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Photochemistry of Molecules Adsorbed on Alkali Ion Exchanged Zeolites. A "Lebensraum" Effect on Product Formation.

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Abstract

The products of the photolysis of dibenzyl ketone adsorbed on faujasite zeolites are found to be a strong function of the Si/Al composition of the zeolite and of the exchangeable cations associated with the internal framework.

Introduction

The "classical" zeolites[1] are robust, crystalline, porous aluminosilicates of typical composition: $M^+(AlO_2)^-(SiO_2)_nG_n$, where M^+ denotes an exchangeable singly charged cation and G is a physiadsorbed guest molecule (inert gases, water, organic and inorganic materials, etc.). It is the enormous internal surface (up to ca 1000 m^2/g) with its periodic microporous geometric structure, that is capable of adsorbing large quantities of guest molecules and whose void structure allows them to pass from the external "skin" of an individual particle into the internal zeolitic surface that imbues zeolitic materials with their most unusual properties. The framework composition, the presence of exchangeable cations associated with the framework, and the topology of the internal void space all contribute to the special properties that make for widespread use of zeolites as catalysts, ion exchange materials and molecular sieves. The faujasite family of zeolites possesses identical internal surfaces[1] consisting of nearly spherical cavities (supercages) with a mean free internal diameter of ca. 13 Å and tetrahedrally arranged windows of ca. 8 Å (Figure 1). The framework composition of faujasites may be varied between certain limits.[1] In addition, M^+ is an exchangeable cation,[2] e.g., Li^+, Na^+, K^+, Rb^+ or Cs^+, which must be associated with each Al atom to maintain electroneutrality. The number of cations per supercage may be varied by controlling the value of n, and one can vary the open void space or "lebensraum" of the supercage by varying the size of the exchangeable ion.[3] The role of alkali metal cation exchange in the catalytic synthesis of styrene[3f] and in the selective N-monoalkylation of anilines[3g], has been reported. We have developed photochemical probes to explore the structure of zeolites and the dynamics of diffusion and rotation of reactive intermediates that are generally at preselected sites on the internal and/or external zeolite surface. We report here the results of an investigation of how, for a given void space topology (the faujasite structure), the products of a photoreaction can be systematically varied by systematic variation of the framework compostion (Si to Al content) and of the exchangeable cations.

The standard paradigm[4] for the photolysis of DBK is shown in Scheme I. In homogeneous solvents, the exclusive isolated product is diphenyl ethane (DPE), although CIDNP evidence for the formation of the rearranged isomeric ketones (oDBK and pDBK) has been reported.[4] The primary geminate triplet radical pair undergoes rapid diffusional separation in solution, and decarbonylation occurs efficiently.[5] If the primary geminate radical pairs could be constrained to a reaction space that inhibits diffusional separation, rearrangement to isomeric ketones such as oDBK and pDBK should become more efficient. Indeed, evidence has been presented that the surface of porous silicas and the crystalline framework of zeolites can provide such constraints.[6] The quantitative aspects of the rotational and diffusional motion of the primary radical pair are expected to depend on the number and the size of the exchangeable ions contained by the supercage. In order to test these ideas experimentally, we investigated the photolysis of DBK adsorbed on three faujasites of differing Si/Al content and of differing ion content (Table 1). In one of the faujasites (MX where M = Li, Na, K, Rb or Cs), the number of mobile cations per supercage is about 4, whereas for the other faujasites (MY where M = Li, Na, K, Rb or Cs), the number of mobile cations is less than one per supercage.[7] Thus, in proceeding from LiX to KX or from MY to MX the degree of lebensraum in a supercage is significantly decreased.

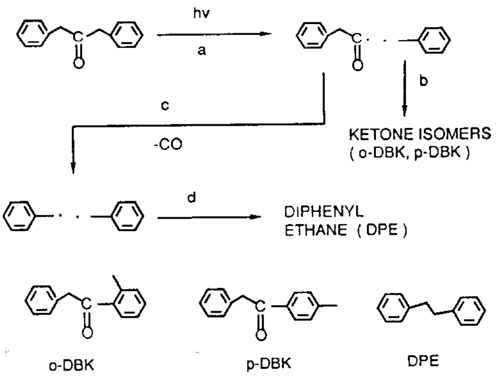
We postulate that product formation is reporting the steric constraints experienced by the radical pairs in a supercage, and that the yield of DPE and the ratio of oDBK/pDBK are two parameters that characterize these constraints. The yield of DPE, according to the conventional paradigm for homogeneous phases, will be related to the ease of diffusional separation of the primary radical pair, which, in turn, will increase as the lebensraum available in the supercage increases. The ratio oDBK/pDBK, in turn, will be related to the ease of rotational motion of the primary radical pair, which will increase as the lebensraum in the supercage increases. Thus, the greater the lebensraum, the greater the yield of pDBK relative to oDBK, and the greater the extent of decarbonylation relative to isomerization.

The data and parameters listed in Table I are consistent with the lebensraum assumption for the X zeolites with M = Li, Na and K. Thus, the yield of DPE decreases monotonically 81% to 40% in going from LiX to NaX to KX, yet DPE is essentially the only product (ca 95%) for LiY, NaY or KY with the lowest Al content. These results are consistent with an increase in lebensraum in going from KX to LiX and with a further increase in going from LiX to MY. Likewise, the ratio oDBK/pDBK and the absolute yield of the isomers decrease monotonically in going from LiX to NaX to KX, yet only traces of isomers are formed on MY. Measurement of the cage effect[8] in the photolysis of pMeDBK adsorbed on MX and MY provides further support of the lebensraum hypothesis: the % cage decreases in going from KX to LiX, and comparable, low values (ca. 20-30 %) of the cage effect are found for MY. It is interesting to note that the effect of exchanging K for Na in the X series has the same qualitative effect on the yield of DPE and on the oDBK/pDBK ratio as adding benzene vapor to NaX[6b]. The lebensraum effect was suggested to explain the influence of added benzene and other hydrocarbons on the photolysis of DBK adsorbed on NaX.

The results for the Rb and Cs exchanged X and Y systems have established that ion exchange is not complete, so that the zeolites are in reality Na,Rb and Na,Cs forms. In the case of the Y exchanged zeolite, the lebensraum trend is maintained in the yield of DPE for all the ions, but Cs breaks from the trend for the oDBK/PDBK test. In X exchanged zeolite, the Cs form corresponds to the extreme lebensraum situation, i.e., quantitative return of the primary radical pair. The Rb form does not follow the lebensraum trend, however, in either the DPE yield or in the oDBK/pDBK ratio. We speculate that this may be due to incomplete exchange (so that the system behaves as a mix of Na and Rb forms, or that the Rb does not

Table I DBK photolysis on ion-exchanged zeolites

zeolite	ion	DPE	oDBK	pDBK	oDBK/pDBK
MX	LiX	81±4%	3±1%	16±2%	0.19
Sio_2/Al_2O_3=2.4	NaX	55±4%	17±2%	26±2%	0.65
	KX	40±4%	40±6%	16±3%	2.50
	RbX	66±7%	16±6%	18±4%	0.89
	CsX	0%	0%	0%	----
MY	LiY	98±1%	0%	1± 0%	----
SiO_2/Al_2O_3=3.5	NaY	83±4%	3±1%	11±2%	0.27
	KY	88±2%	7±1%	5±1%	1.40
MY	LiY	100%	0%	0%	----
SiO_2/Al_2O_3=4.7	NaY	95±1%	0%	5±1%	----
	KY	94±4%	2±0%	4±1%	0.50
	RbY	88±4%	6±2%	6±2%	1.0
	CsY	63±5%	8±2%	29±3%	0.28



Scheme I. Schematic representation of the photolysis of dibenzyl ketone (DBK). Step (a) consists of absorption, formation of S_1, intersystem crossing to T_1, and cleavage to produce a primary geminate radical pair. The latter may either undergo coupling to produce ketone isomers (b) or lose carbon monoxide (c) to produce secondary geminate radical pair, which may either undergo cage coupling (d) or diffusional separation to form random free radicals which couple eventually (not shown here).

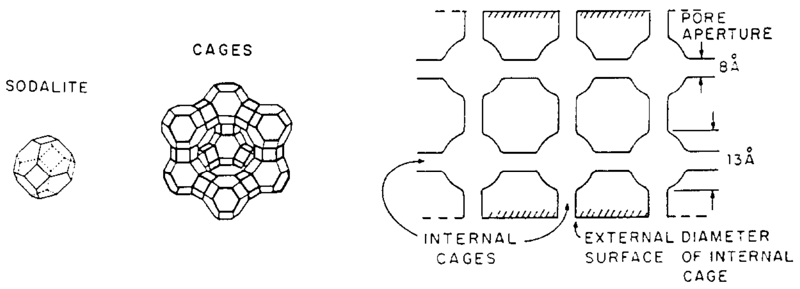


Figure 1. Representations of the building blocks, structure, and simple topological picture of the faujasite zeolite.

position itself in the supercage in a manner that exerts its lebensraum effect in a manner that is directly related to its size. It is also possible that there may be some modification of the zeolite structure during the exchange process. This possibility is presently being investigated. Interestingly, the relative rates of photolysis qualitatively follow the lebensraum expectation for the MX system for all of the ions investigated.

In summary, a very simple product analysis appears to be capable of reporting on the space available for rotational and diffusional motions of radical pairs produced in faujasite supercages. For a given Si/Al ratio, the lebensraum increases as the size of the mobile ions decreases, and, for a given ion, the lebensraum increases as the Si/Al ratio increases. This information, since it is derived from direct product analysis, should be pertinent to the understanding of catalytic action of the faujasites, which represent industrial catalysts of wide use and versatility.[9]

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2. The discussion of exchangeable ions in this manuscript is restricted, with respect to the mechanism of product formation, to the site III ions which are loosely bound in the supercages[3] and factors such as ion polarizability[3], are unnecessary to explain the data.

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