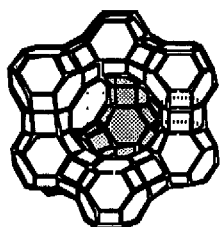


RELATIVE SIZE OF THE HOST AND THE GUEST DETERMINE THE REACTION PRODUCT SELECTIVITY: NORRISH TYPE II REACTION OF ALKANONES WITHIN ZEOLITES

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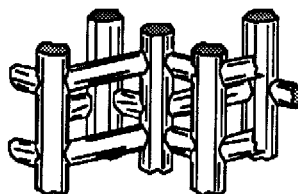
Abstract: Results of the photolyses of alkanones in faujasites and pentasils point out the importance of the relative size of the reaction cavity to that of the reactant guest in controlling the chemical behavior of host-guest systems.

By nearly curtailing the freedom of motion of a reactant molecules, organic crystalline media provide very high selectivity in certain photochemical reactions.¹ Selectivity or the modification imposed by other less organized media (eg. micelles, liquid crystals, inclusion complexes) has not been very high.² Differences in product selectivity obtained for a particular reaction in various media is attributable, although not solely, to the differences in size, shape and nature (texture or flexibility) of the reaction cavity³ available for the reactant guest molecules. We illustrate in this letter that the relative size of the reaction cavity to that of the guest reactant plays a crucial role in controlling selectivity in a chemical reaction. In this context we have utilized zeolites which crystallize with well-defined internal structures consisting of channels/cages/cavities as the reaction medium⁴ and the alkanones capable of undergoing the Norrish Type II reaction as the guests.⁵ The internal structure of the two types of zeolites (faujasites; X and Y and pentasils: ZSM-5 and ZSM-11) that we have utilized as media vary in size and shape (Figure). The Norrish Type II process (Scheme) is a mechanistically well understood reaction and has been extensively studied in both isotropic,⁶ and anisotropic media.⁷ Results of the product study when compared between aryl alkyl ketones, reported previously,⁸ and alkanones, presented here, and that between faujasites and pentasils as the media brings out a powerful message that in order to obtain a high product selectivity, one should utilize a reaction cavity that is large enough to respond to the shape changes that occur along the reaction coordinate but at the same time hard and small enough to provide relatively different extents of restriction on various reaction pathways available to the reactive intermediates.



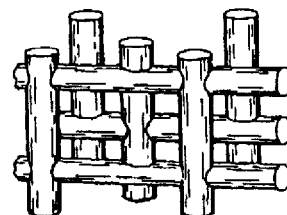
X and Y

Window Size (dia): 7.4 Å
Cage/Channel Size (dia): 12 Å
Si/Al ratio X= 1.2; Y = 2.4



ZSM-5

same as channel
5.3 x 5.6 and 5.1 x 5.5 Å
>550



ZSM-11

same as channel
5.3 x 5.4 Å
>600

Figure

(Table 2, S.Nos. 1-5). The ratio of *trans* to *cis* over 50 corresponds to less than 2% of the *cis* isomer. Such a preference for the *trans*-cyclobutanol in the channels of ZSM-5 and ZSM-11, we believe, is the result of the differences in size and shape of the two isomers and their diradical precursors. Between the *trans*- and the *cis*-cyclobutanol and their precursor diradicals, the *cis* isomer and its precursor 1,4-diradical possess shape and size which are relatively large to fit into the channels. Consequently, the *trans*-cyclobutanol is favored.

Table 1. Elimination (olefin and ketone of shorter chain length) to cyclization (*cis*- and *trans*-cyclobutanols) product ratio upon photolysis of aryl alkyl ketones and alkanones in zeolites

| S. No. | Alkanones | Hexane | Na X | NaY | ZSM-5 | ZSM-11 |
|--------|--------------------|--------|------|-----|--------|--------|
| 1 | Valerophenone | 2.8 | 1.2 | 1.1 | only E | Only E |
| 2 | Octanophenone | 1.8 | 0.9 | 0.6 | Only E | Only E |
| 3 | Dodecanophenone | 1.8 | 0.6 | 0.5 | only E | Only E |
| 4 | Tetradecanophenone | 3.5 | 0.5 | 0.2 | Only E | Only E |
| 5 | 2-Tridecanone | 2.8 | 1.0 | 0.9 | 4.3 | 4.5 |
| 6 | 4-Tridecanone | 1.9 | 0.3 | 0.5 | 4.0 | 4.1 |
| 7 | 6-Tridecanone | 1.6 | 0.7 | 0.8 | 2.7 | 3.2 |
| 8 | 4-Tetradecanone | 1.9 | 0.4 | 0.7 | 3.3 | 4.1 |
| 9 | 5-Decanone | 1.3 | 1.0 | 0.8 | 3.0 | 3.5 |

Table 2: *Trans* to *cis* cyclobutanol ratio upon irradiation of alkanones in zeolites

| S.No | Alkanones | Hexane | Na X | NaY | ZSM-5 | ZSM-11 |
|------|-----------------|--------|------|-----|-------|--------|
| 1 | 4-Nonanone | 1.8 | 0.6 | 1.3 | 60 | 60 |
| 2 | 4-Undecanone | 1.8 | 0.4 | 0.7 | 60 | 60 |
| 3 | 4-Dodecanone | 1.7 | 0.7 | 0.9 | 65 | 70 |
| 4 | 4-Tridecanone | 1.7 | 0.7 | 1.1 | 70 | 68 |
| 5 | 4-Tetradecanone | 1.7 | 0.8 | 1.1 | 72 | 66 |
| 6 | 4-Decanone | 1.8 | 0.4 | 0.7 | 60 | 60 |
| 7 | 3-Decanone | 1.8 | 0.4 | 0.9 | 16 | 14 |
| 8 | 2-Decanone | 1.5 | 0.6 | 1.0 | 6.0 | 6.5 |
| 9 | 3-Octanone | 1.8 | 0.7 | 0.8 | 20 | 18 |
| 10 | 4-Octanone | 1.8 | 0.7 | 1.3 | 15 | 18 |
| 11 | 2-Octanone | 1.4 | 0.8 | 1.2 | 8.0 | 7.1 |
| 12 | 2-Heptanone | 1.7 | 0.8 | 0.9 | 3.8 | 4.1 |
| 13 | 3-Heptanone | 1.5 | 0.6 | 0.9 | 2.8 | 2.6 |
| 14 | 2-Hexanone | 1.5 | 0.8 | 1.3 | 2.4 | 2.7 |

On the basis of the above argument, one would expect the alkanones, in which the *trans*- and the *cis*-cyclobutanols have closely similar shape and size, to yield *cis*-cyclobutanol along with the *trans* isomer. This is certainly the case. Alkanones such as hexanone, heptanones and octanones (Table 2, S.Nos. 9-14) give both *trans*- and *cis*-cyclobutanols. It is of interest to note that there is a correlation between the size or length of the alkyl chain and the selectivity: octanone > heptanone > hexanone. Such a trend is also seen with 2-, 3-, and 4-substituted decanones (Table 2, S.Nos. 6-8). When the carbonyl substitution is moved along the chain (2-, 3-

and 4- positions) one generates a *cis*-cyclobutanol of increasing bulkiness. The fact that the selectivity for the *trans* isomer increases with the bulkiness of the *cis*-cyclobutanol (from 2- > 3- > 4- decanones) further confirms our model that relative size of the reactant to the reaction cavity is an important parameter to be considered.

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- Zeolite 13-X and LZ-Y in Na form were obtained from Aldrich. ZSM-5 and ZSM-11 were prepared by literature procedure by D. R. Corbin and P. Hollins and given to us. Rollman, L. S.; Volyocsik, E. K. in *Inorganic Synthesis*, Wiley, New York, 1983, pp. 61-68. 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 trimethylpentane. This was followed by filtration, washing with hexane or trimethylpentane 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 (Hewlett Packard Model 5390, capillary column coated with SPB-35). Conversions were less than 20%. For experimental details see: Ramamurthy, V.; Corbin, D. R.; Eaton, D. F. *J. Org. Chem.*, **1990**, *55*, 5269; Ramamurthy, V.; Caspar, J. V.; Eaton, D. F.; Kuo, E.; Corbin, D. R. *J. Am. Chem. Soc.*, In press.
- Trans*- and *cis*-cyclobutanols from 2-decanone were characterized by their ir, nmr and mass spectral data. GC elution pattern of the photolysis mixture of 2-decanone was identical to that of other alkanones. Therefore, products from other alkanones were not characterized. GC peaks of product Type II alkanones and Type II olefins were identified by authentic samples obtained from either Aldrich or Wiley Chemicals. Type II products from most of the alkanones studied here have been reported earlier. The order of GC elution (Hewlett Packard Model 5390, capillary column coated with SPB-35) of the irradiated mixture is as follows: Type II alkanone, Type II olefin, *trans*-cyclobutanol, *cis*-cyclobutanol and starting ketone. The elution pattern was identical to that of ketones investigated by Weiss and his co-workers. We thank Professor R. G. Weiss for sharing the information.
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