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.

ZSM-5 same as channel 5.3 x 5.6 and 5.1 x 5.5 A >550

ZSM-11 same as channel 5.3 x 5.4 A >600

Figure

Photolysis of aryl akyl ketones such as valerophenone, octanophenone and other higher analogs included in pentasil zeolites gave via the Nonish type II process only elimination products although both cyclization and

elimination products were obtained in faujasites and in isotropic solution media.8 In order to understand such a behavior we proposed that the relatively large motions required for the conversion of the skew diradical to cyclobutanols either directly or via the cisoid diradicals were not tolerated by the narrow channels of pentasils (Scheme). Such a model would predict that the relative size of the channel to the reactant will play a crucial role in product selectivity. Results presented below on alkanones provide a strong support to the above model.

A number of alkanones where the bulky phenyl group in aryl alkyl ketone is replaced by a long alkyl chain, varying in chain length between 6 to 14, were irradiated in hexane, as included

in faujasites (Na X and Na Y) and in pentasils (ZSM-5 and ZSM-11).^{9,10} In $\frac{all}{all}$ cases both elimination (olefin and alkanone of shorter chain length) and cyclization products *(cis-* and rranr-cyclobutanols) from the initial 1,4 diradical are obtained. The results presented for alkanones in Table 1 contrasts sharply with that of aryl alkyl ketones, a few of which are also presented for comparison. We believe that the formation of cyclobutanols from alkanones clearly is a reflection of the relative cavity size with respect to the reactant. In the narrow channels of pentasils, aryl alkyl ketones $(d-5.5 \text{ Å})$ will be held tightly with little space around the reaction center. On the other hand, alkanones $(d-4 \text{ Å})$ when placed in the channels of pentasils will leave some space around them. This vacant space would be sufficient to permit the motions required for the formation of cisoiddiradical (and cyclobutanol) from the primary skew 1,4-diradical (Scheme). A small increase in E/C ratio in pentasils with respect to those in faujasites and in hexane, probably, is a reflection of the encumberance provided by the narrow channel for the cyclization process. If the the diradical conformer equilibrium is established within the excited state lifetime in the channels of zeolite the product ratio reflects only the kinetics of the process. If in case the equilibrium is not established within the excited state lifetime in the channels, the E/C ratio is a reflection of the population of the transoid and the cisoid conformers.

Most interesting results come from the selectivity seen between the cis- and the trans-cyclobutanols in the channels of pentasils (Table 2). Both trans- and cis-cyclobutanols are obtained from all the fourteen alkanones when they are irradiated in hexane, Na X and Na Y, with the ratio differing slightly between the three media. However, in pentasils the ratio of trans- to cis-cyclobutanols, depending on the alkanone, differed dramatically from those in the above three media. Trans-cyclobutanol was preferentially obtained in the case of 4-alkanones

{Table 2, S.Nos. l-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 *tram-* and the ciscyclobutanol 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.

S. No.	Alkanones	Hexane	Na X	NaY	$ZSM-5$	$ZSM-11$
	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. S	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 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	4-Nonanone	1.8	0.6	1.3	60	60
$\mathbf{2}$	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	17	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

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

On the basis of the above argument, one would expect the alkanones, in which the *tram-* 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 $2 - 3 - 3 - 4$ - 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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- 9. 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 uimethylpentane. 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. Sot., In press.*
- 10. *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, rrans-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.
- 11. It is a pleasure to thank D. R. Corbin and P. Hollins for samples of pentasil zeolites.