new products, *o*-DBK and *p*-DBK, increases as the exchanged cation increases in size ($Cs^+ > Rb^+ > K^+$). It is suggested this effect is caused by the steric constraints imposed by the larger cations and thereby leads to a reduction in void space. If proper separation of the primary DBK radical pair is limited by these steric factors, decarbonylation cannot occur and the radical pair will react to form the isomeric ketones DBK, *o*-DBK, and *p*-DBK depending on the amount of movement allowed by the supercage.[17] The MX faujasites, which have roughly double the amount of exchangeable cations, and thus even more cramped supercages, show an even larger lebensraum effect than their MY counterparts. Other lebensraum effects on Norrish type I and II reactions are also well-known.[18]

The similar HD:BCH product ratios observed in our study of DBO contained in the light cation (Li^+, Na^+, K^+) zeolite and surface photolysis experiments indicate that interior size has little to do with product ratio in our system. The relatively heavy loading of DBO in our samples suggests that many supercages may contain up to three DBO molecules.[19] Even this added steric hindrance inside the void space seems to have little or no effect on the product ratio. This leaves us with no definite explanation for the increase in diene/bicyclohexane ratio for the light cation zeolites relative to the product ratios observed in homogeneous solution photolysis.

It might be argued that an increase in size of the cation (Rb^+, Cs^+) and the added steric hindrance of a multiple-occupied supercage might lead to the increase in the HD:BCH ratio when RbY and CsY are utilized as hosts. We feel this is unlikely, since our previous work with heavy atom containing solutions shows the same enhanced ratio. In addition, since it is generally accepted that the cyclohexane-1,4-diyl must relax into the twist boat or chair conformation[20] (from the initial boat form) to open to the 1,5-hexadiene, any steric interference with this process should lead to more bicyclohexane, and not the diene, being formed preferentially.

Mechanism of Product Formation in the Photolysis of DBO. These results have forced us to slightly modify our initial proposal for the mechanism of product formation in the photolysis of DBO.[6] No bicyclohexane can be formed from the singlet twist boat conformation. Before or simultaneous with deazatization, ISC can be increased by neighboring heavy atoms up to the 75:25 equilibrium between the singlet and triplet electron spin multiplicities. The singlet diazenyl diradical closes to bicyclohexane with concomitant loss of N_2 while the triplet diazenyl diradical relaxes to the twist-boat conformation, extrudes N_2, and eventually undergoes ISC to the singlet diradical and undergoes ring opening to give 1,5-hexadiene (Scheme 1).

Direct irradiation of the diazene chromophore produces the excited singlet state of DBO. This species can lose energy through internal conversion, fluorescence emission, or homolysis of the C−N bond to produce the diazenyl diradical. [Phosphorescence has never been observed in intact DBO.]

Rapid ISC may occur at either of two points in the reaction. Rapid mixing of the spin states may occur in the diazenyl diradical to produce the 3:1 ratio of singlet to triplet cyclohexane-1,4-diyl directly. Alternatively, rapid ISC may occur in the 1,4-cyclohexanediyl, but *only* on a very high energy surface, where the energy of the singlet and triplet electron spin state is equal (hence the 3:1 statistical mixture). Since C−N bond cleavage requires thermal activation ($E_a = 8-9$ kcal/mol), bond homolysis and N_2 extrusion must lie on a reaction surface that is even higher in energy than the reaction surface produced by photochemical excitation alone. Fast loss of N_2 would produce 1,4-cyclohexanediyl in a boat geometry with the unpaired electronic orbitals oriented orthogonally. Calculations at the 6-31G* level reveal than the boat conformation is not an energy minimum, but relaxes to the twist-boat or chair conformers that are local minima on the energy surface.[21] In the boat conformation of 1,4-cyclohexanediyl, the energy gap between the singlet and triplet state is large ($\Delta E_a = 22$ kcal/mol) and this precludes reversible ISC in the true boat geometry. This mechanism is not vastly different than that proposed by Edmunds.[20b]

Conclusions

The spin−orbit coupling afforded by Xe is enhanced through polarization by adsorption in the zeolites or adsorption in a microenvironment that will influence the distribution of the

---

[17] (a) Ramamurthy, V.; Corbin, D. R.; Eaton, D. F. *Tetrahedron Lett.* **1989**, *30*, 5833. (b) Garcia-Garibay, M. A.; Zhang, Z.; Zhang, Z. *J. Am. Chem. Soc.* **1991**, *113*, 6212. (c) Zhang, Z.; Turro, N. J, *Tetrahedron Lett.* **1987**, *28*, 5637. (d) Zhang, Z.; Turro, N. J. *Tetrahedron Lett. 1989*, 30, *3761*.

[18] (a) Ramamurthy, V.; Corbin, D. R.; Turro, N. J.; Sato, Y. *Tetrahedron Lett.* **1989**, *30*, 5829. (b) Ramamurthy, V.; Sanderson, D. R. *Tetrahedron Lett.* **1992**, *33*, 2757. (c) Ramamurthy, V.; Corbin, D. R.; Johnston, L. J. *J. Am. Chem. Soc.* **1992**, *114*, 3870.

[19] This estimation is based on the calculated size of DBO (4.62 Å × 4.28 Å × 3.05 Å) and the space available inside the NaY zeolite. DBO is not assumed to "stack" well.

[20] (a) Engel, P. S.; Horsey, D. W.; Keys, D. E.; Nalepa, C. J.; Soltero, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 7108. (b) Edmunds, A. J. F.; Samuel, C. J. *J. Chem. Soc., Perkins Trans. 1* **1989**, 1267.

[21] Roberson, M.; Simons, J., University of Utah, personal communication.

closed electronic octet through noncovalent interactions. Xenon has the added advantage of being non-reactive toward atom abstraction and it is transparent at the wavelengths commonly used to initiate photolysis.

The product ratio reaches a level of 3:1 1,5-hexadiene: bicyclohexane when DBO is photolyzed inside heavy atom containing faujasites. The heavy atoms may be in the form of exchangeable cations (Rb^+, Cs^+) or adsorbed Xe. The product ratio of 1,5-hexadiene:bicyclohexane is controlled by the electron spin multiplicity of the intermediate diradical. The spin multiplicity reaches an equilibrium of 3:1 (three triplet states for each singlet state) when ISC crossing, via SOC, is maximized by the use of heavy atoms in the zeolite cage. The zeolites also have the advantage of keeping the diradical in close proximity to the heavy atom.

Rapid ISC induced by heavy atoms may take place in the diazenyl diradical or in the high-energy cyclohexane-1,4-diyl. The singlet diazenyl diradical closes to form bicyclohexane, whereas the triplet diazenyl of the diyl relaxes from the boat conformation to the twist-boat, and then possibly to the chair, before undergoing ISC to the singlet and ring opening to the 1,5-hexadiene product.

Experimental Section

General. The synthesis of DBO[22] and the identification of products for DBO photolysis[6] have been reported previously. All solvents used for loading and extracting zeolites were of the highest possible purity.

Zeolite Preparation and DBO Loading. The NaY zeolite powder was purchased from Aldrich. The zeolite was calcined at 565 °C for 12 h to destroy any organic contaminants. Cation exchange (Li^+, K^+, Rb^+, Cs^+) of the zeolite was carried out according to literature methods.[18c,23] The cation of interest was exchanged into the NaY zeolite by contacting the powder with the appropriate 10% nitrate solution ($LiNO_3$, $NaNO_3$, etc.) at 90 °C for 4 h. For each gram of zeolite, 10 mL of the cation nitrate solution was used. This cycle was repeated three times. The zeolite was filtered, washed thoroughly, and dried at 120 °C for 30 min. The zeolite cake was crushed into a fine powder and heated under vacuum (0.02 Torr) at 300 °C for 3 h. This process was also carried out with $NaNO_3$ to ensure that all samples were manipulated in the same manner. From this point, the zeolite sample was handled in a N_2 atmosphere.

To load the dry zeolite, 50 mg of DBO was dissolved in 4 mL of dry pentane (Omnisolv). To this solution was added 350 mg of the dry NaY and the slurry was stirred for 10 h. The excess pentane was removed and the zeolite was washed with three 4-mL aliquots of fresh pentane. The mother liquid and the three washings were combined and the solvent was removed by rotary evaporation. Typically, <2 mg unadsorbed DBO was recovered.[24] The DBO/zeolite powder was dried by passing N_2 gas over the surface for 15 min. The sample was evacuated at 0.02 Torr for 48 h until the amount of pentane was <0.5% of that of DBO. The high loading level of DBO (14%) is needed because the zeolite absorbs at the wavelength for photolysis of DBO (366 nm) and the quantum yield for deazatization of DBO at 25 °C is low ($\Phi_r = 0.018$, C_6H_6).[25] Lower loading levels do not produce sufficient of product for analysis. The DBO loaded zeolite (≈70 mg) was placed in a closed end Pyrex tube (10 cm long, o.d. 9 mm, i.d. 5 mm). The sample tube was evacuated at 0.02 Torr for 30 min and flame-sealed.

The DBO/zeolite samples were photolyzed for 6 h using a 450-W compact Hg arc lamp that was filtered to allow passage of a 100-nm band centered at 366 nm. After 1 h, the sample was rotated 180°, and after 2 h, the sample was agitated thoroughly. This process was continued for the entire photolysis period to provide the maximum conversion of azoalkane to products. After photolysis, the zeolite was stirred in 0.5 mL of dry toluene (Omnisolv) for 10 h to extract the photolysis products and any excess DBO. The zeolite was separated from the toluene by centrifugation. Several samples were extracted three times to determine if either product was preferentially adsorbed. The first extraction typically yielded ≈85% of the products, the second ≈10%, and the third ≈5%. GC analysis indicated there was no difference in product ratio from one extraction to the next. The extent of photolysis was typically 1−2%. It should be noted that the samples must be sealed under vacuum and photolyzed soon after removal of all pentane (1−2 days). Older non-vacuum sealed samples (≈2 weeks) showed a small amount of 1,5-hexadiene and bicyclohexane product upon extraction even without photolysis. Freshly prepared (<2 days), vacuum sealed samples showed no products in the absence of photolysis.

DBO/NaY/Xe Sample Preparation. A Pyrex sample tube was attached to a 4 in. section of 3/8 in. copper tubing with Torr Seal. The connection was cured at 110 °C for 12 h. The Pyrex/copper tube assembly was filled with the NaY/DBO and a 200 test stop valve was fitted to the assembly. The assembly was connected to a 25 L tank of Xe gas (Spectra Gases, 99.999%) equipped with a 200 psi regulator. The sample and gas line were evacuated at 0.02 Torr for 30 min. The system was flushed with Xe gas to pressures of 5−120 psi. The valve was closed and the sample was allowed to incubate for 30 min prior to photolysis. The DBO/zeolite/Xe samples were photolyzed and extracted, and the products were analyzed as described above.

Fluorescence Studies (Available as Supporting Information). Fluorescence studies on DBO/*n*-octane, DBO/*n*-octane/Xe, DBO/NaY, and DBO/NaY/Xe systems were carried out with an Aminco-Bowman spectrofluorimeter. The apparatus was used in the reflectance mode for all measurements. The excitation wavelength was 337 nm (the $n-\pi^*$ transition of the $-N{=}N-$ chromophore) and the emission wavelength was scanned from 350 to 500 nm. No change in emission intensity or any shift in λ_{max} (405 nm) was observed for any of the four measurement conditions.

Acknowledgment. The authors would like to thank Mr. Mark Roberson for his helpful discussions of the mechanism of DBO photolysis and his help with the 6-31G* calculations. We would also like to thank Professor William Breckenridge for his discussions of SOC values. This work is supported by a grant from the National Institute of Environmental Health Sciences (ES 05728).

Supporting Information Available: Fluorescence emission spectra of (a) DBO/heptane (0.03 M); (b) DBO/heptane (0.03 M)/60 psi Xe; (c) DBO/NaY zeolite (14% loading); and (d) DBO/NaY zeolite (14% loading)/60 psi Xe (1 page). See any current masthead page for ordering and Internet access instructions.

JA961546H

---

(22) (a) Cohen, S. G.; Zand, R. *J. Am. Chem. Soc.* **1962**, *84*, 586. (b) Askani, R. *Chem. Ber.* **1965**, *98*, 2551.

(23) Ramamurthy, V.; Sanderson, D. R.; Eaton, D. F. *Photochem. Photobiol.* **1992**, *56*, 297.

(24) Considering the entropic driving forces that derive from the ratio of internal to external surface areas (1000−10000) and the enthalpic driving forces from the electronic interactions between guest molecules and the cations of the zeolites, we assume that the majority of the DBO is taken into the supercage and not adsorbed onto the outer surface. (a) Turro, N. J.; Zhang, Z. In *Photochemistry on Solid Surfaces*; Anpo, M., Matsuura, T., Eds.; Elsevier: New York, 1989. (b) Turro, N. J. *Pure Appl. Chem.* **1986**, *58*, 1219. (c) Suzuki, I.; Oki, S.; Namba, S. *J. Catal.* **1986**, *100*, 219.

(25) Engel, P. S.; Keys, D. E.; Kitamura, A. *J. Am. Chem. Soc.* **1985**, *107*, 4964.