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Persistent carbocations from 4,4′-dimethylaminodiphenylethylenes within CaY zeolite: intrazeolite-water controls the structure of the carbocation

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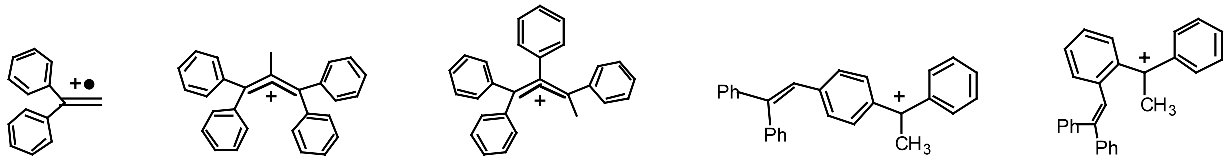
Abstract—Inclusion of 4,4′-dimethylaminodiphenylethylene and related olefins within activated CaY results in the formation of persistent monomer carbocations. The structure of the cation, consequently the color of the zeolite, is controlled by water molecules present within zeolites. Under 'dry' conditions the zeolite is light yellow and under 'wet' conditions it is blue colored. Blue color results from the quininoidal structure adopted by 1,1-bis-(4-dimethylaminophenyl)ethyl cation through participation of the lone pair electrons present on the amino substituent at the para position. © 2003 Elsevier Science Ltd. All rights reserved.

1,1-Diphenylethylene in acidic media such as acetic acid, silica gel and HY zeolites generates a green color with absorption maxima at ~410 and ~620 nm.[1–3] Although the shorter wavelength absorption has been identified to be due to 1,1-diphenylethyl cation, no consensus has been reached regarding the species responsible for the longer wavelength absorption. In a publication in 1997, we attributed the blue color (λ_{max} ~ 610 nm) that persisted for several days after washing the 1,1-diphenylethylene included CaY zeolite to the radical cation of 1,1-diphenylethylene **1**.[4] However, our transient studies later revealed that 1,1-diphenylethylene radical cation absorbs at ~400 nm and has no absorption at ~610 nm.[5] Currently, the conjugated dimeric cations **2**–**4** (Scheme 1) are suspected to be the species responsible for the persistent blue color.[3,5–7] Similar to 1,1-diphenylethylene, 4,4′-disubstituted (fluoro, chloro, methyl and methoxy) 1,1-diarylethylenes upon inclusion within CaY gave persistent colors[7] suggesting that the structure **4** suggested by Rooney[3d] should include a vinylene unit attached at the *ortho* position as well (structure **5**, Scheme 1). The colors generated by the above olefins were permanent and not reversible. However, 4,4′-dimethylamino-1,1-diphenylethylenes **6**–**8** (Scheme 2) were unique in their behavior. These olefins upon inclusion within activated CaY showed different colors (pale yellow versus blue) depending on the humidity conditions of the laboratory. We had originally attributed the absorption in the visible region (~620 nm) to 4,4′-dimethylaminodiphenylethylene radical cation.[4] Prompted by the transient results on 1,1-diphenylethylene[5] we have reexamined the systems **6**–**8** and the results presented here



1 2 3 4 5

Scheme 1.

Keywords: carbocation; zeolite; diarylethylenes.

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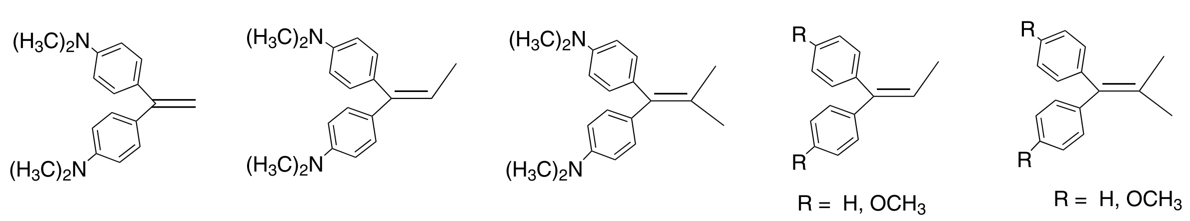


6 **7** **8** **9** **10**

Scheme 2.

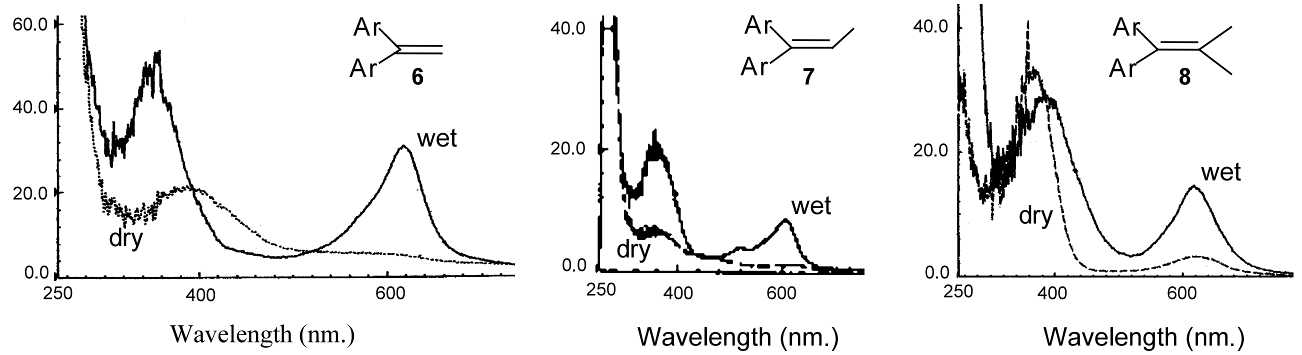
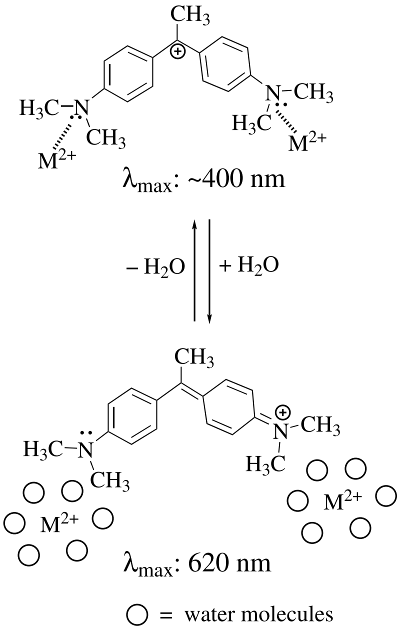


Figure 1. Diffuse reflectance spectra of 4,4′-dimethylamino-1,1-diphenylethylenes **6**–**8** under dry and wet conditions. Note that under 'dry' conditions the long wavelength absorption is weak.

suggest that the visible color is likely to be due to the carbocation of quininoidal structure.[8]

Upon stirring the olefins **6**–**8** (5 mg) with activated CaY (300 mg) in hexane under dry conditions gave a light yellow solid. As shown in Figure 1 the diffuse reflectance spectrum of the dry sample of 4,4′-dimethylamino-1,1-diphenylethylene–CaY consisted of an absorption mainly in the 400 nm region. Similar absorptions were earlier reported in the case of 1,1-diphenylethylene as well as eight other related olefins included in CaY.[7] The absorptions in the 400 nm region in all these cases were attributed to the corresponding monomer cations. On this basis one would expect the absorption recorded in the case of dry samples of 4,4′-dimethylamino-1,1-diphenylethylene included CaY also to be due to the corresponding monomer cation. In the case of 1,1-diphenylethylene and 4,4′-disubstituted (fluoro, chloro, methyl and methoxy) 1,1-diarylethylenes a longer wavelength absorption (>600 nm) grew in intensity with time and upon extraction with either diethyl ether or tetrahydrofuran the blue color was retained by the zeolite. However, no such change in absorption spectrum occurred in the case of 4,4′-dimethylamino-1,1-diphenylethylene–CaY samples. The dry samples, those that have been washed with diethyl ether or tetrahydrofuran, remained light yellow colored. Surprisingly, when 4,4′-dimethylamino-1,1-diphenylethylenes **6**–**8** included CaY samples were exposed to ambient laboratory conditions, they turned blue in color and showed absorptions in the >600 nm region (Fig. 1) and as discussed below this color disappears once the sample is dried on a vacuum line.

Although it is tempting to assign the longer wavelength absorption of 4,4′-dimethylamino-1,1-diphenylethylene included CaY sample to the dimer cation of structures similar to **2**–**5**, we believe that this is unlikely to be the case. In order to form the persistent dimer cations of the structure **2**–**5**, the olefin must contain two terminal hydrogens. For this reason, methyl capped diarylethylenes **9** and **10** (R = H and OCH_3) did not yield the dimer cations and did not become blue within CaY.[7] On this basis, one would not expect methyl capped dimethylamino substituted olefins **7** and **8** to yield the corresponding dimer cations **2**–**5**. Therefore, the species responsible for the >600 nm absorption in the case of 4,4′-dimethylamino-1,1-diphenylethylene and related methyl capped olefins **7** and **8** included CaY samples must have different structures from the ones listed in Scheme 1. Fortunately a clue to the structure of the species was found in the literature, where Mischler's hydrol blue (i.e. 1,1-bis-(4-dimethylaminophenyl)methyl cation) under acidic conditions was reported to give the same blue color (610 nm) as compound **6** did in CaY.[8] Barker and his co-workers have suggested that the absorption in the 600 nm region is due to the monomer cation present in the quininoid form (Scheme 3).[8] Similar observations have been made with 4,4′-dimethylamino substituted triarylmethyl cationic dyes.[9] Based on literature precedence we suggest that the long wavelength absorption in the case of 4,4′-dimethylamino-1,1-diphenylethylene included in CaY (exposed to ambient conditions) must be due to the monomer cation present in the quininoid form.



Scheme 3.

Since the blue color (the 620 nm absorption) in the case of the olefins **6**–**8** included in CaY resulted only when the sample was kept under laboratory conditions, we carefully examined which one of the three—nitrogen, oxygen or water—present in the atmosphere is responsible for the color. A dried sample of olefin **6** in CaY was placed in a dry box under nitrogen atmosphere. The sample remained light yellow as long as it was left in the dry box. Next the sample was transferred to a dessicator under dry conditions and continuously purged with oxygen. During this time the sample remained light yellow. Continuous purging with nitrogen also did not result in coloration of the zeolite sample. When the sample was taken out of the dessicator and left on top of a workbench it turned blue in a few minutes. These observations led to the conclusion that neither nitrogen nor oxygen but water in the atmosphere was responsible for the generation of this colored species. The above experiments were repeated for olefins **7** and **8** with the same results.

The above assignment of the quininoid structure for the long wavelength absorbing species is consistent with the observed effect of water on the absorption spectra. Under ambient laboratory conditions the zeolite would be expected to have water molecules present within the cages and the Ca^{2+} and H^+ ions would be solvated by these molecules. However, when the zeolite is dried/degassed on a vacuum line, the Ca^{2+} ions would become free and co-ordinate with the lone pairs of the 4,4′-dimethylamino group. Thus under 'dry' conditions due to absence of conjugation between the amino nitrogen lone pair and the cationic center, the 4,4′-dimethylaminodiphenyl ethyl cation would have non-quininoidal structure and would absorb at ~400 nm. The parent diphenyl ethyl cation is reported to have an absorption maximum at 425 nm.[10] In this system substitution with an electron donor group such as methoxy at the *para* positions shifts the absorption to near 500 nm. In our case, interaction of the dimethyl amino groups at the *para* positions with the Ca^{2+} makes them highly electron withdrawing groups. Observed blue (400 nm) instead of red shift is consistent with the expectation that electron withdrawing groups at the *para* position would shift the absorption maximum to the blue of 425 nm. Under 'wet' conditions the cationic center would be stabilized via conjugation with the lone pair of 4,4′-dimethylamino group resulting in longer wavelength absorption. This cation-controlled process is schematically illustrated in Scheme 3. The fact that the process could be reversed suggests that the 1,1-bis-(4-dimethylaminophenyl)ethyl cation once formed is stable within a zeolite. The visible color change easily detected by human eyes could even serve as an indicator of the 'dryness' of a zeolite.

We believe that upon inclusion of 4,4′-dimethylamino-1,1-diphenylethylenes within activated CaY a proton rather than an electron transfer process takes place. The carbocations thus generated are persistent within CaY. The ability of the amino group to stabilize the cationic center is determined by the presence of water within the cages of a zeolite. Generation of persistent carbocations upon inclusion of aryl alkenes within acidic zeolites is general and one needs to be careful in using such zeolites for photochemical studies.[11,12] We have shown earlier that aggregation of dye molecules such as thionin, excimer formation of molecules such as pyrene and naphthalene, the reactive state of carbonyl compounds such as acetophenone and cyclohexenone and the enantio and diastereoselectivity in photochemical reactions are influenced by intrazeolite water molecules.[13] In the current study we have provided an example in which the structure of a carbocation is controlled by intrazeolite water molecules.

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