

Photochemistry of Macrocyclic Ketones within Zeolites: Competition between Norrish Type I and Type II Reactivity

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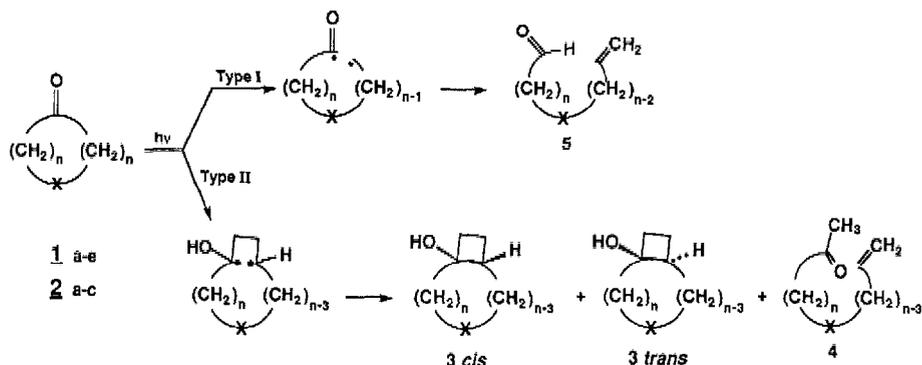
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Abstract: Photolysis of macrocyclic mono- and diketones (**1** and **2**) included in X and Y zeolites gives Norrish type I products in addition to the products obtained via the Norrish type II process, the only observed process in isotropic media. Enhancement of the type I over the type II process is cation-dependent and especially large enhancements are obtained with Li and Na as cations. The zeolite effect is attributed to a reduction in the rate of the Norrish type II γ -hydrogen abstraction process.

The photochemistry of cycloalkanones has been extensively investigated.¹ Smaller ring systems up to cycloheptanone are known to undergo only α cleavage (Norrish type I reaction) from both singlet and triplet $\pi\pi^*$ excited states. Larger ring systems above cyclononanone have been shown to undergo only intramolecular hydrogen abstraction (Norrish type II). The absence of the Norrish type I reaction in larger ring systems is attributed to low rate constants compared to the Norrish type II process.^{2,3} We provide here a strategy by which one can induce normally reluctant systems to undergo the Norrish type I reaction. This involves photolysis of ketones included in zeolites.



<p>1 a x = CH₂ n = 4</p> <p>b x = CH₂CH₂ n = 4</p> <p>c x = CH₂ n = 5</p> <p>d x = CH₂CH₂ n = 5</p> <p>e x = CH₂CH₂ n = 6</p>	<p>2 a x = CO; n = 7</p> <p>b x = CO; n = 8</p> <p>c x = CO; n = 9</p>
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Photolysis of cycloalkanones **1a-e** and cyclic diketones **2a-c** in isotropic solvents yields products derived only *via* the Norrish type II process (Scheme 1).^{4,5} To our surprise, irradiation of these molecules when included in cation (Li, Na, K, Rb and Cs) exchanged X and Y zeolites gave products derived from both Norrish type I and type II processes.^{6,7} *Cis* and *trans* cyclobutanols (**3**), type II fragmentation product (**4**) and type I product (**5**), whose yields varied with the cation, were obtained.⁸ The ratio of type I to type II products [5/(3+4)] in Na Y with respect to hexane (**2**) or pentane (**1**) as solvent is shown in the form of a graph in Figure 1. The remarkable dependence of the ratio of type I to type II products on the cation is illustrated in the form of a bar graph in Figure 2. It is evident from these figures that there is a dramatic enhancement of the Norrish type I process within zeolites. The yield of Norrish type I product increased from 0% in isotropic media to as high as 60% in zeolite. 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; both X and Y zeolites gave similar enhancement. It is also important to note that the extent of enhancement is dependent on the ring size of the ketone. The smaller the size the larger the effect.

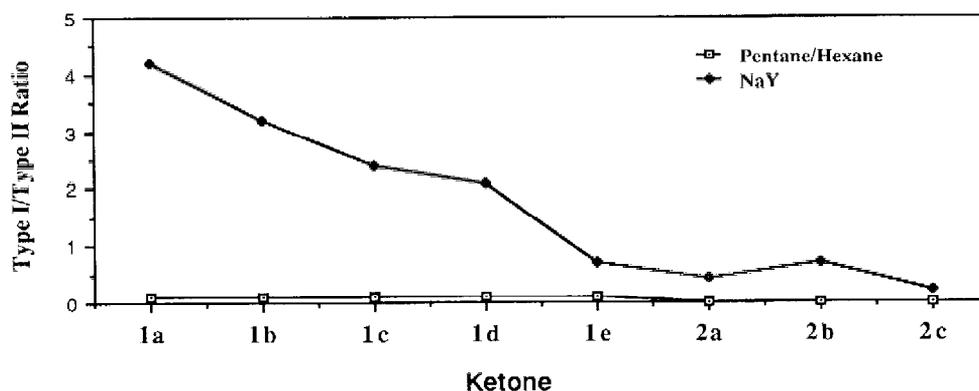


Figure 1: Enhancement of type I products in zeolite Na Y. Note in pentane (**1**) or hexane (**2**) as solvent no type I product was obtained with **2** and <2% in the case of **1**.

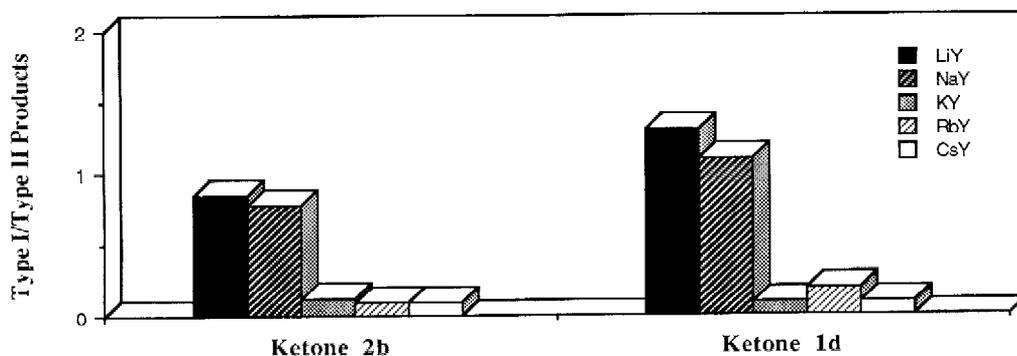
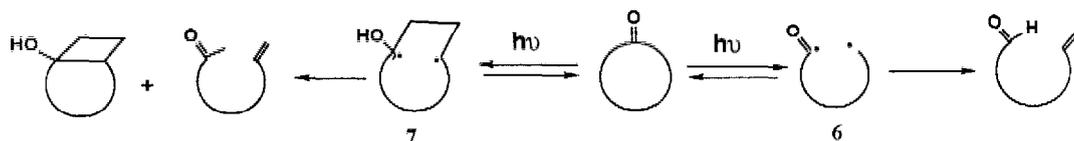


Figure 2: Dependence of type I to type II product ratio on the cation.

The results obtained with cyclododecanone (**1c**) indicate that the occurrence of the Norrish type I reaction is unique to the zeolite medium. No type I products were obtained when irradiation was conducted in micellar media, within cyclodextrin cavities and on silica gel surface. Further, irradiation of the above ketones either as a mixture with NaCl (solid salt mixture) or in benzene solution containing NaOMe gave only the Norrish type II product. This indicates that both zeolite cages and cations are required to bring out the type I activity.



Scheme 2

Zeolites can influence the photobehavior of **1** and **2** by altering the rates of decay of the excited states via type I and type II processes or by changing the partitioning of the reactive intermediates **6** and **7** between return to starting ketone and decay to products (Scheme 2). Increased rate of type I, decreased rate of type II, decreased cage return of **6** and/or increased intramolecular hydrogen return of **7** should give rise to a greater proportion of type I product. Of these four possibilities, the last two are less likely. An increased cage effect, which has been demonstrated in zeolites, would only reduce—not increase—the efficiency of the type I process.⁹ Also in a polar medium and a medium containing a large number of oxygens (capable of forming hydrogen bonds) such as within the zeolite cavity,¹⁰ internal hydrogen return is not expected to be favored over cyclization and fragmentation of the 1,4-diradical **7**.¹¹ Therefore the primary reason for the formation of type I products in zeolites is most likely to be a reduction in the rate of the competing type II process. It has been established through solid state NMR and diffusion measurement studies that the translational and rotational motions of aromatic as well as aliphatic molecules are reduced within zeolites.¹² This predicts that reactions requiring segmental motion of the reacting molecule will be slowed within zeolites. Indeed this has been found to be the case for valerophenone (VP) and α,α -dimethylvalerophenone (DMVP). The triplet lifetimes of VP and DMVP in various zeolites clearly indicate that the γ -hydrogen abstraction process is considerably slowed when these ketones are adsorbed onto zeolites.¹³ For example, the lifetime of VP triplet when adsorbed onto Li X and Na X is much longer than in solution ($\sim 5 \mu\text{s}$ and $1 \mu\text{s}$ vs ~ 5 ns). Similar behavior is observed with DMVP triplet (Na X: $0.5 \mu\text{s}$ vs solution: ~ 1 ns). In macrocyclic ketones also only a few of the many conformers are expected to be suitable for γ -hydrogen abstraction. Furthermore, the conformational interconversion is expected to be restricted within the zeolite supercages due to electronic interaction between the cation and the carbonyl chromophore of **1** and **2** and due to van der Waals interactions between the zeolite surface and the ketone molecule. Under such conditions, an inherently slow type I process would be able to compete with the type II process. The relatively large effect of Li^+ and Na^+ , which are expected to bind strongly to the carbonyl chromophore, is consistent with this.

The strategy that we have presented here is general. Earlier we showed that enhanced yields of type I products can be obtained in systems where both type I and type II processes compete in solution.¹⁴ The present study establishes that one can bring about type I processes even in systems which do not show any sign of such reactivity in solution.¹⁵

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6. X and Y zeolites possess supercages of dia~12Å with an entrance pore of dia~7.5Å. The largest molecule used here, namely, **2c**, has dimensions smaller (length 11.3Å and width 6.2Å as per crystal structure) than the sizes of the above window and cage. Therefore all molecules investigated here are expected to enter and fit within a single cage of X and Y zeolites. The internal structure of X and Y zeolites is identical except for the difference in the ratio of aluminum to silicon in the framework and the cation density.
7. Zeolite 13-X and LZ-Y in Na form were obtained from Aldrich and were exchanged with alkali cations. The extent of cation exchange was monitored by ICP analysis. In all cases the exchange was above 75%. Ketones were included into zeolites by stirring (~4-12 h) known amounts (~5 mg) of ketone with known amounts (250 mg) of zeolite in hexane or pentane. This was followed by filtration, washing with hexane or pentane and degassing in Pyrex or quartz tubes fitted with Teflon stopcocks. White zeolite powders containing ketones were irradiated with a 450 W medium pressure mercury lamp for 2 h. Products were extracted by stirring the zeolite in ether (5 mL) for about 6 h and analyzed by gc (capillary columns were used: SE-30 for **1a-e** and SPB-35 for **2a-c**). Conversions were less than 20%. For experimental details see: V. Ramamurthy, D. R. Corbin and D. F. Eaton, *J. Org. Chem.*, **1990**, *55*, 5269; M. A. Garcia-Garibay, Z. Zhang and N. J. Turro, *J. Am. Chem. Soc.*, **1991**, *113*, 6212.
8. Products from all the ketones were characterized by their ir, nmr and mass spectral data. Type II products have been reported earlier.^{4,5} The order of elution of the irradiated mixture in gc is as follows: Type II alkenone, Type I alkenal, *trans* cyclobutanol, *cis* cyclobutanol and starting ketone.
The ratio of the type II products (elimination vs cyclization products from type II 1,4-diradicals and *cis* and *trans* cyclobutanols) also showed small dependence on the zeolite and the cation. Possible reasons for such dependence are not discussed here.
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