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PHOTO-FRIES REACTION OF NAPHTHYL ESTERS WITHIN ZEOLITES

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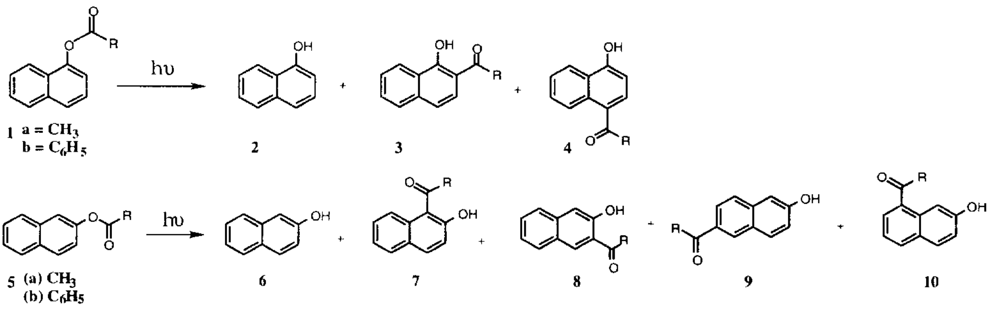
Photolysis of naphthyl esters within zeolites leads to the photo-Fries rearrangements as in isotropic solution. However, a high level of product selectivity is obtained using 'cation as the key'. A key component for predicting the selectivity of photoreactions within zeolites, namely the location of reactants, is missing at this stage. Copyright © 1996 Elsevier Science Ltd

Photochemistry has reached the stage of maturity where the reaction course of some excited state molecules can be controlled. In this context, photochemistry in organized assemblies has attracted considerable attention during the last two decades.[1] This letter is concerned with one such assembly–zeolites.[2] Results presented here on the photo-Fries rearrangements of 1-naphthyl and 2-naphthyl esters (Scheme 1) illustrate how the product distribution in a chemical reaction can be controlled with judicious choices of zeolite types and the cations present in it as a medium.[3-5] The choice of the naphthyl system is motivated by the following factors: (a) the reaction has been investigated extensively in solution;[6] (b) attempts have been made previously to control the product distribution with varied success;[7] and (c) since the naphthyl esters give a larger number of products than the phenyl esters, they provide a greater opportunity to test the limitations of zeolite as a medium to achieve selectivity. The medium that we have exploited is faujasite (X and Y zeolites). The topological structures of X and Y zeolites consist of an interconnected three-dimensional network of relatively large spherical cavities, termed "supercages" (diameter ~ 12Å).

The experimental procedure consisted of stirring known amounts of **1** or **5** and activated X or Y zeolite in hexane, followed by washing with excess hexane and drying under reduced pressure (10^{-4} Torr). Filtration and thorough washing with hexane gave zeolites loaded with **1** or **5**. These were irradiated in hexane as a slurry. The absence of reactants and the products in the hexane solvent portion was established by GC analyses and UV absorption spectra. Following irradiation, the products were extracted from the zeolites with ether and analyzed by GC. Mass balances were excellent (>95%). Spectra for the products matched well the reported data.[4,5] Since the results obtained in X zeolites are closely analogous to that in Y zeolites, the former are not elaborated in this letter (Tables 1 and 2).



Scheme 1

The photo-Fries rearrangement of naphthyl esters proceeds via a general mechanism: Excitation to the excited singlet state results in homolytic fragmentation of the naphthyl ester. Cage escape, recombination and hydrogen migration result in several isomeric products. In solution, the relative yield of the various isomers depends on the π-electron densities at various carbon atoms on the naphthoxy radical and on the distance between the site at which the acyl (or the benzoyl) radical is generated and the site to which it migrates. The photo-Fries reaction has been established to occur predominantly from the S_1 state.[4-6]

Table 1: Product Distributions Upon Photolyses of 1-Naphthyl acetate and 1-Naphthyl benzoate

	1-Naphthyl benzoate (**1b**)^{a,b,c}				1-Naphthyl acetate (**1a**)^{a,b,c}			
Medium	Product Yield			Singlet	Product Yield			Singlet
	2^{d}	**3 a**	**4 a**	Lifetime (ns)^{e,f}	**2**	**3 b**	**4 b**	Lifetime (ns)^{e,f}
Hexane	4	70	26		6	81	13	
Methanol	8	63	29		10	72	18	
LiY–Hexane	10	89	1	13.2 (21); 4.7	2	94	4	9.2 (45); 4.0
NaY–Hexane	3	96	1	13.5 (26); 5.3	1	96	3	8.8 (37); 3.7
KY–Hexane	2	98	<1	12.2 (13); 4.7	4	94	2	8.1 (34); 3.1
RbY–Hexane	2	98	<1	10.6 (4); 1.5	42	57	<1	5.6 (7); 2.4
CsY–Hexane	6	94	<1	12.9 (4); 1.1	31	69	<1	3.9 (3); 0.7

a: Irradiations were conducted to about 30% conversion. Ratio of products was independent of the conversion in the range 15 to 90%. All yields presented are an average of at least four independent runs. Error limit on yields ±2%. Time required for 30% conversion was dependent on the cation. For example, this amount of conversion was achieved within 2h in the case of LiY and 24h in the case of CsY.

b: Occupancy level was kept at ~1 molecule per supercage.

c: Results similar to these reported here were also observed when Mg, Ca, Sr, and Ba Y zeolites were used.

d: Reported naphthol yield is a sum of blank (thermal) and photochemical reactions. The extent of blank reaction varied with the cation.

e: A decent fit ($\chi^2 < 1.2$) of excited singlet decay required at least two components.

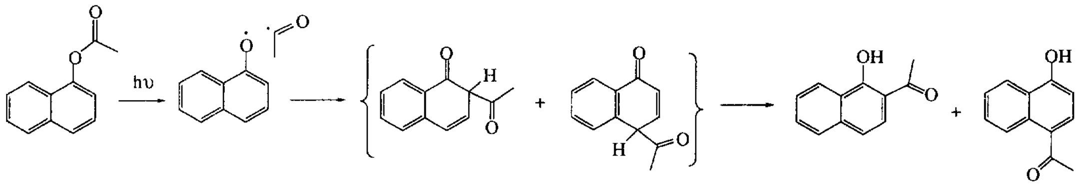
f: Numbers in brackets refer to the contribution by the longer lifetime component, e.g., in LiY the component with lifetime 13. 2 ns contributes 21% and the one with 4.7 ns 79%.

Table 2: Product Distribution Upon Photolysis of 2-Naphthyl acetate (**5a**)^{a}

Medium	Product Yields					Singlet Lifetime,
	6	**7**	**8**	**9**	**10**	$\tau_{S(1)}$ (ns)
Hexane	2	79	13	-	3	
Methanol	32	51	3	9	4	
LiY–hexane	18	42	39	3	-	10.5; 4.7
NaY–hexane	9	65	22	2	2	11.3; 4.6
KY–hexane	19	71	10	-	-	9.1; 4.4
RbY–hexane	34	57	3	-	-	7.8; 2.8
CsY–hexane	62	38	-	-	-	2.7; 0.4

a: Same footnotes as in Table 1 apply.

Naphthols **2** and **6** may originate either via an in-cage or an out-of-cage process. Since attempts to obtain evidence for the in-cage disproportionation process were not successful, we believe that naphthols are formed via an abstraction of hydrogen from the hexane present within the zeolite supercage.[8] In addition to the above photochemical pathway, a dark process, probably catalyzed by acidic/basic sites present in zeolites, also contributes to the total yield of naphthol. The contributions of zeolite catalyzed naphthol formation were higher in **1a** and **5** than in **1b**. The primary products of the photo-Fries reaction are the keto isomers (Scheme 2). However, we were unable to trap this intermediate. It is quite likely that the keto isomer enolizes to the acyl (or benzoyl) naphthols very readily within a supercage.



Scheme 2

A remarkable control of product selectivity is obtained in 1-naphthyl esters **1a** and **1b**. While in solution, both 2-acetyl (or 2-benzoyl) naphthol and 4-acetyl (or 4-benzoyl) naphthol are formed, within zeolites the acyl and benzoyl radicals seek the 2-position of the naphthoxy radical (Table 1). Even more spectacular control of product distribution is obtained with 2-naphthyl acetate (Table 2). In solution four isomers are formed; within Cs Y, a single isomer is obtained. The above selectivity is not the result of shape exclusion since all isomeric products fit well within the supercage: when these isomers were included independently, they were readily incorporated within X and Y zeolites; also they can be easily extracted from the zeolites. Selectivity, we believe, results from the restriction imposed on the mobility of the naphthoxy and the acyl (benzoyl) fragments by the supercage framework and cations. The cage free volume, determined by the cation also, plays an important role as evident from the increased selectivity with the increase in the cation size.[9] While the increased cation size results in higher selectivity, it also has an adverse effect on the efficiency of photoreaction. Photoreactions within Rb and Cs X and Y zeolites, while highly selective, are much slower than in LiY. (Table 1, footnote a). The origin of this effect is evident from photophysical studies of **1** and **5** in cation exchanged Y zeolites.[10] The heavy cations quench the excited singlet state by enhancing intersystem crossing.[11] In general, excited singlet state decay monitored by single photon counting has a two component behavior. In addition to the decrease in the contribution of the long lifetime component with the increase in the cation size, the lifetime of both the components is decreased (Tables 1 and 2). Further, the steady state emission, which is predominantly fluorescence within NaY is predominantly phosphorescence within CsY. These observations suggest that cations such as Cs^+ enhance the rate of intersystem crossing from the reactive S_1 to the unreactive T_1 state.

Table 3: Product Distribution Upon Photolysis of 2-Naphthyl benzoate (**5b**)[a]

Medium	Product Yields					Singlet Lifetime
	6	**7**	**8**	**9**	**10**	$\tau_{S(1)}$ (ns)
Hexane	11	67	5	9	3	
Methanol	22	54	5	9	7	
LiY–hexane	6	79	10	5	1	11.1; 4.4
NaY–hexane	10	64	9	8	9	10.5; 2.9
KY–hexane	21	44	12	14	8	7.1; 2.3
RbY–hexane	28	39	13	14	6	6.8; 1.5
CsY–hexane	17	21	19	41	2	1.3; 0.1

a: Same footnotes as in Table 1 apply.

A basic assumption we have made in analyzing the above results is that the reactant molecules reside in the supercages of X and Y zeolites. If the molecules reside in between two cages, the influence of cations on the reaction is expected to be different, and less selectivity may result. Indeed, this appears to be the case with 2-naphthyl benzoate (Table 3). Clearly, there is no discernible selectivity with this system. Although a heavy cation effect is operative, as indicated by the cation-dependent excited singlet lifetimes, no trend between the product yield and the cations emerges. The photobehavior of 2-naphthyl benzoate within the zeolite is a clear indication that chemistry within zeolites has not reached a stage of where the guest sites can be predicted. However, such a knowledge is needed to predict unequivocally the chemical behavior of guest molecules.[12]

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