

Modification of Photochemical Reactivity by Zeolites: Cation Controlled Photodimerisation of Acenaphthylene within Faujasites

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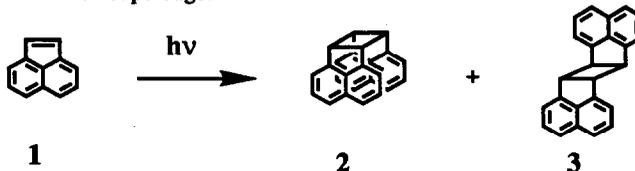
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Abstract: Photolyses of acenaphthylene included in M⁺Y zeolites gave the corresponding cis and trans dimers. The ratio of the dimers formed depends on the type of cation present in the supercage. Dimerization is believed to originate from the excited singlet state in the case of lower atomic weight cations and from the triplet state in the case of higher atomic weight cation exchanged zeolites. Dimerization provides insight into the distribution and migration of molecules within the zeolite internal structures.

The internal surfaces of zeolites have recently been demonstrated to exert significant influence on the unimolecular photoreactivity of included molecules.¹ However, no such effect on bimolecular photoreactions of guests within zeolite frameworks has yet been reported. We present here our preliminary results on a study of a photochemical bimolecular reaction, the dimerization of acenaphthylene, within a zeolite framework. Further, we also show that the multiplicity of the reactive state can be controlled by careful choice of the exchangeable cations that are present within the supercage.



The photobehavior of acenaphthylene (1), the molecule chosen for investigation, is unique in that it has been extensively studied in various constrained media and has been subjected to one of the largest heavy atom effects on its dimerization.² The irradiation of acenaphthylene in solution yields the cis (2) and the trans (3) dimers; the singlet gives predominantly cis dimer whereas the triplet gives both cis and trans dimers in comparable amounts. The photodimerisation is presumed to occur inside the spherical supercages (of zeolite-Y) which possess a diameter of ca. 13 Å³.

Photolyses of dry solid inclusion complexes of acenaphthylene in various cation (Li, Na, K, Rb, Cs and Tl) exchanged Y zeolites gave the cis and trans dimers.⁴ Cis to trans dimer ratio is dependent on the cation and on the number of guest molecules per supercage ($\langle S \rangle$). The relative efficiency of dimerization was calculated by irradiating all six zeolite complexes under identical conditions. Relative triplet yields and the triplet lifetimes of acenaphthylene included in various cation exchanged Y zeolites were obtained by monitoring the acenaphthylene triplet by its T-T absorption at 470 nm via diffuse reflectance flash photolysis technique.⁵ Results of these studies are summarized in the Table.

Table: Cation Dependent Photodimerization of Acenaphthylene Included in M⁺Y Type Zeolites

Zeolite	Cis/Trans dimer ^a		Relative Efficiency of Dimerization ^b	Relative Triplet Yield ^c	Triplet Lifetime ^d
	$\langle S \rangle = 0.5$	$\langle S \rangle = 0.25$			
Li Y	25	25	0.2	e	--
Na Y	25	22	0.2	e	--
K Y	2.3	1.6	0.4	0.2	9.6 μ s
Rb Y	1.5	1.1	1.0	0.5	5.7 μ s
Cs Y	4.2	2.8	0.8	0.7	2.1 μ s
Tl Y	22	22	0.3	1.0	0.3 μ s

a. $\langle S \rangle$ refers to the average occupancy, i.e., the ratio of the number of acenaphthylene molecules to the number of supercages. Relative efficiency, relative triplet yield and triplet lifetime are for samples with $\langle S \rangle = 0.5$. b. Efficiencies are normalized to Rb Y and the amount of dimer formed was estimated by using pyrene as a gc calibrant. c. Triplet yields are normalized with respect to Tl Y; the amount of the triplet formed was estimated by measuring the intensity of T-T absorption at 470 nm. d. Triplet lifetimes were measured from their decay half lives. e. No triplets were detected.

Absence of triplet formation in Li Y and Na Y is consistent with the solution behavior in which the intersystem crossing yield from S_1 to T_1 is reported to be near zero.⁶ This leads us to conclude that the dimerization in the supercages of Li Y and Na Y is from the excited singlet state. Preferential formation of the cis dimer also supports this conclusion. We attribute the high triplet yield in K, Rb, Cs and Tl Y to a 'heavy atom effect' caused by the cations present within the supercage.⁷ The trends observed in the variation of the triplet yield and the triplet lifetime with the increasing mass of the cation is consistent with the expected spin-orbit coupling induced triplet formation.⁸ Formation of the trans dimer, the triplet derived product, in the cages of K, Rb and Cs Y is in agreement with the triplet generation. Further, formation of the trans dimer is completely quenched when the photolysis is conducted under oxygen atmosphere.

A careful examination of the results reveals that the efficiency of dimerization is controlled not only by the reactive states but also by their lifetime. We believe that the results can be understood on the basis of a model presented in Figure 1. Although at this stage we do not have any knowledge about the distribution pattern, we believe that even at low loading levels there are supercages with double occupancies.⁸ Dimerization occurs within both double and single occupancy cages and the efficiency of dimerization is a sum of both. While dimerization is favored in the double occupancy cages under all conditions, in single occupancy cages such is possible only if molecular migration occurs between cages. One can assume that the extent of participation of single occupancy cages in dimerization depends upon the migratory distance within the excited state lifetime and the effect of cation siting on diffusivity.⁹ On this basis it is expected that short lifetime will disfavor the excited state reaching another molecule before being deactivated. This model would predict the dimerisation efficiency to be low in cases where the reactive state has a short lifetime. Indeed, these predictions are realized. The efficiencies in Li Y and Na Y are low since the dimerization originates from short lived (~ 1 ns) singlets; efficiencies in Rb, Cs and Tl Y show a decreasing trend (in spite of increasing triplet yield) in line with the decreasing triplet lifetime.

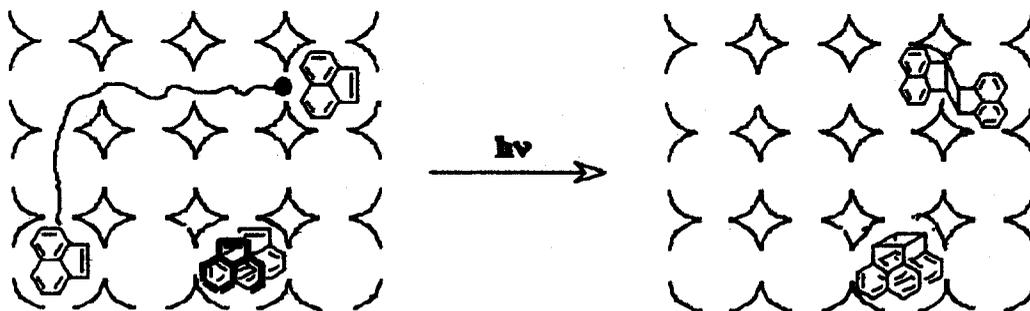


Figure 1

While dominant formation of cis dimer in Li and Na Y is expected since the reaction involves singlets, its formation in Tl Y was not anticipated because the reactive state in this case is triplet. The decrease in trans dimer yield in the series Rb, Cs and Tl Y is also unforeseen. Further, based on the solution behavior (triplet reaction) one would expect the ratio of cis to trans dimer to be in the range of 0.5² whereas in all of our cases it is above 1. These results, in our opinion, reflect, at least partially, the cavity control on the stereochemistry of dimerization. While the cis form is compact (length $\sim 7\text{\AA}$, width $\sim 8\text{\AA}$) and will fit within a supercage, the trans dimer is too long (length $\sim 14\text{\AA}$, width $\sim 8\text{\AA}$) to fit within a single cage. Therefore, it is more likely that doubly occupied cages give rise to cis isomer while when excited molecules present in singly occupied cages meet another molecule in adjacent cages trans dimer is preferentially formed. On the basis of the model presented in previous paragraphs, one would predict short reactive state

lifetimes to favor reaction in doubly occupied cages and the formation of cis isomer (Li, Na and Tl Y). The decrease in trans dimer in going from Rb to Cs Y is simply a reflection of the decrease in triplet lifetime. Higher yields of the cis dimer in triplet reaction within the internal structures of zeolites compared to solution might then be due to the fact that acenaphthylenes are not subjected to a uniform environment as in homogeneous solution and dimerization results from doubly and singly occupied cages.

Present results clearly attest to the vast and untapped potential of zeolites as microenvironments to modify the photochemical and photophysical behavior of organic molecules. The use of cations to effect triplet reactions within the internal structure of zeolite is under active investigation in our laboratory.¹⁰

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