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ROLE OF WATER IN INTRAZEOLITE PHOTOCHEMISTRY

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The photochemical and photophysical behavior of several ketones included within Na X zeolites is dependent upon the adsorbed water within the zeolite. Results suggest that when the zeolite is dry (water free), the guest ketones reside within supercages and when the internal structure is filled with water the guest molecules are displaced to the external surface. Copyright © 1996 Elsevier Science Ltd

Research activity in the area of intra-zeolite photochemistry is progressing from a 'show and tell' to a more 'predictable' period.[1] Zeolites have an extraordinary tendency to adsorb water and therefore, zeolite-organic samples prepared in different laboratories tend to have different amounts of water.[2] Such differences, as illustrated in this letter, may have a significant influence on the photochemical outcome and on our ability to control and predict photochemical reactions in zeolite.

The general method of inclusion of organic molecules within zeolites involved stirring known amounts of activated (at ~480°C) zeolite and substrate in dry hexane. Filtering, washing with hexane and drying on a vacuum line at 10^{-4} torr for at least 4 hours gave dry samples. Degassing at elevated temperatures (~80°C) ensured that the sample was water free. Known amounts of water can be included by exposing the sample to water vapor and monitoring its weight on Metler balance.

In Figure 1, the emission spectra of xanthone included within Na X, recorded at 77K is shown. The fluorescence (350 to 420 nm) to phosphorescence (400 to 550 nm) ratio depends on the water content of the sample; an absence of water favors fluorescence. We believe that the difference in emission properties has its origin in the difference in the nature of the lowest excited triplet state (nπ* and ππ*) under the two conditions. The lifetimes of the excited singlet state of xanthone, as measured by single photon counting, under the two conditions are nearly identical (dry: biexponential, 5.9 and 1.7 ns; wet: biexponential, 5.6 and 1.2 ns) within experimental error. Therefore the difference in the fluorescence to phosphorescence ratio, most likely, does not arise from changes in the inter-system (S_1 to T_1) crossing yield.

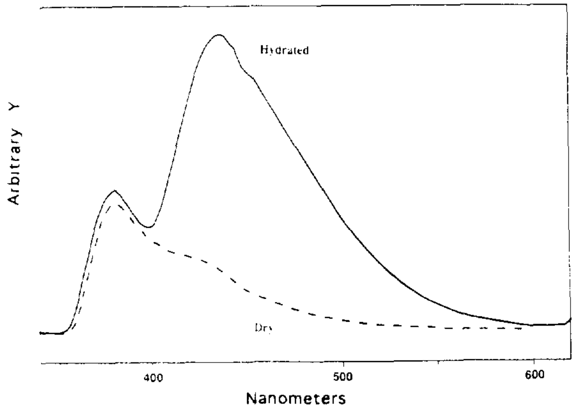
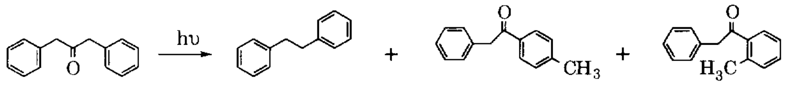


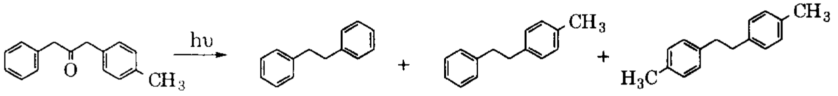
Figure 1: Emission spectra (at 77K) of xanthone included within Na X.

It has been established previously that the character of the lowest triplet state of xanthone is medium dependent (polar medium favors $\pi\pi^*$ character).[3] We propose that when the zeolite is 'dry', xanthone experiences a polar and when 'wet' a less polar microenvironment. This arises due to the difference in location of xanthone molecules under the two conditions; under 'dry' condition xanthone resides within the more polar supercage and when 'wet' on the less polar external surfaces.[4] What is most unique is that dehydration of the wet sample resulted in complete recovery of the fluorescence. Through a dehydration–hydration cycle we were able to control the location of xanthone within zeolites and thereby the fluorescence to phosphorescence ratio.

Results of photochemical reactions of several ketones presented below further support the above paradigm. Dibenzyl ketones undergo Norrish Type I cleavage as illustrated in Scheme 1.[5] The cage effect in the case of *p*-methyl benzyl benzyl ketone (PMBBK) and the product distribution in the case of dibenzyl ketone (DBK) were employed to probe the influence of water on their photochemistry.



	DBK → DPE	p MAP	o MAP
Na X (Dry)	55	26	17
(Wet)	100	0	0
K X (Dry)	40	16	40
(Wet)	98	1	1



PMBBK AA AB BB

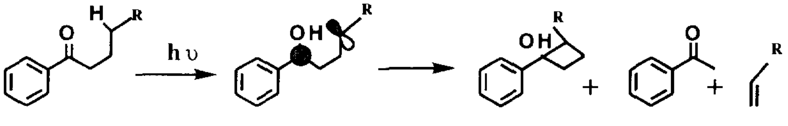
$$\text{Cage Effect} = \frac{\text{AB-(AA+BB)}}{\text{AA+AB+BB}}$$

Na X (Dry)	39	K X (Dry)	49
(Wet)	7	(Wet)	4

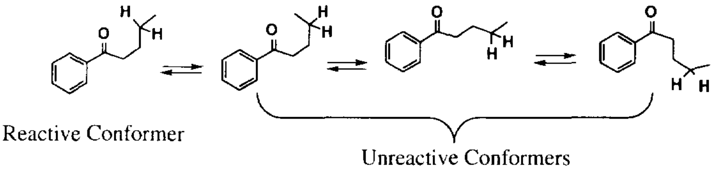
Scheme 1

It is clear from the Scheme that the presence of water has a remarkable influence on the cage effect and the yield of rearrangement products for PMBBK and DBK respectively. We propose that the changes observed are due to differences in the location of the reactive ketones under dry and wet conditions. Similar to xanthone, these ketones stay within the supercages for 'dry' zeolites and are displaced to the external surfaces in wet zeolites. Molecules and intermediates on the external surfaces are expected to experience much less restriction to their diffusional and rotational motion. Therefore, as observed in this study, cage and rearrangement products are expected to be less likely than when the ketones are present on the internal surfaces of the zeolite.[6]

The third example deals with the Type II reaction of aryl alkyl ketones.[7] Aryl alkyl ketones listed in Table 1 undergo the Norrish-Yang reaction to yield elimination and cyclization products via γ-hydrogen abstraction (Scheme 2). We have shown earlier that these ketones when present within the supercages of X and Y zeolites, as a result of interaction with the cations, adopt conformations that are unfavorable for γ-hydrogen abstraction (Scheme 2).[8,9] Consistent with this model, the excited triplet state of valerophenone has a relatively long lifetime (900 ns) within 'dry' Na Y. Most surprisingly, the lifetime decreased to less than 200 ns in wet zeolite. The decrease in lifetime is consistent with the general model in which the guest ketone tends to be displaced to the external surface when water enters the supercage. When the arylalkyl ketone resides on the external surface, the absence of interaction with the cations is expected to permit a fast equilibriation between various conformers. Further, interaction of 1,4-diradicals with water molecules should favor a transoid geometry which is established to undergo, preferentially, the elimination reaction.[7] Therefore, wet samples are predicted to have shorter triplet lifetimes and higher percentages of elimination products. These predictions have come true. All five aryl alkyl ketones investigated show a larger elimination/cyclization ratio when the zeolite is 'wet' (Table 1). The results presented in Table 1 correspond to a loading level of 1 molecule of ketone per six supercages. All irradiations were carried out as a hexane slurry. Analysis of the hexane solvent after photolysis did not show the presence of any products indicating that both cyclobutanol and the ketones (acetophenone and starting ketone) tend to stay on the surfaces of the zeolite.



Scheme 2



Scheme 3

Table 1: Dependence of the Type II Elimination to Cyclization Ratio on Water Content

Zeolite	Valero-phenone		Octano-phenone		Dodecano-phenone		Tetradecano-phenone		Henei-cosanone	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
LiX	0.68	4.2	0.58	2.8	0.38	2.1	0.51	1.5	1.7	3.0
NaX	0.37	3.4	0.41	2.1	0.13	1.9	0.41	1.4	1.2	3.2
KX	0.36	2.3	0.38	2.6	0.1	2.3	0.7	1.8	1.0	2.5

Very interesting results were observed when controlled amounts of water were titrated into the zeolite. The results presented in Figure 2 are remarkable. While the first five water molecules have a dramatic effect on the triplet lifetime, they have no effect at all on the product distribution. It has been shown before that the first five water molecules that enter the supercage co-ordinate with the Type III ions (4.75 per supercage located on the walls of the supercage) while additional water co-ordinates to Type I (2 per supercage present within sodalite units) and Type II ions (4 per supercage located at the open hexagonal faces) and then fills the void space within the supercage.[10] We believe that the triplet lifetime serves as a probe for the changes within the supercage where as the product distribution is an indication of the location of the ketone (internal vs. external surface). More than five molecules are needed to displace the ketone to the external surface. It may be of interest to note that it took us almost a year to recognize the influence of water on the lifetime. When the reproducibility of lifetime measurements for a number of samples became a major problem (although product yields for the same samples did not vary), samples were prepared under controlled conditions. This demonstrated the dramatic effect of the water content on the triplet lifetime.

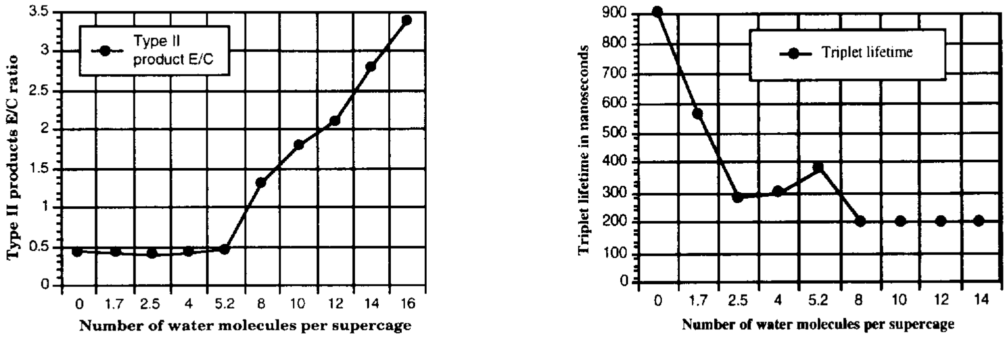


Figure 2: Variation of product distribution (right) and triplet lifetime (left, in nanoseconds) of valerophenone included within Na X as a function of the water content.

Based on the above observations, we conclude that guest molecules reside within the supercage when the zeolite is dry and on the outside surface when the zeolite is wet. Consistent with this conclusion, when wet zeolite containing guest ketones was washed with excess hexane, the hexane wash contained significant amounts of the ketone. However, similar washing of anhydrous zeolite containing ketone did not result in ketone loss into the hexane layer. We have shown with three examples that the photochemical and photophysical behavior of ketones included within zeolite depends on the water content. More importantly, the exact number of water molecules present within zeolites can have a dramatic influence on the observed results.[11]

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