

MODIFICATION OF PHOTOCHEMICAL REACTIVITY BY ZEOLITES: CATION ENHANCED α -
CLEAVAGE OF ARYL ALKYL KETONES INCLUDED IN FAUJASITES.

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Contribution Number 5132

Abstract: The yield of Norrish type I products are significantly enhanced when aryl alkyl ketones are photolyzed in the cages of faujasite type zeolites. Exchangeable cations present within the supercages are suggested to be responsible for such an enhanced α -cleavage.

Zeolites are robust, crystalline, porous aluminosilicates possessing an enormous internal surface area that is capable of adsorbing large quantities of guest molecules whose structures allow them to pass from the external to internal zeolite surface.¹ The framework composition, the presence of exchangeable cations and the topology of the internal void space all contribute to imbue these materials with special properties that contribute to their widespread use as catalysts. Although the use of zeolites as catalysts has been fairly well established, their utility as a 'micro-reactor' to conduct phototransformations has been less explored.² With this in mind, we have investigated the photobehavior of faujasite (M^+X and M^+Y) included α , α -dimethyl valerophenone, 1-methylcyclohexyl phenyl ketone and 1-methylcyclopentyl phenyl ketone. Striking alteration in the product distributions (with respect to benzene) brought about by exchangeable cations Li and Na highlights the important role played by the electronic interaction between the cation and the adsorbed molecules in influencing the reactivity of the included molecules.

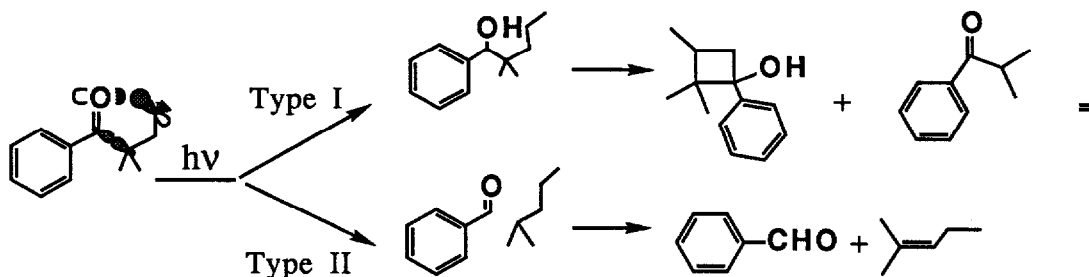
Faujasites (zeolites X and Y), the zeolites used in this investigation, are composed of so-called sodalite or β -cages that are linked to adjacent ones via hexagonal prisms.¹ The supercages that are formed by such a type of construction possess an internal diameter of ~ 13 Å, which is accessible through four twelve membered rings (ca ~ 8 Å in diameter). Because of the presence of aluminum atoms in the zeolite structure, there is a net negative charge in the lattice, and charge compensating cations are required to balance the anionic framework charge. The cation will be distributed among the different sites depending upon various factors.

Photolysis of ketones 1-3 in benzene and as complexes of zeolite M^+X and M^+Y ($M = Li, Na, K, Rb$ and Cs) gave products resulting from both Norrish type I and type II processes (Scheme and Table)³. No products other than benzaldehyde, the alkenes and the corresponding cyclobutanols were obtained in any of these cases both in benzene and in zeolites.⁴ It is clear from the Table that the yield of benzaldehyde, a product of the Norrish type I process, is increased significantly in all zeolites with respect to benzene. It is also to be noted that Li and Na generally exert larger influences than other cations.

Table: Product Distribution upon Photolysis of Ketones 1-3 in Faujasites

Medium	Dimethyl valerophenone (1)		1-Methylcyclohexyl phenyl ketone (2)		1-Methylcyclopentyl phenyl ketone (3)	
	A	B	A	B	A	B [#]
Benzene	23	60	32	68	2	98
LiX	95	5	65	35	50	50
NaX	85	15	57	43	35	65
KX	34	66	43	57	39	61
RbX	32	68	34	66	29	71
CsX	42	58	59	41	38	62
LiY	94	4	76	24	43	57
NaY	90	10	50	50	26	74
KY	59	41	25	75	11	89
RbY	20	80	21	79	8	92
CsY	68	32	17	83	5	95

Yields of benzaldehyde (A) and cyclobutanol (B) as analyzed by GC at < 20 % conversion.

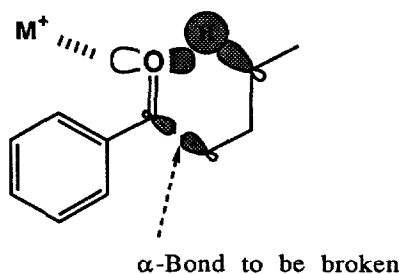


Scheme 1

The enhancement of type I products over type II can be due to the influence of the cage either on the reactivity of the triplet (increased rate of α -cleavage, reduced rate of γ -hydrogen abstraction) or on that of the reactive intermediates (reduced geminal recombination of the type I radical pair, enhanced rate of γ -hydrogen reversion of the type II 1,4-diradical). Our earlier studies⁵ have shown that the cage effect is much larger in zeolite supercages than in isotropic solvents ruling out decrease in geminal recombination of type I radical pair being responsible. It has been established⁶ that Lewis bases and hydrogen bonding solvents favor cyclization of the type II 1,4-diradical over reverse hydrogen transfer; supercages possessing both these characteristics⁷ should indeed enhance the type II products over benzene although the reverse is the case.

Adsorption and spectral studies have indicated that if the molecules with a π -bond or polar functional groups are adsorbed on zeolites, they interact strongly with the exchangeable cations.⁸ The interaction energy depends on the type, radius, and the concentration of the exchangeable cations, type of zeolite and structure of adsorbed molecules. Such cations as lithium and sodium show stronger interaction than the larger potassium, rubidium and cesium

cations.⁹ We also have noticed the significant influence of the cations on the electronic absorption spectra and on the ²H-MAS NMR spectra of aromatics such as naphthalene, anthracene, phenanthrene and pyrene.¹⁰ Although no clue to such interaction is obtained from the absorption spectra of ketones 1-3 when included in faujasites, thermogravimetric analyses indicate that the temperature required to desorb these ketones from LiX is much higher than from CsX; the temperature of desorption decreases in the order Li > Na > K > Rb > Cs. For example in the case of 1-methylcyclohexyl phenyl ketone¹¹ the temperature at which desorption occurs is as follows: LiX 515°, NaX 508°, KX 492°, RbX 471°, and CsX 464° C. The extent of cation influence on the product distribution also follows the same trend: the extent of influence decreases from Li to Cs as cations. We propose that the cations present within the supercage interact with the carbonyl chromophore of the ketones 1-3 and such interaction weakens the α-bond (Figure 2). According to this model, the enhanced yield of benzaldehyde is a direct consequence of the increased rate of α-cleavage with respect to γ-hydrogen abstraction. However, the argument that the carbonyl oxygen binds strongly even in the triplet state and impede hydrogen abstraction sterically can not be ruled out with the present data.



No significant change in product distribution is observed upon irradiation of α,α-dimethylvalerophenone in benzene in the presence of H⁺ (H₂SO₄) and in tert-butanol in the presence of sodium methoxide. Furthermore, irradiation of the above ketone on a silica gel surface did not result in increased yield of benzaldehyde. These point out that a constrained medium, such as the faujasite supercage, and a cation are required to enhance the α-cleavage. The interaction between the cation and the ketone must not be strong enough to effect the α-cleavage of valerophenone, cyclohexyl phenyl ketone and cyclopentyl phenyl ketone, the ketones which normally do not undergo Norrish type I process in isotropic solvents.^{4,6} Cations present within the supercage of faujasites have earlier been established by us to influence the photochemical and photophysical behavior of molecules through 'labensraum effect',¹² via heavy atom effect¹³ and through controlling the conformations of the included molecules via specific interactions.¹⁴ Present results clearly attest to the vast and untapped potential of zeolites as microenvironments to modify the photochemical and photophysical behavior of organic molecules.¹⁵

References and Notes

1. "Zeolite and Molecular Sieves Structure, Chemistry and Use", Breck, D. W. John Wiley, 1974.; "Zeolite Molecular Sieves", Dyer, A. John Wiley, 1988.
2. Turro, N. J. Pure & Appl. Chem. 1986, 58, 1219.; Tetrahedron 1987, 43, 1589.
3. Scaiano, J. C.; Casal, H.L.; Netto-Ferreria, J. C. In "Organic Phototransformations in Non-homogeneous Media" ed. Fox, M. A. American Chemical Society, 1985, pp 211-222.
4. Ramamurthy, V. In "Inclusion Phenomena and Molecular Recognition", (Ed) Atwood, J. L. Plenum, in press.

3. Ketones **1-3** were included in zeolites by stirring known amounts of the guest and the host zeolite in trimethylpentane for 10 h. The complex was filtered and washed with ether under a dry nitrogen atmosphere. Known amounts of the complex were degassed (10^{-4} torr) and irradiated under sealed conditions. Products were extracted by stirring the irradiated complex in 10 mL of ether for 12 h. For comparison the products were also extracted by dissolving the zeolite with HCl. Material balance was ~ 85% in most cases. Amounts of the guest included were estimated by elemental analysis of the zeolite and by gc analysis of the reextracted material. Loading in all cases was about 2.5% and the water content was ~ 3%. Products were analyzed by a Hewlett Packard GC 5890 with SE-30 capillary column and flame ionization detector. Conversions for analyses were kept to < 20%.

4. For solution irradiations see: Lewis, F. D.; Johnson, R. W.; Johnson, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 6059. Lewis, F. D.; Johnson, R. W.; Ruden, R. A. *J. Am. Chem. Soc.* **1971**, *94*, 4292. Wagner, P. J.; Mc Grath, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 3849.

5. 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.

6. Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.

7. Baretz, B. H.; Turro, N. J. *J. Photochem.* **1984**, *24*, 201.
Experiments using pyrene aldehyde (λ_{max} of fluorescence) and pyrene (Ham effect on emission bands I and III) as probes (Dong, D. C.; Winnik, M. *Photochem. Photobiol.* **1982**, *35*, 17. Kalyanasundaram, K.; Thomas, J. K. *J. Phys. Chem.* **1977**, *81*, 2176) indicate that the interior of the faujasite supercage is polar. Details to be published.

8. Angell, C. L.; Howell, M. V. *J. Colloid. Interfac. Sci.* **1968**, *28*, 279. Freeman, J. J.; Unland, M. L. *J. Catalysis* **1978**, *54*, 183. Unland, M. L.; Freeman, J. J. *J. Phys. Chem.* **1978**, *82*, 1036. Fitch, A. N.; Jovic, H.; Renouprez, A. *J. Phys. Chem.* **1986**, *90*, 1311.

9. Tsitsishvili, G. V.; Andronikashvili, T. G. in "Molecular Sieve Zeolites" (Ed.) Flanigen, E. M.; Sand, L. B. American Chemical Society, Washington, D. C. **1971**, pp 217-228.
Avgul, N. N.; Bezus, A. G.; Dzhitig, O. M. in "Molecular Sieve Zeolites" Ed. Flanigen, E. M.; Sand, L. B. American Chemical Society, Washington, D. C. **1971**, pp 184-192.

10. ^2H -MAS NMR of anthracene and phenanthrene indicate that their motions are restricted within LiX when compared to that within NaX and KX. The first absorption band which is very weak (forbidden band) for naphthalene, phenanthrene and pyrene becomes relatively pronounced within LiX and NaX. These we believe are the result of electronic interaction between the adsorbent and the supercage. Details to be published.

11. Ketones **1** and **3** show a similar trend.

12. Turro, N. J.; Zhang, Z. *Tetrahedron Letters* **1987**, *28*, 5637. Ramamurthy, V.; Corbin, D. R.; Eaton, D. F.; Turro, N. J. *Tetrahedron Letters*, in the press.

13. Ramamurthy, V.; Caspar, J. V.; Corbin, D. R.; Eaton, D. F. *J. Photochem. Photobiol.*, in the press.

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

15. VR and DC thank A. Pittman and P. Hollins for their valuable technical assistance and Professor F. D. Lewis for useful discussion. NJT thanks Air Force Office of Scientific Research, the National Science Foundation, the Office of Naval Research and IBM Corporation for financial support.

(Received in USA 12 May 1989; accepted 22 August 1989)