

Modification of Photochemical Reactivity by Zeolites: Consequences of Rotational Restriction on Norrish Type II Reaction of Alkanophenones

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The photolysis of several alkanophenones in monovalent cation exchanged faujasites and in pentasil zeolites, occurred with expected γ -hydrogen abstraction and the ratio of the products derived differed; cyclobutanol formation was completely suppressed in pentasils, probably due to restriction of the rotational motion of the central σ bond present in the Norrish type II derived 1,4-diradical.

In this Communication, we show that a 'tight fit' between the host and the guest is essential to bring about marked selectivity in photochemical transformations.¹ Faujasites and pentasils² are used as hosts to conduct the Norrish type II hydrogen abstraction of alkanophenones. Although they possess completely interconnecting three dimensional pore structures both types of zeolite have fundamentally different void space topologies. While the former consists of relatively large and spherical cages (diam. ~ 13 Å; entrance pore diam. ~ 8 Å), the latter contains only interconnecting channels (diam. ~ 5.5 Å). The free space in the supercage of faujasites can be further fine-tuned by varying the size of the exchangeable cation and adjusting the Si/Al ratio.

Results of photolyses of several alkanophenones in benzene and in several zeolites are summarized in Table 1.[‡] When compared to benzene solution photolysis, a striking alteration in the product distribution was observed with pentasils

(ZSM-5, ZSM-8, and ZSM-11; all in Na⁺ exchanged form) as hosts.³ In these zeolites the cyclization process of the 1,4-diradical is fully suppressed leading to acetophenone as

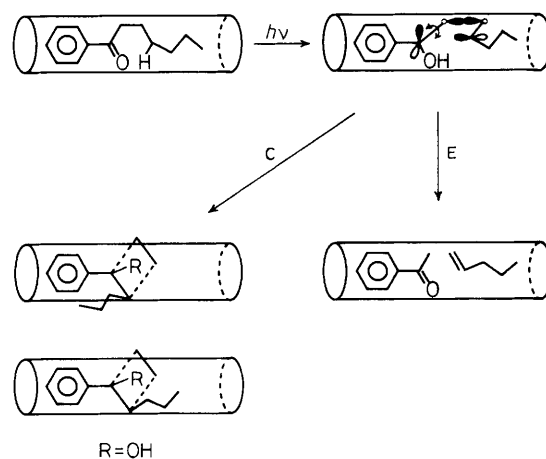


Figure 1. Schematic representation of the Norrish type II reaction within the ZSM channel (intersecting channels are not shown).

† Contribution Number 4769.

‡ Dry zeolite (100 mg) and the ketone (10 mg) were stirred in 2,2,4-trimethylpentane (10 ml) for about 10 h under dry nitrogen. The complex was filtered, washed several times with dry ether, degassed under reduced pressure (10^{-4} mm), and irradiated in sealed Pyrex tubes with a 450 W medium pressure mercury lamp. Loading in all cases was $\sim 2\%$ and the water content was $\sim 3\%$ by weight.

Table 1. Photolysis of aryl alkyl ketones in zeolites with variation in product distribution.^{a-c}

Medium	Butyrophenone	Valerophenone	Octanophenone		Dodecanophenone		Tetradecanophenone		Octadecanophenone	
	E/C	E/C	E/C	CB _t /CB _c	E/C	CB _t /CB _c	E/C	CB _t /CB _c	E/C	CB _t /CB _c
Benzene	6.2	3.0	1.9	2.6	1.2	2.4	2.7	2.4	2.7	2.7
Li-X	3.9	1.3	1.6	2.6	0.6	1.4	0.4	2.1	2.5	1.8
Na-X	2.7	1.1	1.5	1.8	0.6	1.4	1.4	0.8	2.7	1.3
K-X	3.3	1.1	1.9	1.1	0.5	1.1	1.5	1.3	4.3	2.0
Rb-X	1.9	1.6	1.9	1.6	0.7	4.2	1.9	2.2	6.2	3.4
Cs-X	2.3	1.3	1.9	3.2	1.2	6.7	1.7	5.1	6.8	4.9
ZSM-5	73	≥100	≥100		≥100		≥100		≥100	
ZSM-8	82	≥100	≥100		≥100		≥100		≥100	
ZSM-11	56	≥100	≥100		≥100		≥100		≥100	
Zeolite-β	0.54	1.3	0.62		0.68		0.31		0.48	

^a Analysed by g.c. using SE-30 capillary column; numbers reported are the average of at least four independent runs assuming identical detector response; error limit: ±5%; conversion in all cases was maintained at less than 15%. Product distribution was independent of the conversion in the range 10–60%. ^b E/C correspond to the ratio of acetophenone to cyclobutanols; CB_t/CB_c represents the ratio of *trans*- to *cis*-cyclobutanols. *trans*-Cyclobutanol had longer retention time than the *cis* isomer on the above column; however, the reverse was the case during silica gel flash chromatography. ^c Similar results were obtained in Li-Y, Na-Y, K-Y, Rb-Y, and Cs-Y. No variation in product distribution was noticed between the various cation exchanged faujasites of Y type.

the sole product of the γ -hydrogen abstraction process. Although the ratio of the products resulting from elimination and cyclization was not altered by faujasites (M⁺-X), the ratio of the *cis*- to *trans*-cyclobutanol was changed such that the larger cation Cs⁺ favoured the *trans* isomer. Similar, but less dramatic behaviour was observed in the cavities of M⁺-Y type zeolites. This is expected as Na⁺-Y contains fewer cations inside the super cages due to their higher Si/Al ratio compared to Na⁺-X.

Coupling (C) of the Norrish type II derived 1,4-diradical to yield cyclobutanols is sterically more demanding than fragmentation (E) (Figure 1). Furthermore, cyclobutanol formation requires a large permanent displacement of the phenyl group.⁴ The absence of cyclobutanols in pentasils, we believe, is the result of the restriction provided by the channel walls for the rotation of the central σ bond (Figure 1) leaving elimination as the only mode of decay for the diradical.⁵ Consistent with this proposal are the results in Na- β , a pentasil zeolite with a larger channel dimension⁶ (Table 1). The larger channel not only allowed formation of cyclobutanols, but in fact caused them to become the major photoproduct. In the case of smaller guests, like butyrophenone, cyclization occurred to a small degree even in ZSM zeolites⁷ with more narrow channel size than in Na- β . Apparently, the alkyl chain is not held rigidly in the channels of any of these zeolites as indicated by the occurrence of γ -hydrogen abstraction. The supercage of faujasite is large enough to allow the formation of cyclobutanol from the diradical. We used two approaches to induce a tighter fit. One, variation of the cation size, was moderately successful. Attempts, however, to fill the void space by lengthening the alkyl chain did not provide the necessary tight fit. We suspect that the alkyl chain extended itself into adjacent cages. When the free volume of the supercage was reduced by the introduction of a larger cation, Cs⁺ (diam. 3.4 Å), the diradical was compelled to cyclize into the *trans* isomer.

Photolyses of ketones in a variety of anisotropic media has been carried out in recent years.^{1,5} The constraint offered by zeolites is more severe than by the hosts used in the above studies. Furthermore, it is clear from the present work that proper choice of the host zeolite is important to observe a dramatic influence on reactions.

We thank A. Pittman and J. H. McCartney for their technical assistance.

Received, 26th January 1989; Com. 9/00451C

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- Based on *ortho*-xylene adsorption measurements carried out by L. Abrams it has been inferred that the channel size increases in the following order: ZSM-11 > ZSM-5 > ZSM-8. We thank Dr. Abrams for the information. Interestingly, the cyclization yield in the case of butyrophenone also increases in the same order (Table 1).