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Intrazeolite Photochemistry. 18. Detection of Radical Cations of Amine Dimers upon Amine Photosensitization with Acetophenone in the Zeolite NaY

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Abstract. Laser flash photolysis (308-nm) of acetophenone (**AcP**)-aliphatic amine mixtures in the cavities of NaY zeolite generates **AcP** triplets, ketyl radical and dimers of amine radical cations. In contrast, photolysis of the same **AcP**-amine system in acetonitrile-water allows to detect exclusively **AcP** triplets and **AcP**$^{-\bullet}$. In the zeolite cavities amine radical cation appear to interact with a second neutral amine to afford the dimer radical cation detected as a longer-lived species absorbing from 480 to 580-nm. These radical cations of amine dimers have never been observed in solution except for special cyclic diamines having two nitrogen atoms rigidly held in close proximity. Product studies have revealed the formation of hydrazines in the photosensitized **AcP**-triethylamine irradiation adsorbed in NaY, but not in acetonitrile solution.

Intrazeolite photochemistry has attracted considerable attention in recent years as a methodology to modify and control the photophysical and photochemical behavior of adsorbed organic guests.[1-3] The internal voids of Y zeolite are formed by spherical cavities of 1.3 nm of diameter interconnected tetrahedrally through smaller openings of 0.74 nm diameter.[4] The very special properties of the reaction cavity provided by the zeolite host arise from the intense internal electrostatic fields and the confinement effect may result in a change in the operating pathways compared to apolar solvents. Besides direct photolysis of an organic compound, the relatively large dimensions of Y zeolite supercages allow studies of sensitized photolysis by selective excitation of a sensitizer that produces a chemical transformation in a non excited molecule in its proximity.[5]

Herein we report that photosensitization of aliphatic amines by acetophenone (**AcP**) inside the NaY zeolite shows a distinctive pattern including detection of amine dimer radical cations not observed for the same reaction in polar solvents. This distinctive behavior arises from the combined contribution of a polar environment stabilizing positively charged intermediates and a confined reaction cavity favoring aggregation of amine radical cation.

Samples of NaY zeolite (supplied by P.Q., Si/Al 2.6)[6] containing **AcP** and three different amines were prepared by sequential adsorption of **AcP** from a CH_2Cl_2 solution, followed by drying under reduced pressure and subsequent incorporation of the corresponding amine either from the vapor phase (triethylamine and 1,4-butanediamine) or from a CH_2Cl_2 solution (DABCO). Samples were stored in closed vials and it can be assumed that partial rehydration has taken place prior to irradiation. Flash photolysis experiments were carried out using 308-nm excimer laser excitation.[7] The diffuse reflectance set-up is similar to that described by Wilkinson.[8] At this wavelength, none of the aliphatic amines absorbs. Exclusive excitation of **AcP** occurs, reaching its triplet excited state which can be easily characterized by its T-T absorption band at 320-nm (Figure 1B). Photolysis of a series of phenones including **AcP** inside NaY zeolite has been the subject of a comprehensive study aimed at the determination of their lifetimes and the influence of coadsorbed water.[9]

The transient diffuse reflectance spectra obtained upon irradiation of the **AcP**-amine mixtures inside NaY exhibit as the most salient common feature the presence of a broad absorption between 480 and 580 nm, depending on the amine. Other accompanying intense absorptions are due either to **AcP** triplets (λ 320 nm) or to **AcPH**$^\bullet$ ketyl radical (λ 415 nm). Two representative spectra are shown in Figure 1A and 1B. The different decay kinetics established that the medium intensity absorptions between 480-580 nm do not correspond to any known **AcP**-derived transient. Assignment of the transient in heterogeneous media is normally based on the comparison with the spectral characteristics of the same transient in solution. In our **AcP**-amine system, the long wavelength (480 to 580 nm) transients can be confidently attributed to the radical cation of the amine dimer.[10,11]

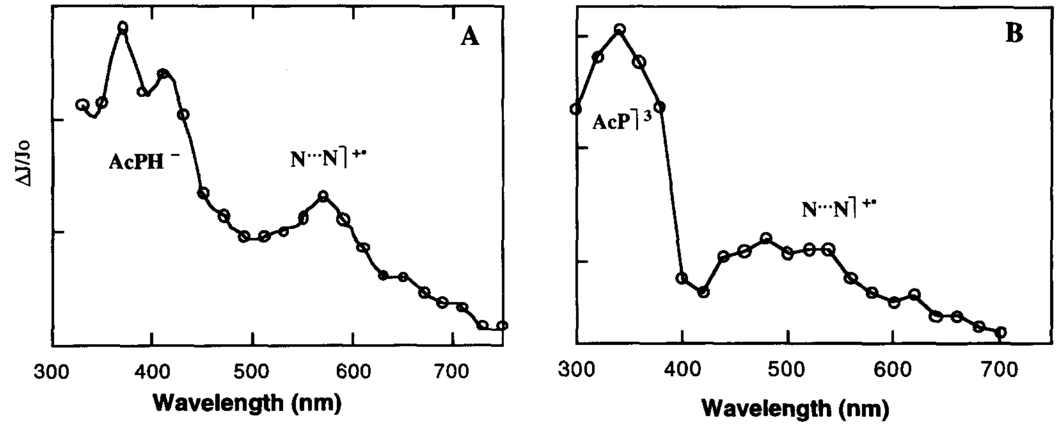


Figure 1. Transient spectra of the **AcP**-1,4-diaminobutane (A) and **AcP**-DABCO (B) mixtures inside NaY 10 µs after 308-nm excitation.

Interestingly, we performed the laser flash photolysis of the same **AcP**-amine system in a 4:1 acetonitrile-water mixture. The transient absorption spectrum obtained in solution is presented in Figure 2. In this case, the transients observed are totally different. The 445 nm band that is completely quenched by the presence of oxygen corresponds to the acetophenone radical anion (**AcP**$^{-\bullet}$). This is coincident with earlier studies that showed that quenching of **AcP** by amines in polar solvents involves single electron transfer (SET) from the amine as donor to acetophenone as acceptor. However, while the **AcP**$^{-\bullet}$ is easily detectable by its characteristic absorption at 445 nm, the radical cations of simple aliphatic amines show a broad structureless absorption expanding a wide range of wavelengths and having the maximum below 300-nm, in a region difficult to access with typical laser photolysis systems and UV-absorbing samples; therefore, no bands corresponding to the triethylamine radical cation are detectable in the spectrum of Figure 2. In contrast, it was reported in the same work that using cyclic diamines having the two nitrogen atoms rigidly held in close proximity exhibit a specific absorption band appearing between 480-580 nm characteristic of N······N$]^{+\bullet}$ interaction.[10]

A reasonable rationalization to explain the features observed in the photolysis of **AcP**-amine system in NaY is outlined in the Scheme. Thus, upon light absorption a SET from amine to **AcP** triplet excited state takes place both in polar solvents and inside the zeolite supercages (path SET in the Scheme). In solution the contact ion pair would evolve to the free radical ions stage allowing the detection of **AcP**$^{-\bullet}$ due to its characteristic absorption band at 445 nm, while the monomer amine radical cation would be undetectable under these conditions. In contrast, **AcP**$^{-\bullet}$ is undetectable inside zeolite and **AcPH**$^\bullet$ ketyl is the observable transient. As SET takes place inside the zeolite cages (as evidenced by the appearance of species derived from amine radical cation), the lack of detection of **AcP**$^{-\bullet}$ radical anion must reflect its shorter lifetime inside zeolite media probably owing to its fast protonation to the corresponding ketyl. In this context, it is worth noting that while zeolites are very appropriate hosts to stabilize positively charged species, the reactivity of negative ones must be enhanced by the internal negative electrostatic fields. Protonation of **AcP**$^{-\bullet}$ could be achieved by coadsorbed water (which the dry zeolite may regain during work-up) or by any intermediate derived from the primary amine radical cation.

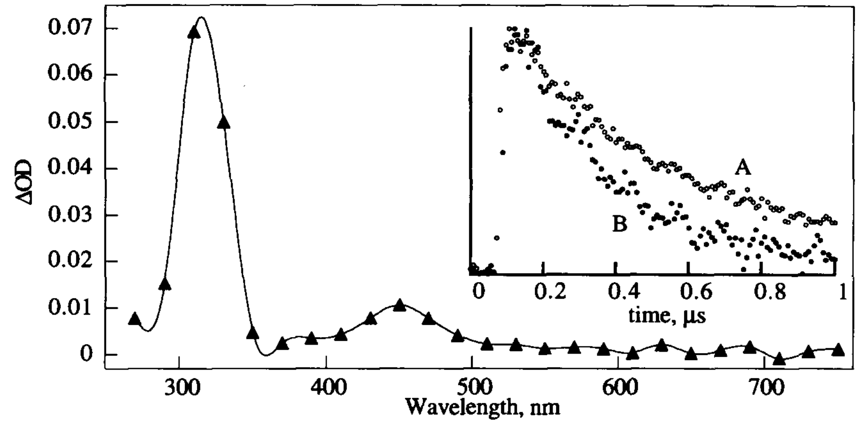
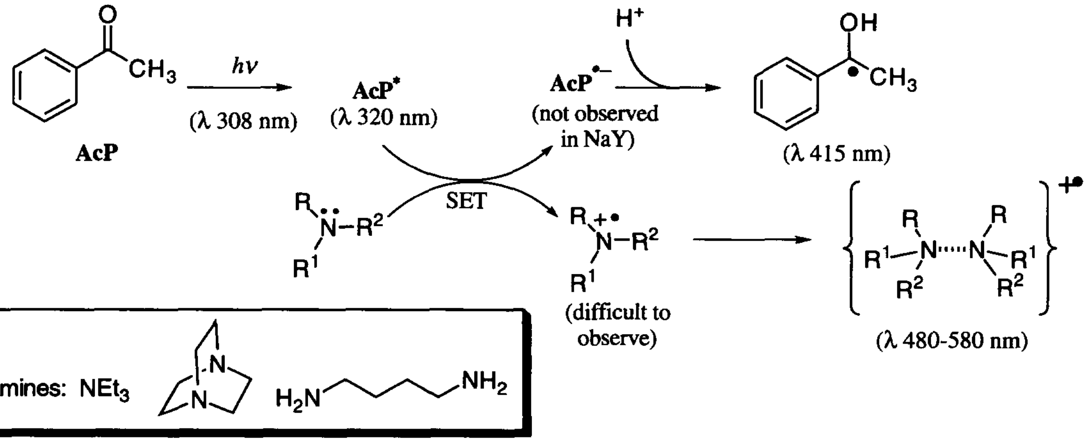


Figure 2. Transient spectrum of **AcP**-triethylamine in acetonitrile-water (4:1) 1 µs after 337 nm excitation. The insert shows the normalized decays monitored at 320 (A) and 450 nm (B).

The most remarkable observation of the **AcP**-amine system inside zeolite is the detection of radical cations of amine dimers. These species have not been observed in solution, except in the case of rigid diamines holding the two nitrogen in close proximity.[10] This may probably reflect the fact that the photolysis is taking place in a confined space. Thus, for those amine radical cations sharing the zeolite cage with another molecule of neutral amine, interaction $N\cdots\cdots N]^{+\bullet}$ has to be favored with regard to solution as the result of mobility and conformation restriction imposed by the rigid framework.[12] This so-called *internal pressure effect* has been previously observed for charge-transfer complexes between methyl viologen and arene donors.[13,14] Similar absorptions (around 600 nm) were also detected when dicumyl peroxide was photolyzed in the presence of triethylamine in NaY.



Scheme. Species involved in the photolysis of **AcP**-amine mixtures inside NaY.

We were interested in establishing whether the distinctive $N\cdots\cdots N]^{+\bullet}$ interaction observed in the intrazeolite photolysis eventually leads to the formation of an isolable product. For this purpose, we carried out a preparative steady irradiation (Rayonet, λ 320 nm) of the **AcP**-triethylamine mixtures adsorbed on NaY and in acetonitrile. Besides **AcP** derived products, analysis by GC-MS of the reaction mixtures established as the most characteristic feature the presence of significant amounts of tetraethylhydrazine when the photolysis is conducted inside NaY but not in acetonitrile solution. The identity of tetraethylhydrazine was confirmed by comparison with an authentic sample prepared by alkylation of hydrazine with ethyl iodide.[15] A control photolysis of the amine incorporated inside NaY without **AcP** did not lead also to the hydrazine.

In summary, photoinduced electron transfer from aliphatic amines to **AcP** triplet excited state inside NaY zeolite exhibits a distinctive pattern characterized by the formation of **AcPH**$^{\bullet}$ ketyl and radical cation of amine dimers different to what is observed in acetonitrile. These behavior is reasonably due to a very short life of **AcP**$^{-\bullet}$ and a cage effect favoring $N\cdots\cdots N]^{+\bullet}$ interaction that eventually leads to product formation.[16]

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(6) The zeolite (1.0 g) was calcined overnight under air at 550 °C. The zeolite was then added to a solution of acetophenone (200 mg) in 10 mL of dichloromethane in a dry-box and stirred for 12h. After filtration, the zeolite was added to a solution of the amine (200 mg in 10 mL) in dichloromethane and stirred for 12 h. The sample was filtered and dried in air.

(7) The laser system uses a Lumonics EX-530 for excitation at 308 nm. Pulse durations are <10 ns and typical pulse energies between 15 and 40 mJ. The signals from the monochromator/photomultiplier system were initially captured by a Tektronix 2440 digitiger and transferred to a PowerMacintosh computer that controlled the experiment with software developed in the LabVIEW 3.1.1 environment from National Instruments. Other aspects of the system are similar to those described earlier: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747; Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396

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