1-Azaxanthone as a Probe for Radical Reactions in Faujasite Zeolite NaY

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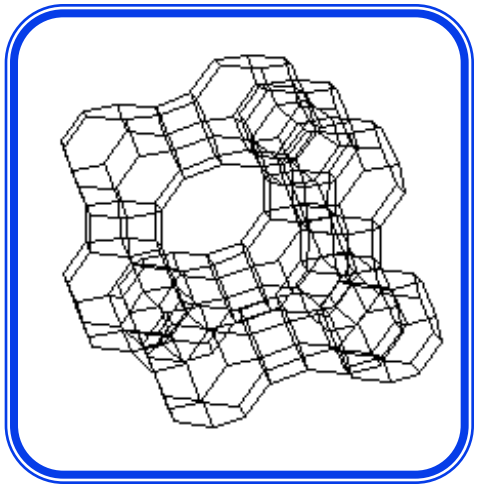
Objectives

- Examine photophysical properties of 1-azax in NaY
- Examine photochemical reactivity of 1-azax with good H and electron donors co-included in NaY
- Determine whether 1-azax is a convenient probe for radical reactions in NaY

Why use 1-azaxanthone as a probe for radical reactions?

Initial studies on the reactivity of 1-azax in organic solvents revealed that it is even better than benzophenone in H abstraction reactions. It is also structurally similar to xanthone, which is used as a polarity probe in hetergeneous systems. Thus if 1-azax also shows the same polarity dependence as xanthone, and is still able to photoreduce efficiently in heterogeneous systems, then it would be an ideal probe to study both polarity and radical reactions in heterogeneous systems such as zeolites.

Structure of NaY



Molecular Formula

$M_{56}(AlO_2)_{56}(SiO_2)_{136}H$ $2O_{253}$

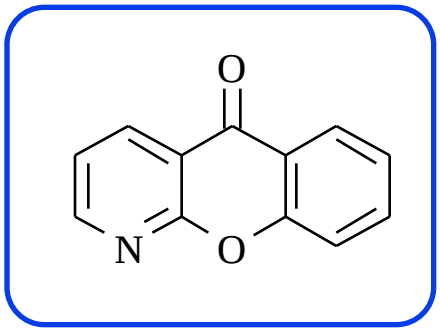
Si/Al = 2.4

Supercages diameter = 12 Å

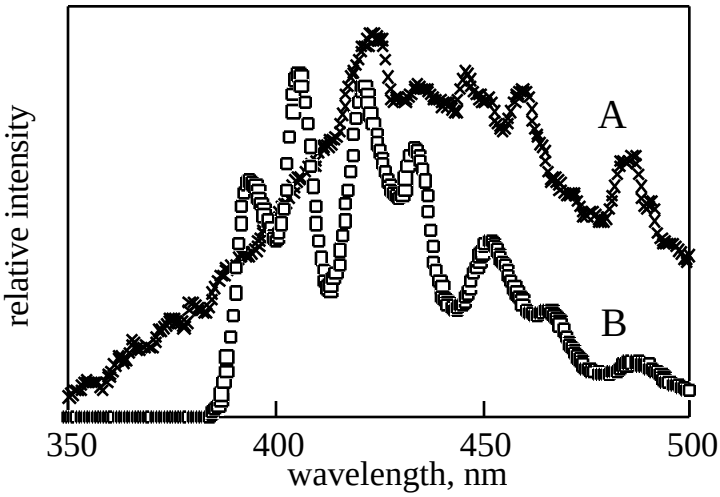
pores size = 7.4 Å

Some properties of 1-azax in solution

- more reactive than benzophenone in H-abstraction reactions (in organic solvents)
- switching from n,π* to π,π* when ε > 60
- small S-T gap (6 kcal / mol)

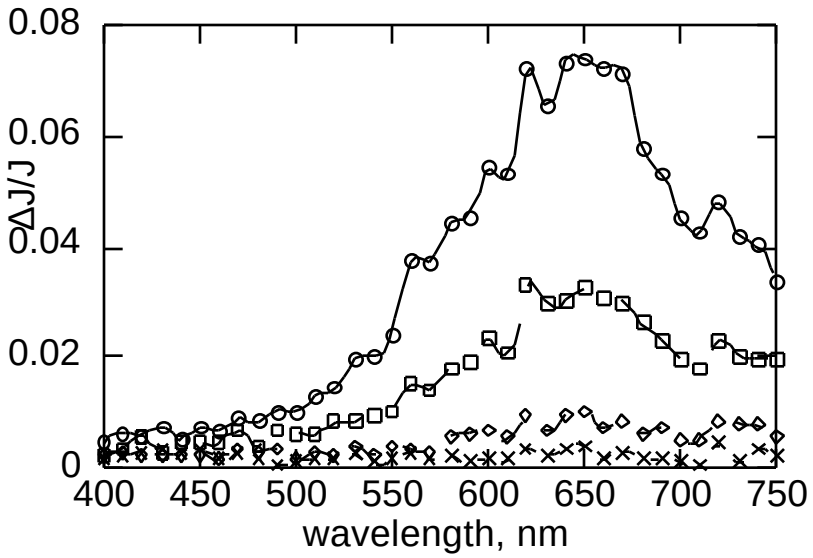


The similarity of the phosphorescence of 1-azax at low T and the emission that is detected for 1-azax in NaY leads to the conclusion that the emission in NaY is due to room T phosphorescence. There may also be contributions from fluorescence as well, given the small S-T energy gap.



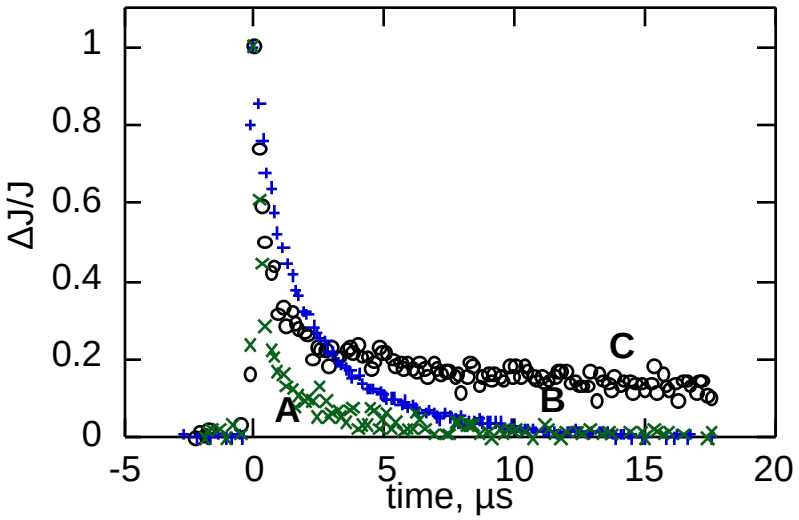
A = RT emssion from NaY
B = emission in EtOH / MeOH glass at 77 K

Transient absorption spectrum of 1-azax in NaY shows a triplet absorption at 660 nm. This will be the region that will be monitored when other organics are coincluded with 1-azax in NaY



0.72, 2.8, 7.92, 15.7 μs after laser pulse

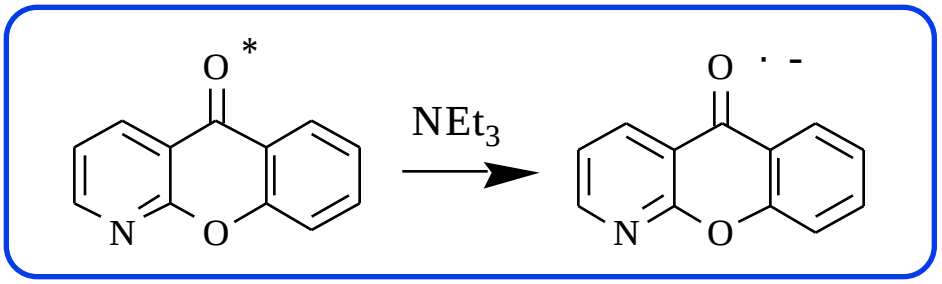
We wanted to see what the effect of NEt_3 addition on the decay kinetics of 1-azax in NaY would be, i.e. how efficiently the ketyl radical anion is formed



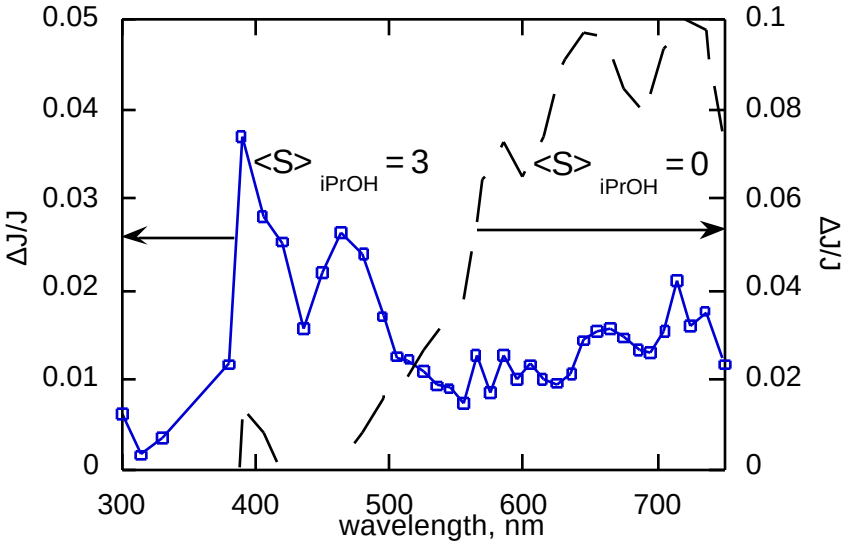
A = no NEt_3 added
B = 0.6 molecules of NEt_3 per supercage
C = 1.7 molecules of NEt_3 per supercage

λ_{mon} = 660 nm (where triplet 1-azax absorbs)

- small amounts of NEt_3 results in a significant increase of triplet lifetime of 1-azax, with no evidence of ketyl radical anion formation
- larger amounts of NEt_3 results in a residual absorption due to the formation of the ketyl radical anion



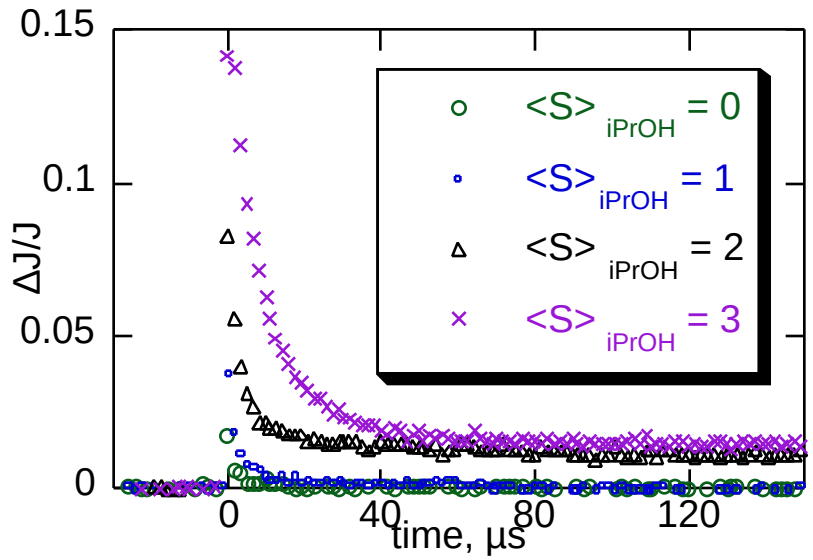
Effect of iPrOH addition on the transient absorption spectrum of 1-azax in NaY



<S> = # of molecules per supercage

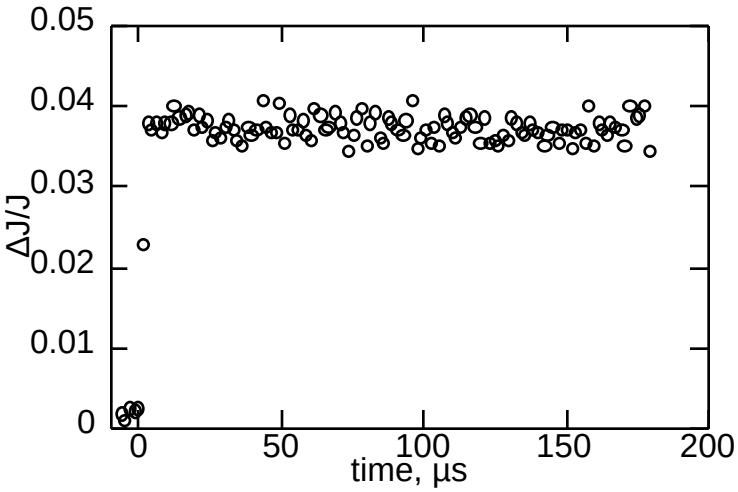
At large loadings of iPrOH, there is very little triplet left. We see two main peaks in the spectrum, one at 390 nm and the other at 480nm.

How do the triplet decay kinetics of 1-azax change when iPrOH is added? At high loadings, there is some residual being formed (the ketyl radical) but not as much as was initially expected, given the high reactivity of 1-azax towards H abstraction in organic solvents.



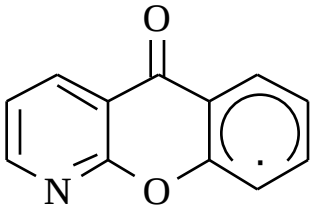
Why the small amount of ketyl radical formation?

When monitoring at 390 nm (one of the maxima in the spectrum) there is a large residual absorption. It is known that cyclohexadienyl-type radicals absorb in this region.

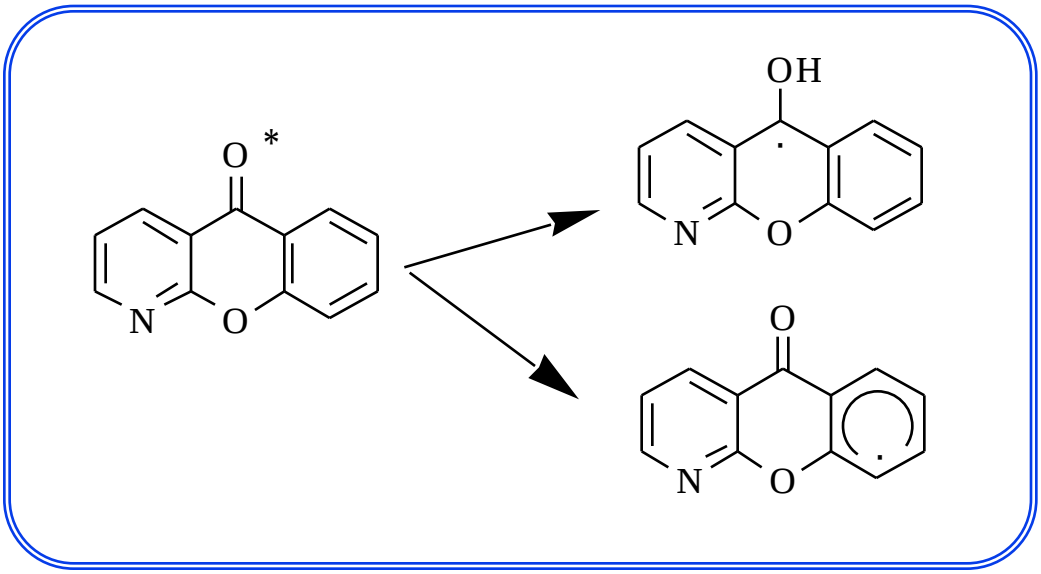


Sample of NaY / 1-azax containing 3 molecules of iPrOH / supercage

The residual absorption is thus assigned to the cyclohexadienyl radical of 1-azax



- The addition of iPrOH to 1-azax in NaY results in the formation of two radicals; ketyl and cyclohexadienyl radicals.



Comparison of the kinetics of the triplet upon inclusion of NEt_3 and iPrOH

When small amounts of $NEt_3$are added, there is a large increase in the triplet lifetime of 1-azaxanthone. No similar effects are seen with iPrOH. Based on our previous results that NaY contains acid sites, we conclude that initial amounts of NEt_3 act to quench the zeolite acid sites.

As more NEt_3/iPrOH is added, there is a gradual increase in the triplet lifetime of 1-azaxanthone. Thus, as the most accessible triplets become quenched, the ones that remain are more protected andas a result become longer lived

Conclusions

① Small amounts of NEt_3 neutralizes the acid sites present in NaY, which leads to the significant increase in triplet lifetime

② Larger amounts of NEt_3 or iPrOH quenches the most accessible triplets: the triplets that survive become longer lived

③ 1-Azaxanthone may not be the ideal radical probe for NaY since it forms other transients (in the case of H donors) and is sensitive to the mild acid sites located in the zeolite