Novel approaches towards the generation of excited triplets of organic guest molecules with zeolites

Kasi Pitchumani,[a] Manoj Warrier,[a] John R. Scheffer*[b] and V. Ramamurthy*[a]†

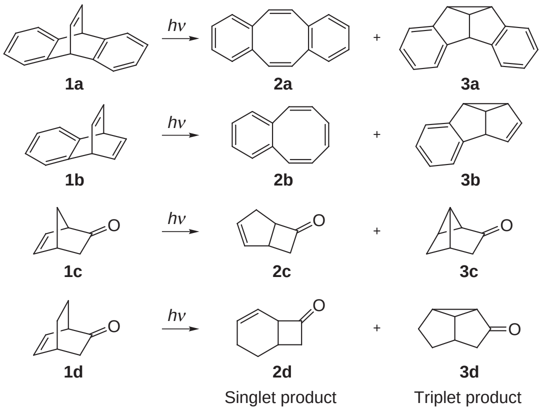
[a] *Department of Chemistry, Tulane University, New Orleans, LA 70118, USA*
[b] *Department of Chemistry, University of British Columbia, Vancouver, Canada V6T 1Z1*

Alkali metal cation-exchanged zeolites (M$^+$X or M$^+$Y) can be used as 'microreactors' in which to carry out photochemical rearrangement reactions of organic guests.

Considering that a number of reactions originate from excited states that are not efficiently reached by direct excitation, it is important to establish strategies that generate molecules in their excited triplet states within zeolites.[1] We show below that three approaches can be used to generate triplets of organic molecules within zeolites. The 'heavy and light atom effects' employ the cations present within zeolites to perturb the excited state dynamics of the guest molecules; the sensitization technique utilizes a second guest molecule (a sensitizer) to turn on triplet reactivity.

Dibenzobarrelene **1a** and benzobarrelene **1b** and enones **1c** and **1d** were chosen as probe molecules for the present study because their photochemical behavior is known to be multiplicity-dependent and relatively simple (Scheme 1).[2] As shown in Fig. 1, molecules such as **1a** can easily be accommodated within the supercages of a zeolite.

To conduct cation-dependent photochemistry, **1a–d** were introduced into the cavities of zeolites M$^+$X by adsorption from hexane solution and irradiated either as powders or as hexane slurries. Experiments were also carried out with M$^+$Y zeolites. The approach involving the use of a triplet sensitizer employed acetophenone, *p*-methoxyacetophenone, α-aminoacetophenone hydrochloride and xanthone as the second component. These were introduced into zeolite K$^+$Y by adsorption from hexane solution. The resulting vacuum-dried, sensitizer-containing zeolite complexes were then transferred to hexane solutions of **1a–d** to produce a series of 'double-loaded' complexes. The mole ratio of sensitizer to reactant was maintained at 1 : 1 in every case, but the amount of material loaded onto the zeolite, the loading level, was varied from 13 to 85, a loading level of 13 referring to an average of one molecule of sensitizer and one reactant molecule for every 13 zeolite supercages. The double loaded zeolite complexes were photolyzed as hexane slurries or as powders at $\lambda > 290$ nm (Pyrex), where reactants do not absorb significantly. Following photolysis, the organic materials were extracted from the zeolites with diethyl ether or tetrahydrofuran and analyzed by capillary gas chromatography. Mass balances were excellent ($>$85%), indicating that the photoproduct ratios were not skewed by selective inclusion of one of the products. The results for cation dependent chemistry are summarized in Table 1. Results from sensitization studies (only a few sensitizers) are compiled in Table 2. Since the behavior of enones **1c** and **1d** was identical to that of **1a** and **1b** upon sensitization results are not shown.



Scheme 1

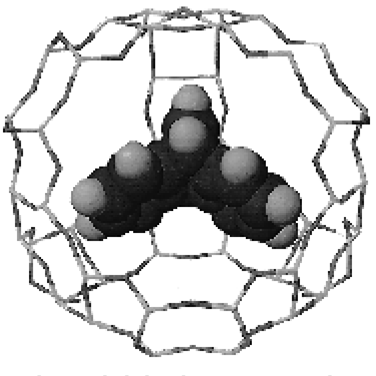


Fig. 1 Dibenzobarrelene included within a supercage; drawing generated by Chem X program

Table 1 Photoproduct distribution from irradiation of compounds **1a** and **1b** in M$^+$X and M$^+$Y zeolites[a]

Medium	Compound	Conv. (%)	Slurry[b] % COT **2**	 % SBV **3**
MeCN	**1a**		77	23
Acetone	**1a**		0	100
LiX	**1a**	4 (23)[c]	33 [80][d]	67 [20]
NaX	**1a**	6 (20)	38 [72]	62 [28]
KX	**1a**	17 (30)	53 [57]	47 [43]
RbX	**1a**	16 (26)	25 [31]	75 [69]
CsX	**1a**	24 (41)	13 [17]	87 [83]
TlX	**1a**	98 (88)	< 1 [+]	> 99 [> 99]
Hexane	**1b**		96	4
Sens.[e]	**1b**		0	100
NaX	**1b**	77	95	5
KX	**1b**	59	92	8
RbX	**1b**	63	86	14
CaX	**1b**	84	88	12
TlX	**1b**	90	8	92

[a] The product ratios were independent of % conversion within the estimated error limits of ±2% and represent an average of at least 5 independent runs. [b] Slurry irradiations were conducted in hexane for 2 h. Solid state irradiations were carried out for 20 h. Conversions are comparable, since all irradiations were conducted under identical conditions. [c] Numbers in parentheses are for solid state irradiations. [d] Numbers in brackets are for zeolites saturated with water. [e] Acetophenone sensitization in hexane solution.

Table 2 Photoproduct distribution from irradiation of compounds **1a** and **1b** in K$^+$Y zeolite containing various triplet energy sensitizers[a]

Compound (Sensitizer)	Loading level[b]	Slurry[c] % COT **2**	Slurry[c] % SBV **3**	Solid[c] % COT **2**	Solid[c] % SBV **3**
(4-Methoxyacetophenone)					
1a	25	< 1	> 99	< 1	> 99
1a	40	4	96	< 1	> 99
1a	85	13	87	< 1	> 99
(α-Aminoacetophenone HCl)					
1a	25	8	92	5	95
1a	40	16	84	10	90
(4-Methoxyacetophenone)					
1b	13	10	90	1	99
1b	25	34	66	2	98
1b	40	51	49	20	80
(α-Aminoacetophenone HCl[d])					
1b	13	39	61	18	82
1b	25	54	46	63	37

[a] The product ratios were independent of % conversion within the estimated error limits of ±2% and represent an average of at least 5 independent runs. [b] Loading level refers to the average number of supercages per guest molecule. For example, a value of 25 indicates one probe molecule and one sensitizer molecule per 25 supercages. [c] Slurry irradiations were conducted in hexane for 2 h. Solid state irradiations were carried out for 20 h. Conversions are comparable since all irradiations were conducted under identical conditions. [d] In this case, the sensitizer is anchored to the zeolite *via* an ionic bond, which allows the photoproducts to be removed selectively and the complex reused. No decrease in zeolite efficiency was seen after as many as 6 runs.

Of the three techniques, the sensitization method was found to be general. Triplet–triplet energy transfer occurred in every case (**1a**–**d**) in the doubly loaded K$^+$Y zeolites. In the presence of an equimolar amount of sensitizer, triplet yields of well over 90% are readily attainable. *p*-Methoxyacetophenone is the sensitizer of choice among those tested. Sensitization works well even when there is only one sensitizer and one acceptor molecule present in 40 or more zeolite cages.

The heavy atom response of compounds **1a** and **1b** is stronger than that observed in the oxadi-π-methane rearrangement of **1c** and **1d**. Essentially 100% triplet state behavior is observed with **1a** and **1b**. The triplet state product observed with **1c** and **1d** never exceeded more than 30% even with Tl$^+$ as the cation.[3,4] Based on the observations made with the above four systems we conclude that 'El Sayed's rule' holds good within zeolites as well: the degree of heavy atom effect on mixing the states of different multiplicity depends on the electronic configuration (nπ* and ππ*).[5]

An unusual observation was made with light cations in the case of **1a**. For **1a**, the Li$^+$ and Na$^+$ exchanged zeolites lead to surprisingly large amounts of triplet photoproduct **3a** (67 and 62%, respectively), but the reaction is relatively slow. This 'light atom' effect disappears, however, when the complexes are equilibrated with water before use. The exact mechanism by which Li$^+$ and Na$^+$ bring about triplet chemistry in the case of **1a** is not clear. We speculate that by binding strongly to the guest molecule, the light atoms perturb its symmetry characteristics and thus influence the intersystem crossing rates relative to an unperturbed molecule. Consistent with this suggestion, the effect falls off with N$^+$ (62%) and K$^+$ (47%), which are expected to bind less strongly. Further where solvation of the cations by water disrupts their strong binding to dibenzobarrelene, the 'light atom' effect of Li$^+$ is completely eliminated (20% triplet), and there is a normal progressive increase in perturbing power for the others (Na$^+$, 28%; K$^+$, 43%; Rb$^+$, 69%; Cs$^+$, 83%; Tl$^+$, > 99%); the classical heavy atom effect becomes increasingly important as the atomic number of the perturbing ion increases.

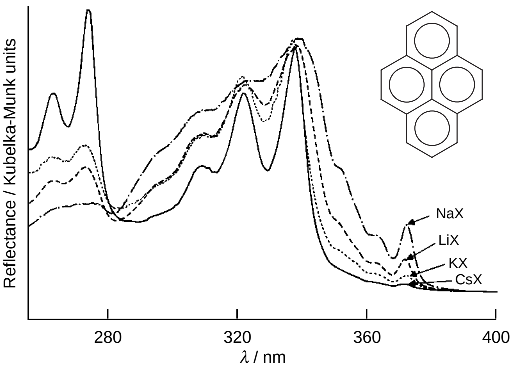


Fig. 2 Diffuse reflectance spectra of pyrene within 'dry' M$^+$Y zeolites. The intensity of the S_0 to S_1 band is dependent on the cation.

Interactions between light cations and included guest molecules such as benzene and anthracene adsorbed on zeolites were noted as early as 1963.[6] The perturbations of electronic states as well as the modifications of the vibrational modes are explained by a lowering of the symmetry of aromatic molecules in the adsorbed state. Our own observations with pyrene are consistent with the above suggestions.[7] Diffuse reflectance spectra recorded for pyrene, at a low loading level (Fig. 2), within a number of cation exchanged X and Y zeolites suggest that the interaction between the cation and pyrene is strong and that the strength of interaction depends on the polarizability of the cation. In Fig. 2, the intensity of the 0–0 transition of the S_0 to S_1 band is dependent on the charge density of the cation present within supercages. Our working model is that the symmetry reduction of the aromatic molecule occurs due to strong interaction between the cation and the aromatic along the π face resulting in slight bending of the aromatic plane. The example provided here indicates that such symmetry reductions also may influence the S_1 to T_n intersystem crossing process as well.

The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (V. R. and J. R. S.). Financial support by the Natural Sciences and Engineering Research Council of Canada (J. R. S.) and Chemical Sciences Program, The US Department of Energy (V. R.) is also gratefully acknowledged. J. R. S. thanks M. D. Fryzuk for helpful discussions.

Notes and References

† E-mail: murthy@mailhost.tcs.tulane.edu

1 D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry and Use*, Wiley, New York, 1974; H. van Bekkum, E. M. Flanigen and J. C. Jansen, *Introduction to Zeolite Science and Practice*, Elsevier, Amsterdam, 1991; A. Dyer, *An Introduction to Zeolite Molecular Sieves*, Wiley, Chichester, 1988.
2 Dibenzobarrelene **1a**: E. Ciganek, *J. Am. Chem. Soc.*, 1966, **88**, 2882; Benzobarrelene **1b**: H. E. Zimmerman, R. S. Givens and R. M. Pagni, *J. Am. Chem. Soc.*, 1968, **90**, 6096.
3 B. Borecka, A. D. Gudmundsdottir, G. Olovsson, V. Ramamurthy, J. R. Scheffer and J. Trotter, *J. Am. Chem. Soc.*, 1994, **116**, 10 322.
4 A recent report that appeared after submission of this manuscript claims that oxa-di-π-methane products alone were obtained when **1c** and **1d** were included within Tl$^+$ and Cs$^+$ Y. But in our hands, triplet product was obtained in < 30% yield and the major products were the singlet derived products **2c** and **2d**. R. Sadeghpoor, M. Gandhi, H. M. Najafi and F. Farzaneh, *Chem. Commun.*, 1998, 329.
5 M. El Sayed, *Chem. Rev.*, 1977, **77**, 793.
6 C. L. Angell and M. V. Howell, *J. Colloid. Surf. Sci.*, 1968, **28**, 279; B. Coughlan, W. M. Carroll, P. O.'Malley and J. Nunan, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 3037.
7 V. Ramamurthy, D. R. Sanderson and D. F. Eaton, *J. Phys. Chem.*, 1993, **97**, 13 380.

Received in Columbia, MO, 6th November 1997; 7/08013A