A Comparison between Zeolite–Solvent Slurry and Dry Solid Photolyses[†]

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The use of a zeolite–solvent slurry as a convenient medium to carry out photoreactions is illustrated with four examples, namely Norrish type I reaction of dibenzyl ketones, Norrish type I and type II reactions of α-alkylbenzyl benzyl ketones, Norrish type II reaction of aryl alkyl ketones, and photodimerization of acenaphthylene. Solvent present within the supercages of zeolites X and Y provides constraint on the mobility of the included guest molecules. Such restrictions are reflected in the product distributions. The difference in the product distribution obtained between the zeolite–solvent slurry and a homogeneous solution is often higher than that between the dry powder zeolites and a homogeneous solution.

Introduction

The study of photochemistry of organic molecules adsorbed on solid surfaces has attracted considerable attention in recent years.[1] The majority of these studies are concerned with photolyses of molecules adsorbed on dry surfaces in the absence of solvents. However, early studies by Leermakers were made on silica surfaces in equilibrium with a liquid phase (slurry).[2] More recent investigations by de Mayo on silica surfaces show that photolyses on dry surfaces and solvent slurries give rise to different product distributions.[3] Further, it has been established that the silica–solvent slurries are often complicated by the presence of organic molecules partly in solution as a result of the existence of very weak interactions between the organic molecule and the silica surface. In addition to silica surfaces, the internal structure (pores and cages) of zeolites has also attracted considerable attention as "microvessels" for photoreactions.[4] The photobehavior of organic molecules included in zeolites is routinely investigated only in the dry state. In this report, we show with four examples that the product distribution obtained upon UV irradiation of organic molecules included in zeolite–solvent slurries is distinctly different from conventional dry powder photolysis. In this context, faujasite-type[5] zeolites (X and Y) are used as hosts.

Photoreactions of ketones and aromatics, utilized as probes in this study, occur within the supercages of X and Y zeolites. The topological structure of X- and Y-type zeolites consists of an interconnecting three-dimensional network of relatively large spherical cavities, termed supercages (diameter of about 13 Å; Figure 1).[5] Each supercage is connected tetrahedrally to four other supercages through 8-Å windows or pores. The interior of zeolites X and Y also contain, in addition to supercages, smaller cages known as sodalite cages. The windows to the sodalite cages are too small to allow organic molecules access to these cages. Charge compensating cations present in the internal structure of the zeolites are known to occupy three different positions (Figure 1) in the zeolites X and Y. Only cations of sites II and III are expected to be readily accessible to the adsorbed organic molecule.

Previously, we have shown that the intercage and intracage motions of guests included in supercages are restricted.[6] Such restrictions depend on the cation size, on the strength of interaction between the cation and the included organic molecule, and on the presence of spectator molecules within the supercage.[7] Continuing along this line of reasoning, we envisioned that when a guest organic molecule is included within supercages of X and Y zeolites in the presence of organic solvents, one might be able to modify the photoreactivity of the guest molecule. In this context, the zeolite–solvent slurry appeared as an attractive medium to carry out photoreactions. In order to establish the generality of the zeolite–solvent slurry as a reaction medium, four photoreactions namely Norrish type I α-cleavage of dibenzyl ketone,[8] Norrish type II reaction of phenyl alkyl ketones,[9] Norrish type I and type II reactions of α-alkylbenzyl benzyl ketones,[10] and the dimerization of acenaphthylene,[11] which have been studied in dry zeolite powders, are chosen as probes. Formation of products from the above photoreactions involve considerable intra- and/or intercage motions of the reactants/intermediates.[8-11] We illustrate here that such motions can be restricted to different extents, depending on the solvent content in the supercages of zeolites X and Y. Further, it is also shown that with the proper choice of the solvent and loading levels, $\langle S \rangle$ (where $\langle S \rangle$ is the loading level or the occupancy number defined as the ratio of the number of guest molecules to the number of available supercages),

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[†] Part of the series Modification of Photochemical Reactivity by Zeolites. Contribution Number 5457.

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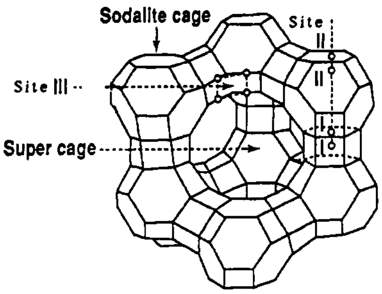

Figure 1.

the zeolite–solvent slurry can be a convenient and experimentally simple medium to carry out selective phototransformations of organic molecules.

Results and Discussion

Methodology. A typical experiment consisted of the following. Zeolites were activated at 500 °C overnight before use. To the guest organic molecule in hexane (or other solvent) was added the activated zeolite, cooled to room temperature, and the mixture was stirred for about 1 h. In the case of yellow acenaphthylene it became apparent during the stirring process that all acenaphthylene molecules (10 mg) dissolved in hexane (5 mL) were adsorbed onto the zeolite (200 mg). No yellow color was left in hexane solvent. In the case of ketones used in this study, color could not be used as an indicator. GC and UV analyses of the hexane layer revealed that no guest organic molecule was left in the hexane portion under the loading levels used in this investigation ($\langle S \rangle$ values: dibenzyl ketone, 0.2; α-butylbenzyl benzyl ketone, 0.05; α-octylbenzyl benzyl ketone, 0.05; valerophenone, 0.2; octanophenone, 0.2; and acenaphthylene, 0.2–1.0). By carrying out experiments at several loading levels ($\langle S \rangle$ varied between 0.1 and 4) and in various solvents such as cyclohexane, benzene, methanol, and diethyl ether, it was concluded that the distribution of organic molecules between the solvent and the zeolite, as expected, depended on the nature of the solvent and on the amount of the dissolved reactant molecule. In general, we found hexane to be the best solvent for the zeolite–solvent slurry preparations since total adsorption of the reactant molecules on zeolites occurred in hexane slurries. In the other solvents, some amount of guest remained in the bulk solvent. This made the interpretation of results difficult as the reaction occurred within and outside (in the solvent medium) of the zeolite.

Magnetically stirred translucent zeolite–hexane slurries were photolyzed under a helium atmosphere (to avoid quenching by atmospheric oxygen). Owing to lesser light scattering problems, the irradiation time required to achieve 20% conversions was less for zeolite–solvent slurry when compared to that for the dry zeolite powders. GC analysis of the hexane portion at the end of the irradiation of the slurry revealed no products in the hexane layer, indicating that the products also remain within the zeolites. However, products and unreacted guests were readily extracted (material balance ~90%) into the ether layer by stirring the reaction mixture in diethyl ether for about 10 h.

A Model. A simple model that we have utilized to understand the photoreactivities of the guests included in the zeolite–solvent slurry is presented in this section. As pointed out above, only the supercages of the X and Y zeolites are large enough to accommodate both the guest as well as the solvent molecules. The supercage of NaX is estimated[12] to have a free volume of ~852 Å^3. When the molecular volumes[13] of the guests investigated here (acenaphthylene, ~281 Å^3/molecule; valerophenone, ~273 Å^3/molecule; and dibenzyl ketone, ~311 Å^3/molecule) are compared with the available free space within the supercages it is clear that singly occupied cages will still be left with some empty space. For example, the free space available for the solvent after being occupied by a single molecule of acenaphthylene would be ~570 Å^3. This space is sufficient for 2.6 molecules of hexane (217 Å^3/molecule). Even cages containing large cations such as Cs have a free volume of ~732 Å^3/cage sufficient for both the guest and the solvent. Therefore, supercages in contact with bulk solvent should be filled with both the reactive guest and the solvent molecules. Solvent molecules present in supercages are expected to occupy the void space left out by the guest molecule and cause serious congestion within the supercage.

Under the conditions of the zeolite–solvent slurry, although the solvent present within the supercages will be in equilibrium with the bulk solvent present outside of the supercage, it ("intracrystalline solvent") is expected to have microproperties different from that of the bulk solvent. The heat of adsorption and the activation energy for self-diffusion of hexane in NaX have been measured to be ~18 kcal M^{-1} and ~5 kcal M^{-1}, respectively.[14,15] The self-diffusion coefficient for hexane within Na X has been measured to be at least 2 orders of magnitude lesser than in the bulk liquid.[16] As a result of reduced diffusivities of the "intracrystalline solvent" and due to reduced space within the supercage, mobility of guests present within solvent-filled supercages are expected to be reduced even further than in solvent-free supercages.

Choice of Photoreactions. The choice of photoreactions is motivated by our desire to establish the generality of the zeolite–slurry irradiations and to explore the extent of restriction provided by the "intracrystalline solvent" on the motions of supercage-included guest molecules. Photoreactions chosen for investigation are Norrish type I α-cleavage of dibenzyl ketones, Norrish type II γ-hydrogen abstraction of aryl alkyl ketones, and dimerization of acenaphthylene (Schemes I–IV). In the case of ketones **1** and **2**, the fragmentation occurs within a single cage and the ease with which the fragments diffuse to adjacent cages defines the product distribution. The photodimerization of acenaphthylene, **3**, presents a reverse situation. In this example, the reactants present in different cages are to diffuse to a single cage and react. Type II γ-hydrogen abstraction in the case of aryl alkyl ketones (**4**) occurs completely within a single cage. Thus the restrictions imposed by the solvent on the inter- and intramolecular

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(12) The accessible volumes of the supercages of zeolites X were calculated from unit cell dimensions assuming: (a) the volume of a MO_2 group (M = Al or Si) to be the same as the volume of a SiO_2 group of quartz (density of 2.66 g/cm^3 which corresponds to a volume of 37.5 Å^3/MO_2); (b) the volume of a supercage is 151 Å^3; (c) cations in site I do not affect the accessible pore volume; and (d) only half of the volume of the cations in site II and all of the volume of the cations in site III occupy accessible volume in the supercage and must be subtracted for a total of 8 cations/supercage for zeolite X. Ionic radii of cations were taken from Liebau, F. *Structural Chemistry of Silicates*; Springer-Verlag: Germany, 1985; Appendix III.

(13) Molecular volumes of the guests were calculated based on their liquid densities and thus refer to liquid packing.

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Scheme I

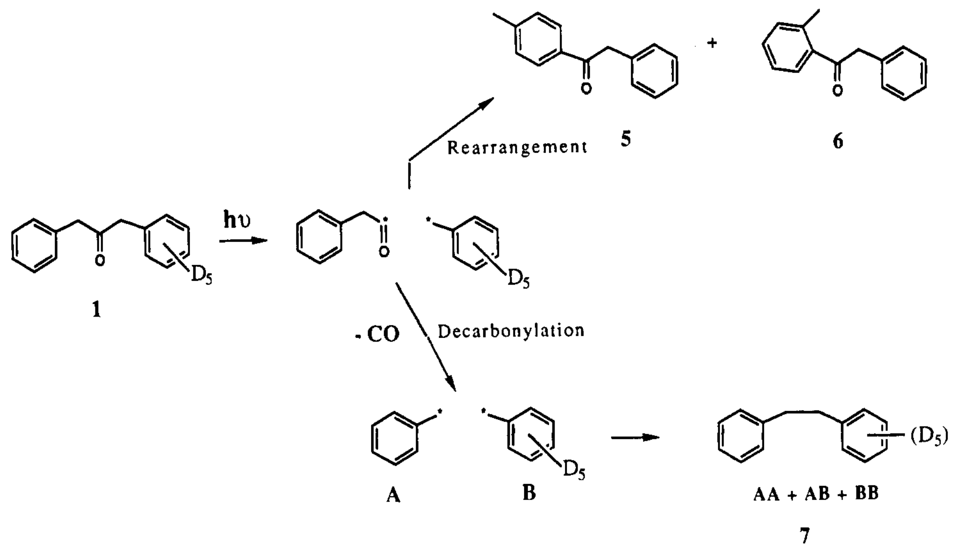

Table I. Product Distribution upon Photolysis of Dibenzyl Ketone Included in LiX and NaX Zeolites: Comparison between Solvent Slurry and Dry Powder Irradiations[a]

	hexane slurry			dry solid		
		rearrangement prod.[c]			rearrangement prod.	
zeolite	cage effect[b]	5	6	cage effect	5	6
LiX	62	74	6	5	11	12
NaX	83	48	36	22	25	12

[a] Both solid and slurry irradiations correspond to the same loading level ($\langle S \rangle = 0.2$). Numbers reported are the average of at least four independent runs. Products were analyzed by GC at ~15% conversion using 4-methylbenzophenone as the internal standard; error limit ±10%. [b] For cage effect, estimation of AA, AB, and BB was measured by GC-MS. Cage effect (%) is defined as follows: 100[AB - (AA + BB)/AA + AB + BB]. [c] For products see Scheme I.

motions of the guest molecules can be probed by the four reactions investigated here.

Photolysis of Dibenzyl Ketone. Norrish Type I Reaction. Results of photolyses of dibenzyl ketone-d_5 (i.e. $C_6H_5CH_2COCH_2C_6D_5$) adsorbed onto LiX and NaX in pentane slurries and as dry powders are presented in Table I. This represents a simple system in which the medium effect on diffusion of the fragments resulting from α-cleavage is reflected in the product distribution. A comparison between the dry powder and the slurry irradiations (Table I) at identical loading levels ($\langle S \rangle = 0.2$) reveals that in the zeolite–pentane slurry the yield of the rearrangement products, 1-phenyl-4-methylacetophenone (**5**) and 1-phenyl-2-methylacetophenone (**6**), is significantly enhanced at the expense of the coupling product, 1,2-diphenylethane (**7**) (Scheme I). Further, the cage effect,[17] defined as 100[AB - (AA + BB)/AA + AB + BB], increases in going from the dry zeolite to the zeolite–pentane slurry (see Scheme I for definitions of AA, AB, and BB).

The preference of photorearrangement in the zeolite–pentane slurry (as compared to dry zeolites) can be understood on the basis of the model presented in an earlier section. The standard paradigm[18] for the photolysis of dibenzyl ketone is shown in Scheme I. In homogeneous solvents, the exclusive isolated product is 1,2-diphenylethane.[19] The primary geminate triplet radical pair undergoes rapid diffusional separation in solution, and decarbonylation occurs efficiently. If the primary geminate radical pair could be constrained to a reaction space that inhibits diffusional separation, rearrangement to isomeric ketones **5** and **6** should become more efficient.[20] Evidence has been presented earlier that the internal porous structure of X and Y zeolites can provide such constraints.[8] In the zeolite–pentane slurry, it is likely that the reactants and intermediates present within supercages will have to push the pentane out of their way before moving to adjacent cages. As a result, recombinations of the primary radicals are encouraged and isomerization becomes competitive or favored relative to diffusional separation and decarbonylation. The observed higher cage effect in the zeolite–pentane slurries during the formation of coupling products (AA, AB, and BB) from the secondary benzylic radical pair is also consistent with the above model.

Photolysis of α-Alkylbenzyl Benzyl Ketones. Norrish Type I and Type II Reactions. The photobehavior of α-alkylbenzyl benzyl ketones **2** is very similar to that of dibenzyl ketone discussed above, except that these systems are inherently capable of undergoing type II hydrogen abstraction in addition to the type I cleavage from the triplet state.[9] Photolyses of α-butylbenzyl benzyl ketone, **2a**, and α-octylbenzyl benzyl ketone, **2b**, in hexane, in dry zeolites, and in the zeolite–hexane slurry give products from both Norrish type I (**8**–**10**) and type II (**1** and **11**) reactions (Scheme II and Table II). Perusal of Table II reveals that there are differences in the distribution of products between the dry zeolites and the zeolite–hexane slurries. The major difference is in the ratio of products derived via type I to type II processes. Significant enhancement of type II products is obtained in the zeolite–hexane slurry at the expense of the rearrangement product 8 resulting from type I process. In the zeolite–hexane slurry, products from the type II γ-hydrogen abstraction process contribute to about 20–40% of the overall products while in hexane and in dry zeolites their contribution is less than 10%.[9]

The above changes in product distribution can be accounted for on the basis of the model utilized to under-

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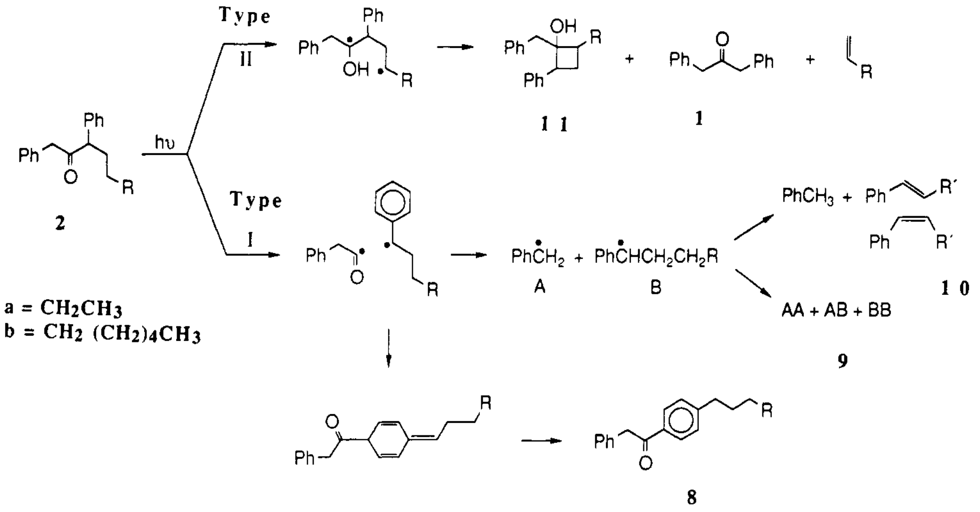
Table II. Product Distribution upon Photolysis of α-Alkylbenzyl Benzyl Ketones Included in LiX and NaX Zeolites: Comparison between Solvent Slurry and Dry Powder Irradiations[a]

	hexane slurry					dry solid				
	type II products		Type I products			Type II products		Type I products		
zeolite	DBK (1)	CB (11)	olefin (10)	AB (9)	RP (8)[b]	DBK (1)	CB (11)	olefin (10)	AB (9)	RP (8)
				α-Octylbenzyl Benzyl Ketone						
LiX	14	5	32	15	34	-	4	28	11	61
NaX	22	18	46	6	7	-	6	27	23	51
				α-Butylbenzyl Benzyl Ketone						
LiX	11	15	27	30	28	-	8	17	11	72
NaX	13	5	43	24	15	-	9	21	17	62

[a] Both solid and slurry irradiations correspond to the same loading level (⟨S⟩ in the case of **1** = 0.2 and **2**, 0.05). Numbers reported are the average of at least four independent runs. Products were analyzed by gc at ~15% conversion using pyrene as the internal standard; error limit ±10%. [b] Ortho and para isomers of **8** were not separated under our GC conditions. RP corresponds to **8**. For products, see Scheme II.

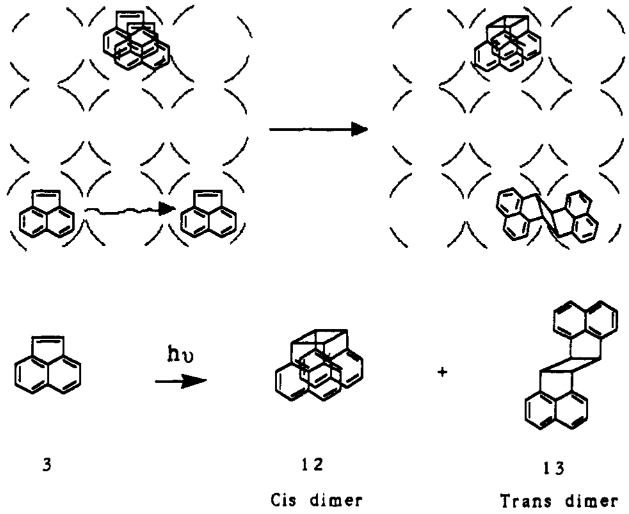
Scheme II



stand the behavior for dibenzyl ketone. As the available space within the supercage is decreased by the presence of solvent hexane molecules, the translational and rotational motions required for the rearrangement of the primary radical pair (Scheme II) becomes increasingly hindered. The above hindrance for rearrangement would favor the competing path, namely coupling of the primary radical pair (after intersystem crossing to the singlet radical pair) to yield the starting ketone. Such an event will decrease the efficiency of type I process. Further, this would allow the normally inefficient type II hydrogen abstraction to compete favorably with the more efficient type I process. This model would also predict that the yield of the rearrangement products would decrease in the zeolite–hexane slurry. These predictions are indeed realized.

Photodimerization of Acenaphthylene. In the two examples discussed above, the guest molecules are photofragmented within a single cage and the ease with which the fragments diffuse to adjacent cages define the product distribution. Photodimerization of acenaphthylene presents a reverse situation.[11,21] In this example, the reactants present in different cages diffuse to a single cage and react. "Intracrystalline hexane solvent" can be expected to play a critical role in this dimerization process also. Indeed this is the case.

Scheme III



Irradiation of acenaphthylene in organic solvents results in both cis and trans dimers, **12** and **13** (Scheme III). The singlet excited state essentially yields the cis dimer whereas the triplet excited state gives both the cis and trans dimers.[21] Photodimerization of acenaphthylene in various cation-exchanged Y zeolites in the dry state has been reported by us previously.[11] The ratio of the two dimers formed depends on the cation present within the supercage. In RbY both the cis and trans dimers are formed, and the dimerization was shown to originate essentially from the triplet state. In this medium, the major part of the dimer is rationalized to come from the reaction between acenaphtylene molecules present in different cages. Therefore, it seemed that if there is going to be an effect

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[21] Cowan, D. O.; Drisko, R. L. *Elements of Organic Molecule Photochemistry*; Plenum Press: New York, 1976; pp 435–443.

Scheme IV

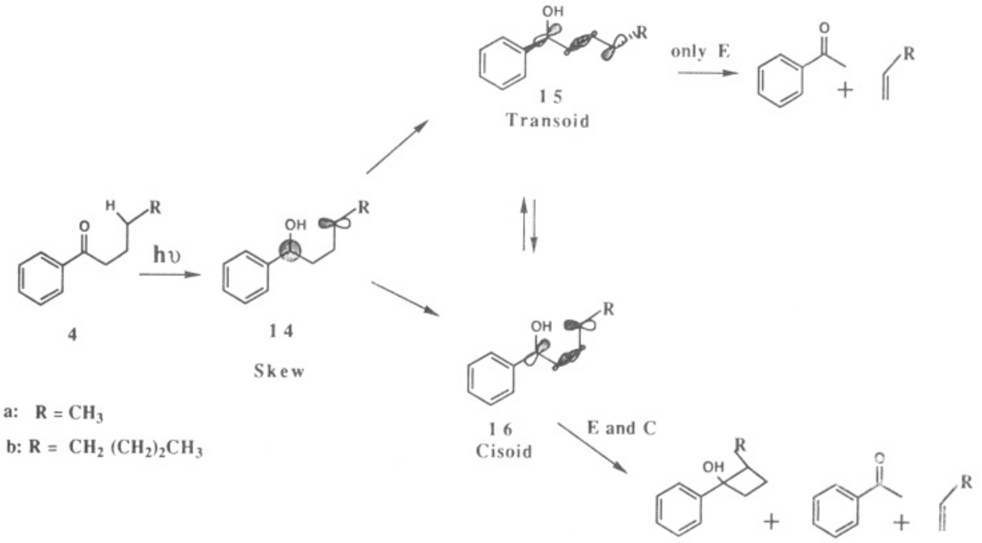

Table III. Photodimerization of Acenaphthylene within the RbY Zeolite Cis to Trans Dimer Ratio: Comparison between Hexane Slurry and Dry Solid Irradiations[a,b]

occupancy number ⟨S⟩[c]	RbY–hexane slurry[d]	RbY dry solid	hexane solvent (no zeolite)[e]
0.2 (5 mg in 250 mg)	2.3	0.6	cis dimer only
0.5 (10 mg in 250 mg)	3.5	1.7	cis dimer only
0.9 (25 mg in 250 mg)	7.2	2.0	9.1

[a] Products yields were measured by GC at ~15% conversion with *trans*-stilbene as the internal standard. Numbers reported are the average of at least four independent runs; error limit ±5%. [b] All three irradiations (slurry, dry solid, and solvent) were conducted under identical conditions. [c] Occupancy number corresponds to the ratio of the number of molecules included to the number of available supercages. [d] No acenaphthylene was to be found in hexane before irradiation, and analyses of the hexane layer after the irradition did not reveal the presence of any dimer. [e] Noted amount was dissolved in 5 mL of hexane and irradiated.

of solvent on intercage migration of guest molecules it will be reflected more readily in RbY than in other cation-exchanged zeolites. Therefore dimerization of acenaphthylene was conducted in RbY both in the hexane slurry and in the dry solid forms at various loading levels. The results of photolyses of acenaphthylene in RbY are presented in Table III.

While in dry zeolites both the cis and the trans dimers are formed, in the hexane slurry the cis dimer alone is obtained. Such a selectivity in the product distribution could arise due to one or more of the following factors: difference in reactive states, variation in distribution pattern (single vs double occupancy) of the acenaphthylene in supercages, and difference in extent of restriction on intercage migration of acenaphthylene molecules between the dry and the solvent–slurry states. We have demonstrated earlier[11] that the reactive state depends on the cation. Since the same cation (Rb) is used in both cases (dry and slurry), it is reasonable to assume that the reactive state remains the same both during dry solid and slurry irradiations. It is not possible at this stage to obtain accurate information or to predict the distribution pattern of guest molecules within zeolite cages. Since the adsorption of acenaphthylene is achieved by the same process (stirring in hexane) both for dry (hexane evaporated off) and slurry (hexane left within the zeolite) irradiations, we assume that the distribution pattern remains the same for both the dry and slurry samples.[22]

The effect of solvent hexane during the dimerization in the zeolite–hexane slurry can be understood on the basis of a scheme proposed previously by us for the photodimerization of acenaphthylene (Scheme III) in zeolites.[11] We proposed that even at low loading levels there are cages with double occupancies. Dimerization occurs within both single and double occupancy cages, and the product formed is a sum of both. While dimerization is expected to be favored in double occupancy cages under all conditions, in single occupancy cages such is possible only if the molecular migration occurs between cages. Further, we have shown earlier[11] that the doubly occupied cages give rise to predominantly the cis dimer while when excited molecules present in singly occupied cages meet another molecule from adjacent cages the trans dimer is formed. Based on the conclusions reached with dibenzyl ketone and α-alkylbenzyl benzyl ketones in zeolite–solvent slurries, one would expect the solvent hexane to block or inhibit the migration of acenaphthylene between cages. This would be expected to selectively reduce reactions between acenaphthylene molecules in singly occupied cages and thus lower the yield of the trans dimer. Therefore, upon photolysis of acenaphthylene in the RbY–hexane slurry dimerization is expected to occur preferentially from doubly occupied cages, and thus a higher yield of the cis dimer (with respect to that in dry RbY) would be predicted. Perusal of Table III reveals that this is indeed the case. At all loading levels investigated, the cis dimer, the dimer formed within doubly occupied cages, is favored in the zeolite–solvent slurry compared to dry zeolites.

Photolysis of Aryl Alkyl Ketones. Norrish Type II Reaction. Product distributions upon photolyses of valerophenone **4a** and octanophenone **4b** included in NaX and KX zeolites in the dry state and as zeolite–hexane slurries are provided in Table IV. Examination of Table IV reveals that in the zeolite–hexane slurry cyclobutanol formation is significantly enhanced with respect to dry zeolites. This remarkable effect, we believe, is once again a manifestation of the restriction on the molecular mobility imposed by the "intracrystalline hexane".

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(22) One could argue that during evaporation of hexane and upon degassing acenaphthylene molecule redistribute themselves differently from the initial distribution. This would mean that the distribution patterns are different in the two cases: dry and slurry. At this stage we have no way of knowing that such has occured. We are in the process of utilizing solid-state NMR to investigate this phenomenon.

Table IV. Photolyses of Valerophenone and Octanophenone Included in NaX and KX Zeolites: Comparison between Hexane Slurry and Dry Solid Irradiations[a]

	hexane slurry		dry solid	
	E/C ratio	*trans*-CB/*cis*-CB	E/C ratio	*trans*-CB-*cis*-CB
	Valerophenone			
NaX	0.3	1.9	1.2	2.2
KX	0.2	3.4	0.8	1.9
hexane solvent (no zeolite)	2.9	3.0		
	Octanophenone			
NaX	0.1	3.1	0.9	0.9
KX	0.1	2.9	0.8	1.0
hexane solvent (no zeolite)	2.7	2.5		

[a] Products yields were measured by GC at ~15% conversion using dibenzyl as the internal standard. Numbers reported are the average of at least four independent runs; error limit ±10%. [b] E/C ratio corresponds to the GC yield of acetophenone to cyclobutanols. [c] *trans*-CB corresponds to the isomer which has a longer retention time on the GC columns: supelcowax capillary and SE-30 capillary. This has been identified to be the isomer in which the phenyl and alkyl groups are on the opposite sides.

The Norrish type II reaction of ketones has been extensively investigated, and the mechanistic details are fairly well understood.[23] The triplet 1,4-diradical, the primary product of γ-hydrogen abstraction, generated in the skew form, **14**, readily transforms to the transoid, **15**, and the cisoid, **16**, conformers via a rotation of the central σ-bond (Scheme IV). As illustrated in Scheme IV these conformers undergo further reaction to yield cyclobutanol, olefin, and enol as final products. While the cisoid conformer transforms to the final products via both the elimination and cyclization processes, the transoid conformer undergoes only the elimination reaction. It is well known that in a medium where the 1,4-diradical is hydrogen bonded, the diradical prefers a transoid geometry and therefore the elimination products dominate the product mixture. This is readily seen as the difference in product distributions between hexane and alcohol as solvents. From the above established mechanistic feature, it is clear that one can understand the influence of the "microenvironment" on the cyclization and elimination (acetophenone) processes on the basis of its effect on the equilibrium distribution of the cisoid and transoid 1,4-diradical conformers.

From Table IV it is clear that the E/C ratio decreases (i.e. cyclization is enhanced) in the order isotropic organic molecule solvent, dry zeolite, and zeolite–hexane slurry. Such a trend can be correlated with the preference of the cisoid geometry for the 1,4-diradical with the change in the medium. Preference for the cisoid geometry would be anticipated with the decrease in the reaction cavity volume. Such a preference would be reflected as an increase in cyclization process. A drop in the E/C ratio from isotropic organic molecule solvent to dry zeolite is indeed consistent with this thinking, when the medium is changed from an organic molecule solvent to a zeolite supercage the reaction cavity volume indeed decreases. Preference for the cisoid conformer would be even more in a supercage filled with the solvent (zeolite–hexane slurry). On this basis one would predict that the type II 1,4-diradical generated within the supercage of the zeolite-solvent slurry would be forced to maintain a compact geometry due to reduction in the available supercage free volume. Thus the first formed skewed 1,4-diradical would be encouraged to relax to the cisoid rather than to the transoid conformer. Severe constraints would be imposed by the "intracrystalline hexane" on the cisoid–transoid interconversion, and the barrier for the cisoid to transoid conversion would be accentuated. Thus the enhanced participation of the cisoid conformer in the transoid–cisoid equilibrium would be expected to give a higher yield of cyclobutanol in the zeolite–hexane slurry. Results observed in NaX- and KX–hexane slurries are indeed consistent with the above predictions.

Conclusions. We have shown in this study that the zeolite–solvent slurry is a good, convenient, and clean medium to carry out photochemical reactions. By the choice of an appropriate solvent and loading level (occupancy number), one can carry out photoreactions completely within zeolite supercages without complication by the bulk external solvent. Solvent present within supercages along with the guest reactants provides constraints on the mobility of the reactants/intermediates. Such restrictions in general are reflected in the product distributions. The selectivity in the product distribution obtained in the zeolite–solvent slurry is often higher than in dry zeolites. A simple method to fully understand the role of "intracrystalline" solvent in controlling the reactivities of the supercage-included guests is needed. One also needs to explore the influence of other solvents having different sizes and shapes. It is quite likely that the mode of packing by other solvents within the supercage is different from hexane. These could have consequences on the photochemical behavior of the included guests. Experiments need to be designed to understand the distribution pattern (single vs multiple occupancy) of the molecules within the zeolite supercages. Attention is being paid to these in our laboratories.

Experimental Section

Materials. Dibenzyl ketone, valerophenone, and octanophenone, (Aldrich) were distilled twice prior to use. Acenaphthylene (Lancaster Synthesis Ltd) was recrystallized four times from ethanol before use. α-Butylbenzyl benzyl ketone and α-octylbenzyl benzyl ketone were prepared by a literature procedure[24] and purified by column chromatography (silica gel/hexane). All samples were more than 99% pure by GC analysis.

Zeolites 13X (NaX) and LZ-Y52 (NaY) were obtained from Linde. The cation of interest was exchanged into these powders by contacting the material with the appropriate nitrate solution at 90 °C. For each gram of zeolite, 10 mL of a 10% nitrate solution was used. This was repeated a number of times. The samples were then thoroughly washed with water and dried. Exchange levels for individual zeolites are as follows: LiX, 46%; KX, 64%; and RbY, 68%. Prior to use these samples were heated in furnace at 500 °C under an aerated atmosphere for about 10 h. Activated zeolites cooled to room temperature were used immediately.

Preparation of the Solid Complex. Known amounts of guest ketones or acenaphthylene and the activated zeolites were stirred together in 10 mL of hexane (pentane in the case of dibenzyl ketone) for about 2 h. In a typical preparation 200 mg of the zeolite and 5 mg of the guests were taken in 20 mL of the solvent. (Amounts taken in each case are as follows: dibenzyl ketone, 4 mg; α-butylbenzyl benzyl ketone and α-octylbenzyl benzyl ketone, 3 mg; valerophenone and octanophenone, 5 mg; acenaphthylene, varied between 2.5 and 25 mg; and RbY, 250 mg.) A white powder (or lightly yellow colored in the case of acenaphthylene) collected by filtration of the solvent was washed with hexane twice (20-mL

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portions) and dried under nitrogen.

Preparation of the Guest-Zeolite-Solvent Slurry. Known amounts of guest ketones or acenaphthylene and the activated zeolites were stirred together in 5 mL of hexane (pentane in the case of dibenzyl ketone) for about 2 h. In a typical preparation 200 mg of the zeolite and 5 mg of the guests were taken up in 5 mL of the solvent. The amounts taken in each case were the same as those listed above in the case of dry solid preparations. At the end of 2 h, the hexane layer was analyzed by GC (Hewlett-Packard Model 5890, supelcowax capillary column) for the presence of the guest. In no case did we find any guest in the hexane layer, indicating that all the guest molecules initially taken have been adsorbed into the zeolite.

Photolysis of Solid and Slurry Samples. Dry solid samples prepared as above were taken in Pyrex tubes (10 mm diameter and 5 cm length) fitted with Teflon stopcocks, degassed thoroughly (10^{-4} mm), and sealed. These were irradiated with 450-W mercury lamps with Pyrex filters. Irradiation cells were rotated periodically to provide uniform exposure. Generally about 15% conversion was obtained in about 2 h of irradiation. After photolyses, products were extracted by stirring the samples in ether (20 mL) for about 10 h. In some cases the zeolite was dissolved with concentrated HCl and extracted with ether. Control experiments established that the products are stable to the acid extraction conditions. A known amount of internal standard (dibenzyl ketone, 4-methylbenzophenone; α-alkylbenzyl benzyl ketones, pyrene; acenaphthylene, *trans*-stilbene; and valerophenone and octanophenone, dibenzyl) was added to the above extracted solutions and products analyzed by GC. The percentage cage effects in the experiments comprising DBK-d_5 were determined by quantitative single ion monitor GC-MS analysis. Analyses were carried out on a Hewlett-Packard (HP 5890) GC connected to a HP 5988 mass selective detector and a HP 9216 work station. The ion intensities (EI 70 EV) corresponding to DPE-d_0 (AA), DPE-d_5 (AB), and DPE-d_{10} (BB) were monitored simultaneously at M$^+$ 210, 215, and 220. The values obtained were corrected for detector response. Structures of all products have been established earlier, and the spectral data are consistent with the literature reports.[8-11,25]

The guest-zeolite-solvent slurry taken in a Pyrex test tube was bubbled with helium (making sure no evaporation of hexane occurred) for about 10 min and sealed. The above slurry while being magnetically stirred was irradiated with 450-W mercury lamps with Pyrex filters for about 15 min. Solvent hexane (or pentane) was decanted and analyzed by GC. Neither starting reactants nor products were found in the supernatent solvent. Products and reactants from zeolites were extracted by stirring them with diethyl ether (10 mL) for about 10 h. To the ether extract a known amount of internal standard was added, and the mixture was analyzed by GC as above. The mass balance in all cases was ~90%.

Irradiation of ketones and acenaphthylene in hexane in the absence of zeolite were also carried out for comparison.

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Palladium-Catalyzed Coupling Reactions of Aryl Triflates or Halides with Ketene Trimethylsilyl Acetals. A New Route to Alkyl 2-Arylalkanoates

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Palladium complexes with phosphines, in the presence of lithium acetate, catalyze the coupling reaction of aryl triflates and ketene trimethylsilyl acetals to yield alkyl 2-arylalkanoates, 1,1′-bis(diphenylphosphino)ferrocene gives the best results. Aryl halides may also be used, provided that a stoichiometric amount of thallium acetate is present. Added acetate anions act both as palladium-bonded groups in the ArPdL$_2$OAc reactive intermediates and as nucleophiles promoting the Si-O bond breaking of the silyl enolate moiety. The reaction represents a novel method for the preparation of alkyl 2-arylalkanoates which, after hydrolysis, afford the corresponding 2-arylalkanoic acids, well known as antiinflammatory and antipyretic drugs.

Introduction

Ketene silyl acetals are extensively used in organic synthesis as enolate equivalents for aldol condensations and Michael addition reactions.[1] The coupling reaction is catalyzed either by Lewis acids as TiCl$_4$[2-5] or by nucleophiles as fluoride anions.[6] Recently it has been found that Pd-phosphine or phosphine free complexes catalyze the coupling reactions of ketene silyl acetals and allylcarbonates to yield α-allylated carboxylic esters.[7,8] Since aryl triflates and aryl bromides are electrophiles widely used in carbon-carbon bond formation reactions catalyzed by Pd complexes,[9-15] we deemed it interesting to study

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