

MODIFICATION OF PHOTOCHEMICAL REACTIVITY BY ZEOLITES: ROLE OF CATIONS IN CONTROLLING THE BEHAVIOR OF RADICALS GENERATED WITHIN FAUJASITES.

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Abstract: α -Alkyldibenzylketones included in cation exchanged faujasite type zeolites show photobehavior different from that in isotropic organic solvents. Rearrangement and disproportionation which do not contribute in solution are the major processes within the cavities of faujasites. Cation size plays a major role in controlling the pathway pursued by the primary and the secondary radical pair.

Photochemical and photophysical properties of organic molecules are considerably altered when they become part of an organized or constrained structure.¹ In this context, the internal surfaces of zeolites have attracted recent attention.² We provide here an example wherein the chemical behavior of primary and secondary intermediates derived from α -alkyldibenzylketones are significantly altered when they are generated and confined within supercages of faujasites that are of molecular sizes. The supercage³ contain exchangeable cations, the number of which depends on the Si to Al ratio of the zeolite framework and on the charge of the cation. The translational and rotational processes that occur on the interior are expected to depend on variables such as the number of cations in a supercage, their size, charge and location within the supercage. For example, the ionic diameters of the alkali ions increase by over a factor of two, implying an increase in volume of a factor of about an order of magnitude in going from Li to Cs ions. Such an increase in ionic volume should lead to a comparable decrease in accessible volume within the zeolite. Such changes as we illustrate below have significant consequences on the behavior of molecules included in supercages.⁴

Photolysis of α -alkyldibenzylketones (1a-e) in benzene and as complexes of faujasites⁵ gave products resulting from the Norrish type I and type II reactions (Scheme 1 and Table). All products except olefins have been characterized earlier⁶ and olefins were identified by their IR, ¹H-NMR and mass spectral properties. Results from three of these ketones are summarised in the Table. There are remarkable differences in product distribution between benzene solution and the solid zeolite complexes: (a) Within the zeolite, the main products are 1,2-diphenyl-1-alkylethanes (AB), 1-phenyl-4'-alkylacetophenones (RP) and olefins, whereas in benzene both olefins and RP are absent. (b) The yields of both olefins and RP are dependent

on the nature of the cation present inside the supercage. As the cation size increases (Li to Cs) the yield of RP decreases and that of olefin increases at the expense of AB.

TABLE: PRODUCT DISTRIBUTION UPON PHOTOLYSIS OF α -ALKYL DIBENZYLKETONES IN ZEOLITES

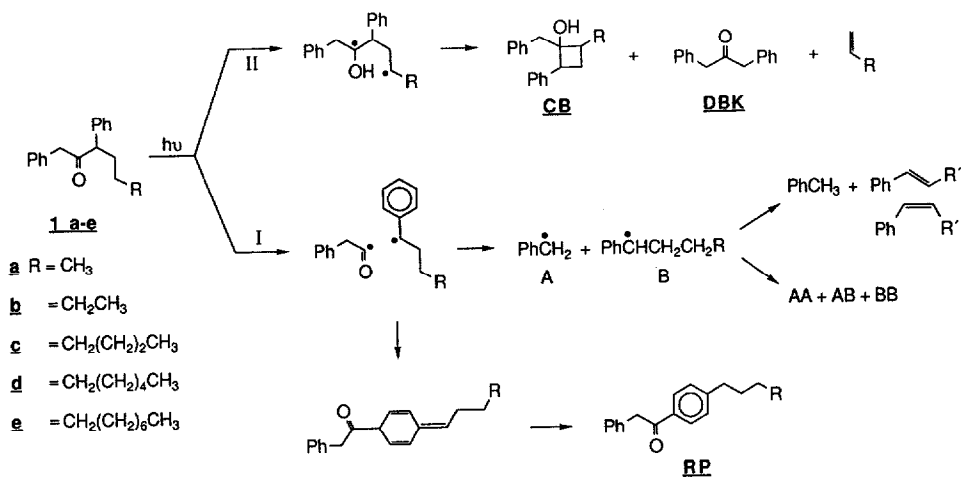
Zeolite [#]	Yields of Olefin, Coupling Product (AB) and Rearrangement Product (RP) [#]								
	(1b)			(1d)			(1e)		
	Ole	AB	RP	Ole	AB	RP	Ole	AB	RP
Na-X	16.8	18.2	62.5	26.3	23.1	50.5	42.4	16.8	40.7
K-X	26.6	18.9	54.5	36.3	28.5	34.6	49.8	18.4	31.7
Rb-X	50.1	12.5	37.4	50.6	23.8	25.3	61.4	11.9	26.6
Cs-X	55.9	10.2	33.6	64.7	20.8	14.4	78.0	7.3	14.1

In benzene **1 b, d and e** gave AA (~20%), AB (~40%), BB (~20%) and type II products (DBK, ~5% and cyclobutanol, ~5%). Neither rearrangement product RP nor disproportionation product olefin were obtained.

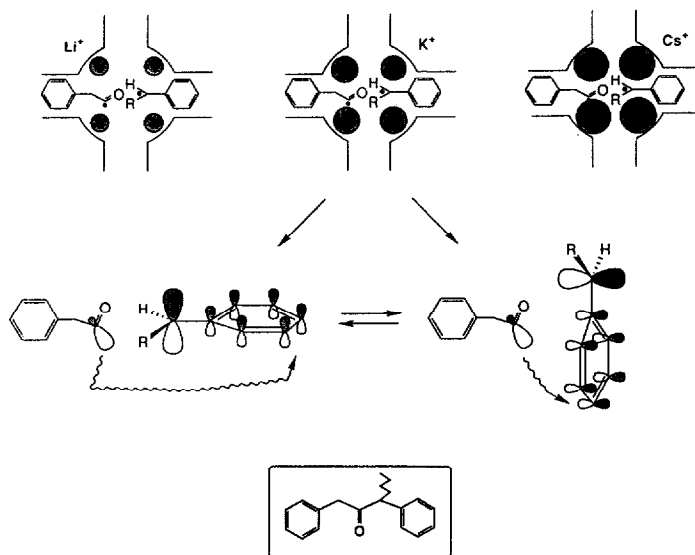
The primary geminate triplet radical pair generated by α -cleavage, in the absence of any significant cage effect, is known to diffuse apart to decarbonylate. However, under conditions where the diffusional motions are hindered (cage effect), the geminate radical pair is predisposed to undergo a rearrangement to yield 4-alkylacetophenones (Scheme 1).⁷ Formation of a single coupling product AB (following decarbonylation) suggests that translational motions of radicals are severely restricted at the internal surfaces of zeolites. Formation of RP as one of the major products from **1** within faujasite is consistent with the above model. As the available space inside the supercage, where the geminate radical pairs are generated, is decreased by the increase of the cation size, the translational and rotational motions required for the rearrangement process become increasingly hindered (Scheme 2). As the cavity free space is reduced, competing paths such as coupling to yield the starting ketone and decarbonylation, requiring less motion, dominate. These expectations are in agreement with our observations of decreased yield of RP as smaller cations are replaced with larger ones (Table). Cations are expected to interact electronically with the intermediates⁸ and such interactions appear not to play any major role in the product distribution.

The effect of cation size on product formation becomes even more obvious in the termination reaction of the benzylic radicals (Scheme 1). In solution the termination process consists only of the coupling between the two benzylic radicals and this results in diphenylalkanes AA, AB and BB in a statistical ratio of 1:2:1. The alternate pathway, disproportionation, is rarely observed in solution in the case of benzylic radical pairs although it is common for alkyl radicals.⁹ Within the supercage, termination proceeds by both

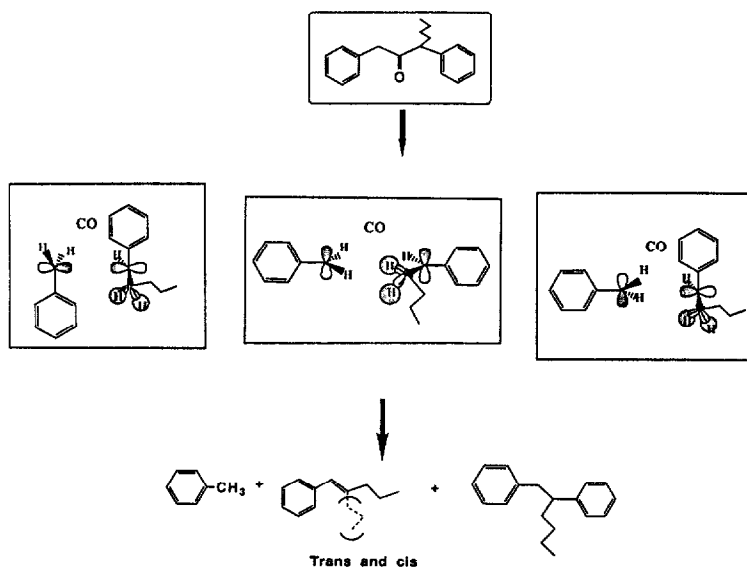
Scheme 1



Scheme 2



Scheme 3



coupling and disproportionation. A schematic diagram for the termination processes between the benzyl radicals is shown in Scheme 3. It has been suggested that the reason for the reactivity differences between alkyl and benzylic radical pairs is that the latter can form dimeric association complexes which could easily collapse to coupling products but whose geometry would be unfavorable for disproportionation.¹⁰ This association would be prohibited inside the cavity, especially in the presence of large cations. Further, more drastic overall motion would be required to bring benzylic radicals together for head to head coupling than to move an alkyl group so that one of its methylene hydrogens would be in a position for abstraction by the benzylic carbon radical. It is logical to expect the radical pair to prefer the least motion pathway as the available free space around them is reduced. Thus, as smaller cations are replaced with larger ones one would indeed expect enhanced yields of olefins as observed in the present study.¹¹

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 6. α -Alkyldibenzylketones 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 ~ 90% in all 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%.
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