

Characterization of Persistent Intermediates Generated upon Inclusion of 1,1-Diarylethylenes within CaY Zeolite: Spectroscopy and Product Studies

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Inclusion of 1,1-diarylethylenes within activated CaY results in the formation of colored samples that are stable for prolonged periods. For example, diphenylethylene generates a green color within CaY. Two reactive intermediates have been shown to be responsible for this color. The species with the short wavelength (λ_{max} 410 nm) absorption has been established to be the diphenylmethyl cation. The identity of the species with the long wavelength (λ_{max} 620 nm) absorption has been debated for three decades. We establish that the diarylethylene radical cation is not responsible for the long wavelength absorption. Laser flash photolysis studies show that a number of diarylethylene radical cations have a characteristic absorption in the 400 nm region in both solution and in NaY zeolite. The absence of this absorption for diarylethylene-CaY samples unequivocally eliminates the possibility that these radical cations are responsible for color formation. This is substantiated by the fact that a number of 2-methyl-substituted 1,1-diarylethylenes generate only the short wavelength cation absorption upon inclusion in CaY; radical cation formation would be expected to be equally facile for the methyl-substituted derivatives. Our results suggest that an allylic dimer cation is the most likely source of the long wavelength (λ_{max} 620 nm) absorption within CaY.

Introduction

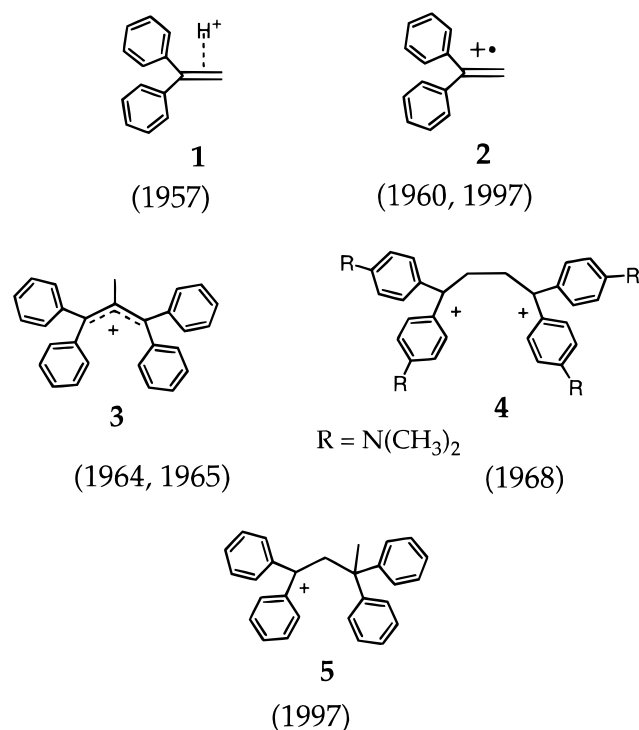
In the past most photochemistry in zeolites has focused on reactions of carbonyl compounds.¹ The extension of these studies to olefinic systems has demonstrated the complexity of zeolites as reaction media.² The chemistry is complicated by both proton and electron-transfer processes in which the zeolites themselves participate. Monovalent and divalent cation exchanged X and Y zeolites do not, generally, contain Brønsted acid sites.³ However, activation of the zeolite can generate acid sites that influence the chemistry of included substrates.⁴ The number of Brønsted acid sites that are generated depends on the cation. For example, activated monovalent cation exchanged Y zeolites contain one acidic site (H^+) per 16 supercages, a relatively small number,⁵ whereas, activated divalent cation exchanged Y zeolites are substantially more acidic with two acidic sites per supercage.⁶ Zeolites also contain Lewis acid sites that include the tricoordinated aluminum sites on the framework, the extra lattice aluminum sites and the charge compensating cations.⁷ The nature, number and strength of Lewis acid sites are less well characterized than are the Brønsted acid sites. Thus the activated, cation-exchanged zeolite, in principle, can serve both as a proton source and as an electron sink (as well as an electron source).⁸

Inclusion of olefins such as indene and vinyl anisole within activated divalent cation and H^+ exchanged zeolites often gives rise to long-lived colored intermediates.⁹ Such intermediates are characterized by their absorption and ESR spectra. Since zeolites can serve as both an electron sink and a proton source, radical cations and carbocations or species resulting from them are often suggested as candidates for the color. The availability of absorption spectral data for radical cations and carbocations of the olefin in question frequently helps to distinguish between

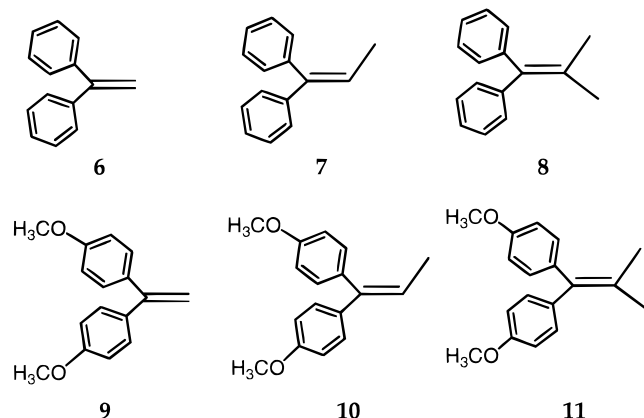
the possibilities. For example, literature data on the absorption spectra for radical cations of vinyl anisole and indene were used to establish that these species were not responsible for the color produced when the precursor olefins were included in zeolites.^{9,10} On the other hand, the origin of the bright color that appears when diphenylethylene is included within zeolites or adsorbed on silica–alumina surfaces has been the subject of controversy for over three decades.^{11–16} The green color that develops upon inclusion of diphenylethylene within CaY and HY is the same as that produced by treatment of diphenylethylene with strong Brønsted or Lewis acids.¹⁷ It has been established that the green color is a combination of yellow (λ_{max} 432 nm) and blue (λ_{max} 615 nm) colors resulting from two independent species. While the 430 nm species has been conclusively identified as the methyl diphenyl carbonium ion by comparison with solution spectra,¹⁸ the origin of the latter is still debated. A number of suggestions have been made to explain the color produced upon addition of diphenylethylene to zeolites and silica/alumina (Scheme 1).^{11–16} We address in this article the question of the nature of the species responsible for the blue color (615 nm absorption) produced when diphenylethylene is included within activated divalent cation exchanged zeolites.

An authentic spectrum of the diphenylethylene radical cation in solution and in a zeolite should in principle help to resolve the above discrepancies. Although a number of groups have reported absorption characteristics of diarylethylene radical cations in glasses at low temperature and in solution, there are a number of inconsistencies in the reported data.^{14,19,20} For example, attempted generation of diphenylethylene radical cation by either γ -irradiation in an organic glass or by pulse radiolysis at low-temperature results in one or more species with λ_{max} at 390, 500–550 and 1200 nm.^{19a–c} It has been suggested that

SCHEME 1



SCHEME 2



the 390 and 520 nm peaks are due to the dimer radical cation^{19a} while the 550 and 1200 nm bands are assigned to the monomer radical cation.^{19b} Later studies suggested that both monomer and dimer absorb in the 390 and 500 nm regions.^{19d,e} The rapid addition of the radical cation to its precursor makes it even more difficult to provide an unambiguous spectrum for the diphenylethylene radical cation in solution at room temperature. Similarly the radical cation of 1,1-di-(4-methoxyphenyl) ethylene has been reported to absorb at 330, 390 and 580 nm in a 1-chlorobutane glass.^{19e} Attempted generation of this radical cation and its 2-methyl substituted analogue by pulse radiolysis is reported to give a 400 nm maximum in dichloromethane,^{20a,b} whereas the 2,2-dimethyl analogue generated by photosensitized electron transfer has a reported λ_{max} value of 760–800 nm.^{20c} Given the difficulty in distinguishing between monomer and dimer radical cations for the 1,1-diarylethylenes, we undertook experiments aimed at characterizing the radical cations of the terminal methyl substituted analogues (7, 8, 10, and 11 in Scheme 2), for which formation of dimeric species is expected to be substantially slower. These studies indicate that the colored species that is formed upon inclusion of diphenylethylene into

CaY is not diphenylethylene radical cation. This led us to carry out additional experiments aimed at characterizing the colored species produced by inclusion of a series of diarylethylenes (Scheme 2) in CaY and these are also presented herein.

Experimental Section

Preparation of CaY. NaY (Aldrich, 10 gm) was added to 200 mL of a 10% Ca(NO₃)₂ solution and the slurry was stirred at 80 °C overnight. The slurry was filtered and the zeolite washed thoroughly with at least two liters of distilled water. The above exchange procedure was repeated at least four times. The zeolite obtained after the wash was then dried at room temperature in air. ICP analysis indicated a composition corresponding to Si_{138.7}Al_{53.3}Na_{7.5}Ca_{23.3}O₃₈₄.

Preparation of 1,1-Diarylethylenes. 1,1-Diphenylethylene (6, Aldrich) was used without further purification. All other olefins (7–11) were prepared from the corresponding ketones by a Grignard reaction followed by dehydration. The standard procedure adopted is described below: One equivalent of ketone was taken in dry diethyl ether under nitrogen atmosphere. To this, 1.5 equivalent of methylmagnesiumbromide (3M in ether) was added and the solution was stirred for 1 h. The ether solution was then quenched with 0.1% aqueous HCl. The organic portion was extracted into ether and concentrated. The alcohol thus obtained was dehydrated by refluxing in 30 mL of benzene with a catalytic amount of *p*-toluenesulfonic acid. The product was purified by column chromatography by using petroleum ether/dichloromethane as the eluant.

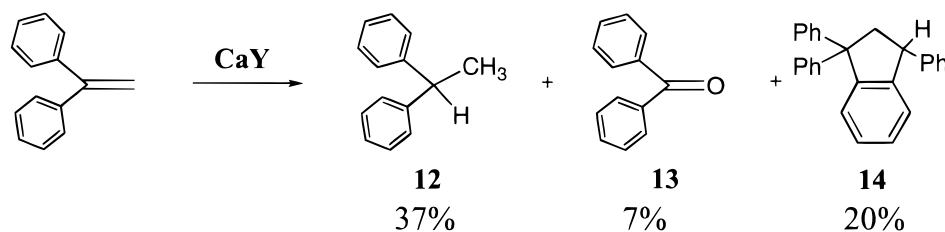
Activation of Zeolites for the Product Studies. A known amount of zeolite was placed in a porcelain crucible in a preheated oven (500 °C) and activated in air for approximately 10 hours.

Inclusion of Olefins in Zeolites. The activated zeolite was cooled to room temperature and added to a hexane solution of the olefin (typically 20 mg of olefin for 300 mg of zeolite; hexane 5 mL) and stirred for 3 h. The products were extracted from the zeolite by stirring the zeolite overnight with either dichloromethane or tetrahydrofuran. Products were analyzed by GC (Hewlett-Packard 5890; SE–30 capillary column). For identification purposes, the products were isolated by flash chromatography and characterized by NMR and GCMS. A similar procedure was used for inclusion of diarylethylenes (with or without sensitizer) in NaX or NaY zeolites for flash photolysis measurements.

Large Scale Product Studies. About 10 g of activated CaY was brought to room temperature and added to a 50 mL solution of cyclohexane containing 1 gm of diarylethylene. The solution was stirred at room temperature under laboratory conditions for 10 h. The green colored zeolite collected by decanting the cyclohexane solution was extracted by stirring with 50 mL methylene chloride. The once extracted zeolite was re-extracted with methanol by Soxhlet extraction (24 h). Finally any remaining products were extracted by dissolving the zeolite with dilute HCl. The zeolite that had been extracted with methanol was treated with 2 mL of HCl and extracted with methanol by Soxhlet extraction (24 h). Products collected during each extraction process were analyzed by GC and GC-MS and characterized by NMR.

Diffuse Reflectance Spectra. Diffuse reflectance spectra were recorded by packing the sample in a 1 mm quartz cell. The background correction was done by recording a spectrum of BaSO₄ in the same cell. The recorded spectrum for the sample was converted into Kubelka Munk by the program supplied with the instrument (Shimadzu Model 2101 PC).

SCHEME 3



Laser Flash Photolysis in Solution and in Zeolites. The laser flash photolysis system used for both transmission and diffuse reflectance studies has been described previously.²¹ For these experiments either a Lumonics HY750 Nd:YAG laser (266 or 355 nm; 10 ns/pulse; < 30 mJ/pulse) or a Lumonics EX-530 excimer laser (XeCl, 308 nm, 6 ns/pulse; < 30 mJ/pulse) was used for sample excitation. Samples for solution experiments were contained in 7×7 mm² quartz cells (flow cells for most experiments and for all spectra) and samples were purged with either oxygen or nitrogen prior to laser irradiation. For the zeolite experiments, the samples were contained in 3×7 mm² quartz cells and were also purged with either nitrogen or oxygen immediately prior to laser irradiation. The samples were moved in the cell holder and shaken frequently in order to provide fresh zeolite surface and minimize complications due to product formation.

Results

Two strategies were employed to distinguish between the radical cations and dimeric cations as the species responsible for the blue color produced upon inclusion of diphenylethylene in CaY zeolite. In one, the chemical and spectral behavior of a series of capped diarylethylenes (Scheme 2) that are less likely to dimerize was investigated. Product studies, and ground-state UV–visible spectra for the various diarylethylenes in CaY zeolite are reported below. In the second approach, the absorption spectra of a series of diarylethylene radical cations were recorded in both solution and in NaX and NaY zeolites by employing nanosecond laser flash photolysis. Diarylethylenes **6**–**11** do not produce colored samples in the sodium exchanged zeolites, making these appropriate models for the generation of zeolite stabilized radical cations for comparison purposes.

Product Studies. The addition of activated CaY to a solution of diphenylethylene in cyclohexane gave a yellow slurry that slowly (~10 min) turned dark green and remained. Following stirring overnight the zeolite was subjected to a series of consecutive extractions: (1) dichloromethane, (2) methanol, and (3) methanol/HCl. While the first two conditions allow the extraction of molecules with diameters <10 Å from the supercage, the latter permit all molecules to be removed from the zeolite interior. Since several prior suggestions for the colored species involve cations of dimeric structure, (**3**, **4** and **5**) we looked for precursors and products of these carbocations. Careful analysis of the product mixture confirmed their absence. The products diphenyl ethane, benzophenone and an indane were isolated in about 70% yield (Scheme 3). Studies carried out with 1,1-bis (4-methoxyphenyl) ethylene (**9**) gave a similar product distribution. Inclusion of olefins **7**, **8**, **10** and **11** in CaY gave only the reduced alkanes.

Spectral Characterization. Diffuse reflectance spectra of CaY included with olefins **6**–**11** were recorded. Inclusion of diphenylethylene in CaY yielded a green sample with two absorption maxima, 432 and 615 nm. After extraction with dichloromethane the zeolite was still colored with a single

absorption maximum at 615 nm. Similar observations were made in the case of 1,1-bis (4-methoxyphenyl) ethylene, **9**, (486 and 680 nm peaks). The intermediates that are responsible for the 432 and 486 nm absorptions are believed to be diarylmethyl cations, by analogy with the known solution spectra for these species¹⁶ and these short wavelength absorptions will not be discussed further.

The time dependent diffuse reflectance spectra of **6** included within CaY are presented in Figure 1. At early times, the absorption due to the monomer cation (432 nm) dominates the spectrum. With time, the longer wavelength absorption grows at the expense of the monomer cation peak. However, the monomer cation cannot be completely converted to the long wavelength absorbing species. As indicated above extraction with methanol or methylene chloride completely removes the monomer cation leaving the long wavelength absorbing species in the zeolite. These observations are consistent with the possibility of a dimeric structure being responsible for the long wavelength absorption. This hypothesis was further explored by examining the methyl-substituted 1,1-diarylethylenes **7**, **8**, **10** and **11**. Diffuse reflectance spectra recorded upon inclusion of olefins **9**–**11** within CaY are provided in Figure 2. Only the uncapped 1,1-bis (4-methoxyphenyl) ethylene gave both the short and the long wavelength absorbing species. The addition of one or two methyl groups at the 2-position led to only modest shifts in the absorption of the monomer cation. A similar observation was made with the olefins **6**–**8**.

Garcia et al. based on semiempirical calculations (ZINDO) suggested that cation **5** might absorb in the visible region.¹⁴ To probe this possibility we synthesized the precursor olefin **15** and the alcohol **16** and included them within activated HY (Scheme 4). As soon as olefin **15** was included into HY, the zeolite turned yellow and showed an absorption band with a maximum at 430 nm. With time the zeolite turned green and showed a new absorption in the region above 580 nm. In about 24 h the short wavelength absorption completely gave rise to the long wavelength band.

Generation of 1,1-Diarylethylene Radical Cations in Solution. Radical cations of the methyl substituted diarylethylenes (**7**, **8**, **10**, **11**) were generated by photoinduced electron transfer (PET) using three different sensitizers that have been extensively used for generation of arylalkene radical cations, as well as by photoionization of the diarylalkene.^{22,23} Typical results obtained are illustrated in Figures 3–5. Figure 3 (top) shows results obtained upon selective excitation (355 nm) of chloranil in the presence 2.5 mM **7** in nitrogen-purged acetonitrile. A shoulder due to triplet chloranil is still visible in the first time window; triplet quenching leads to two new transients, the chloranil radical anion at 450 and 340 nm and a second species with λ_{max} at 390 nm and a weak absorption beyond 700 nm. The 390-nm transient disappears upon addition of 3.5 mM tetramethylammonium bromide. The same species is generated by 355 nm excitation of 9,10-dicyanoanthracene in the presence of 0.2 M biphenyl as cosensitizer and 5 mM **7** in oxygen-saturated

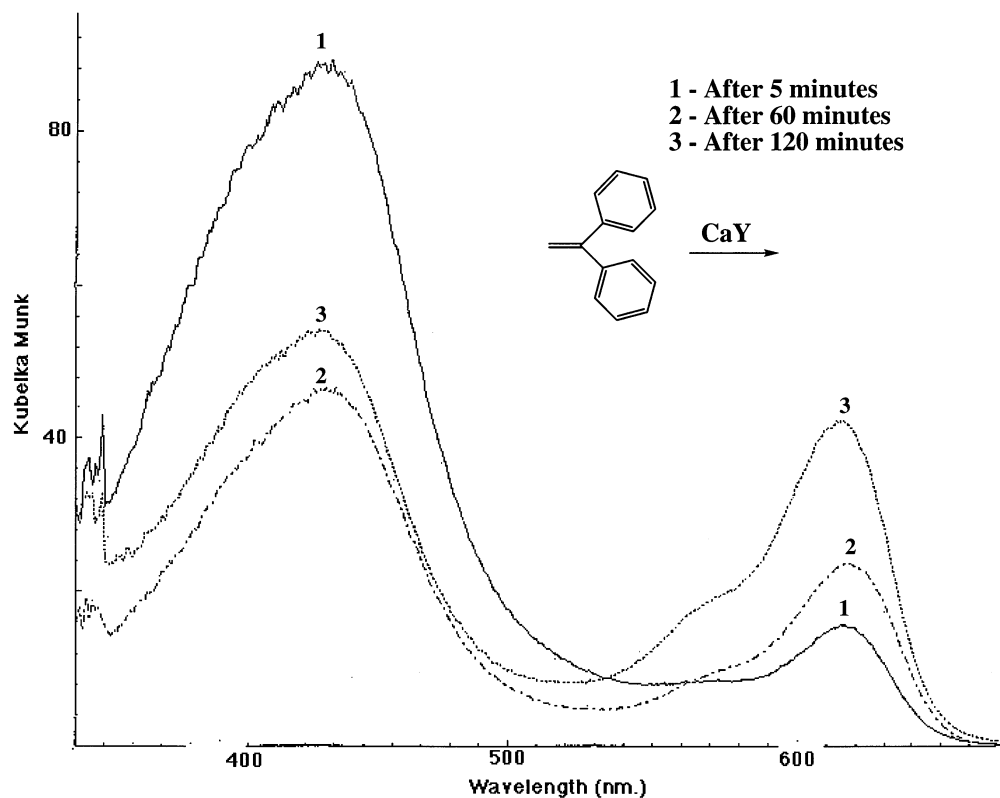


Figure 1. Time evolution of the diffuse reflectance spectra of diphenyl ethylene included within activated CaY. Note the decrease in intensity of the absorption at 430 nm and increase in absorption above 600 nm with time.

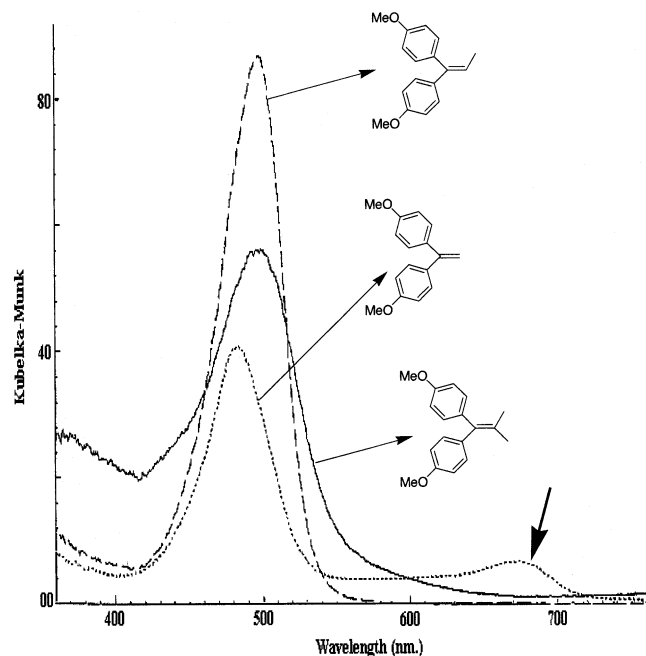


Figure 2. Diffuse reflectance spectra of *p,p'*-dimethoxy diphenylethylenes **9**–**11** included within activated CaY. Note the absence of absorption above 600 nm in the case of **10** and **11**.

acetonitrile. In this case the excited 9,10-dicyanoanthracene singlet reacts exclusively with biphenyl to generate biphenyl radical cation which then oxidizes **7**. The use of either triplet chloranil or 9,10-dicyanoanthracene/biphenyl as sensitizer in the presence of **8** gives very similar results; spectra using the latter sensitizer are shown in Figure 3 (bottom) and show that **8**⁺ has λ_{max} at 410 nm and an additional long wavelength absorption (> 660 nm). Note that the 9,10-dicyanoanthracene radical anion is scavenged by oxygen, resulting in a cleaner spectrum than is

obtained using triplet chloranil. The 390 and 410 nm transients observed upon photosensitized electron transfer for **7** and **8** are assigned to the respective radical cations on the basis of their reactivity toward bromide ion and insensitivity to oxygen.

The generation of radical cations from the methoxy-substituted diarylethylenes **10** and **11** gave somewhat different results from those described above. For example, 355 nm excitation of a solution of chloranil plus 2.5 mM **10** generated the chloranil radical anion as well as additional transient(s) with λ_{max} at 400 and 600 nm. The spectrum obtained using 9,10-dicyanoanthracene/biphenyl also showed both 400 and 600 nm signals, without the added complication of signals due to long-lived radical anions (Figure 4, top). The decay kinetics at 400 and 600 nm were identical and were unaffected by a 10-fold variation in [**10**] (1.3–13 mM). These results suggest that the two absorptions belong to a single transient. To further confirm this, decay kinetics at the 2 wavelengths were measured in the presence of 0.23 mM bromide ion. The signals at both 600 and 400 nm decayed more rapidly in the presence of bromide ion and with similar kinetics, although there are small contributions due to a long-lived residual at 400 nm and a spike due to radical anion at 600 nm. The results of the sensitized experiments indicate that **10**⁺ has two well-defined absorption bands in the UV–visible range. A similar set of experiments show that **11**⁺ has λ_{max} at 420 and 630 nm, demonstrating that the addition of a second methyl group has little effect on the spectrum of the radical cation.²³

Direct 266 nm excitation of the same diarylethylenes was also examined as a source of radical cations. Both **7** and **8** provided evidence for only a small amount of radical cation in the 400 nm region with additional oxygen-sensitive signals between 340 and 400 nm. By contrast, considerably stronger signals were obtained by direct 266 nm excitation of **10**. As shown in Figure 4 (bottom), direct excitation of **10** in oxygen-

SCHEME 4

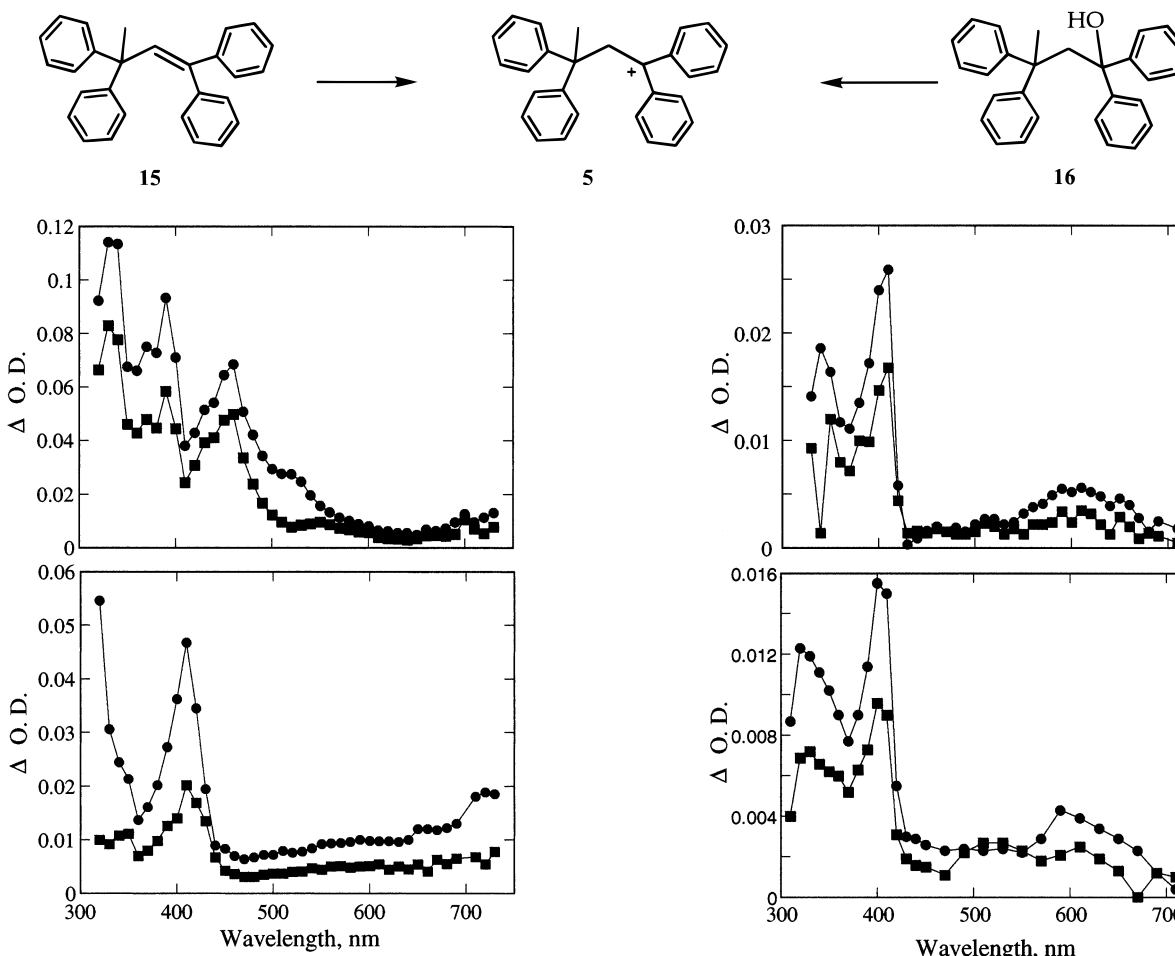


Figure 3. (top) Transient absorption spectra measured 0.3 (●) and 0.7 (■) μ s after 355 nm laser excitation of chloranil in the presence of 2.5 mM **7** in nitrogen-saturated acetonitrile. (bottom) Transient spectra measured 0.4 (●) and 1.8 (■) μ s after 355 nm excitation of 9,10-dicyanoanthracene in the presence of 0.2 M biphenyl and 4.9 mM **8** in oxygen-saturated acetonitrile.

saturated acetonitrile gives the same 390/600 nm species observed in the sensitized experiments, as well as an additional weak absorption at 520 nm. There are also some differences in the 350 nm region from the spectra shown in Figure 4 (top); these may be due to contributions from sensitizer bleaching in the latter case. The decay kinetics at 390 and 600 nm were measured in the presence of several concentrations of bromide ion. In all cases the kinetic traces at the two wavelengths overlap very well, confirming that the two bands are due to a single species, 10^{+} , in agreement with results obtained by PET. A rate constant of $2.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ was obtained from the slope of a combined plot of the decay kinetics at both 400 and 600 nm as a function of bromide ion concentration. The 520 nm signal decays more slowly than the radical cation, and its decay is slightly enhanced in oxygen-purged solution as compared to nitrogen. There is also additional absorption at short wavelengths in the latter case. Based on literature data, it is likely that the 520 nm species arises from addition of 10^{+} to its precursor to give a dimer radical cation.²⁰ Direct excitation of **11** also generates radical cation, although the signals are weaker than those from **10** and there is little evidence for an additional absorption in the 500 nm region.

Literature reports indicate that detection of radical cations from **6** and **9** is complicated by their rapid addition to the

Figure 4. (top) Transient absorption spectra measured 0.4 (●) and 1.8 (■) μ s after 355 nm excitation of 9,10-dicyanoanthracene in the presence of 0.2 M biphenyl and 5.3 mM **10** in oxygen-saturated acetonitrile. (bottom) Spectra measured 0.9 (●) and 2 (■) μ s after 266 nm laser excitation of **10** in oxygen-saturated acetonitrile.

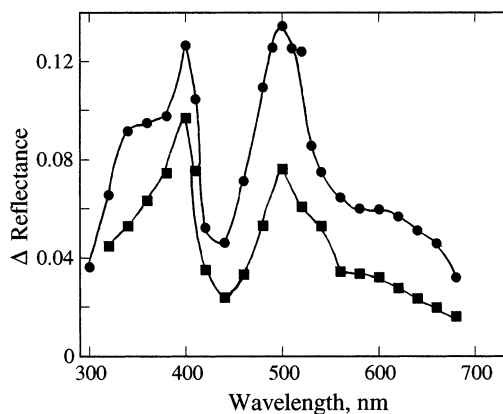


Figure 5. Transient spectra measured following 266 nm excitation of a nitrogen- (●) and oxygen-saturated (■) sample of **10** (150 μ mol/g) included in NaY zeolite.

precursor alkene.^{19,20} Nevertheless, we attempted to generate 6^{+} using the same sensitizers used for the other diarylethylenes. A transient species with λ_{max} at 340 nm and a shoulder at approximately 400 nm was readily detected using *N*-methylquinolinium/toluene as sensitizer. However, the decay of this species was not affected by the concentration of **6** and it is unlikely to be the monomer radical cation, although its reactivity toward nucleophiles is consistent with cationic character.

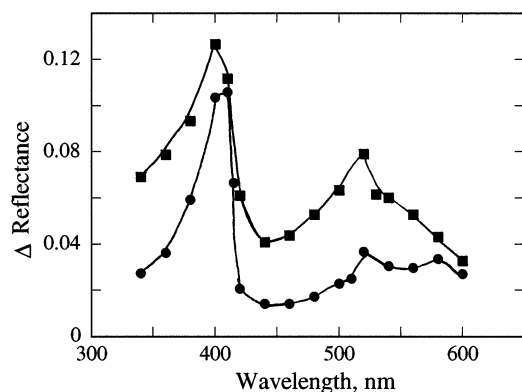


Figure 6. Transient spectra measured after 308 nm excitation of **10** in NaY: (●) 50 $\mu\text{mol/g}$; (■) 200 $\mu\text{mol/g}$.

Generation of 1,1-Diarylethylene Radical Cations in Zeolites. Attempts to generate the diarylalkene radical cations in NaX and NaY zeolites focused on **10** since its radical cation can be easily produced by both photoionization and photosensitization in solution. Direct excitation of **10** in NaY at either 266 or 308 nm gave a transient spectrum with λ_{max} values at 400 and 500 nm (Figure 5). There is also a weaker band between 550 and 650 nm. In some samples of **10** in NaY spectra under nitrogen show additional strong signals with λ_{max} at approximately 550 nm, consistent with the formation of trapped electrons, Na_4^{3+} .^{9e,24} The trapped electron can be efficiently removed by purging the sample with oxygen; the somewhat variable yield of this species is probably related to the water content of the zeolite. Previous studies have shown in the presence of water that the trapped electron exists as hydrated electrons that absorb at longer wavelengths (>700 nm).²⁵ Direct excitation of **10** in NaX under nitrogen gives transient spectra that are dominated by the formation of Na_4^{3+} . However, purging the sample with oxygen removes the latter signal, leaving the same 400 and 500 nm absorptions that are observed in NaY.

$\mathbf{10}^+$ was also produced by photosensitization using 2,3-dicyanonaphthalene which we have previously found to be a useful sensitizer for generating arylalkene radical cations in zeolites.²⁶ Excitation of the sensitizer at 355 nm in the presence of **10** in NaY under oxygen gives a similar spectrum to that shown in Figure 5, with bands at 400 and 500 nm of comparable intensity. Under nitrogen the same sample gives a substantial signal due to Na_4^{3+} in the 500–600 nm region; this presumably results from photoionization of the sensitizer in competition with its quenching by the alkene, as we have observed previously.²⁶ A blank experiment in which **10** in NaY is excited at 355 nm confirms that the transients observed in the presence of sensitizer do not result from direct excitation of **10**.

Kinetic measurements at 400 and 500 nm for both the direct and photosensitized experiments demonstrate that the two bands do not arise from a single species. Although the decay kinetics are complex and occur over a range of time scales, the 500 nm band always disappears more slowly than that at 400 nm. Based on the solution results, it is reasonable to assign the 400 nm band to the radical cation; this is also consistent with the observation of weak signals in the 600 nm region, after removal of the trapped electrons with oxygen. The 500 nm species could arise from either the diphenylethyl cation formed by photoprotonation or a dimer radical cation, both of which might be expected to absorb in this region. To distinguish between these two possibilities, we examined samples with two different loadings of **10** (Figure 6). The relative intensities for the 400 and 500 nm transients were 1.3 and 0.9 for 50 and 200 $\mu\text{mol/g}$

loadings. The decreased yield of the 500 nm species at lower loading is consistent with its assignment to a dimer radical cation. It is also interesting to note that the longer wavelength band shifts slightly to the red in an oxygen atmosphere and shows a growth that is not detected under nitrogen. This may indicate trapping of an initial 1,4-distonic radical cation with oxygen to yield a dimeric cation. Similar results have been observed for intramolecular cyclizations of several radical cations derived from 1, ω -bis (diarylethenyl) alkanes.²⁰

Qualitatively similar results were obtained upon direct excitation of **11**, although the signals were somewhat weaker. This is in agreement with the lower photoionization yield for **11** as compared to **10** in solution, as noted above. Although **7** did not yield an appreciable amount of radical cation upon direct excitation, PET did give weak signals at 400 nm, consistent with formation of $\mathbf{7}^+$.

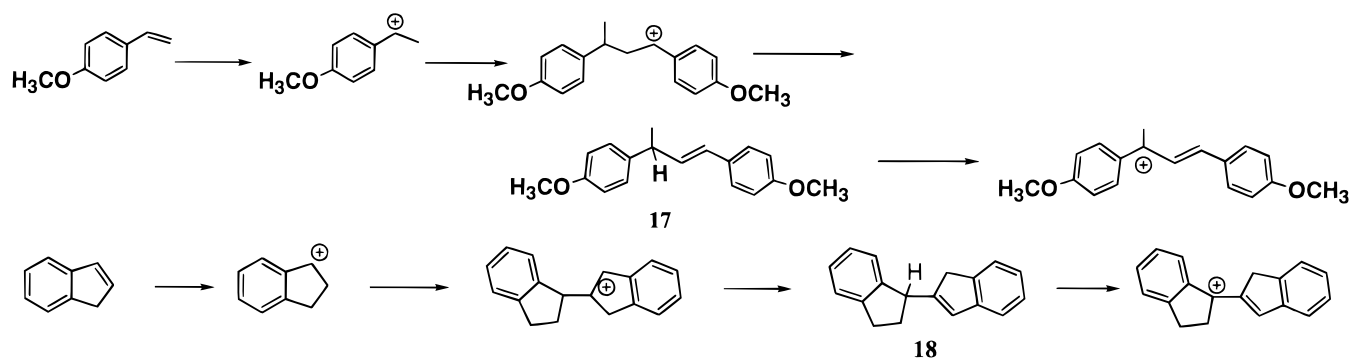
Discussion

The transient studies described above lead to the conclusion that the radical cations for the two 1,1-diphenylethylenes (**7** and **8**) have similar spectra with a strong absorption at approximately 400 nm and a weak band beyond 700 nm. This is in reasonable agreement with spectra obtained for $\mathbf{6}^+$ in matrices. The transient studies do not provide any evidence for addition of these radical cations to the monomer alkene, although it should be noted that a reversible addition as we have observed previously for *t*-anethole would also account for these results.²⁷ There is no evidence for any significant absorption between 500 and 650 nm for any of the 1,1-diphenylethylenes, thus providing conclusive evidence that the 600 nm transient observed upon inclusion of 1,1-diphenylethylene is not $\mathbf{2}^+$. This is further substantiated by the fact that similar long wavelength absorptions are not observed for either **7** or **8** in CaY, even though formation of the radical cations should, if anything, be more facile for these two alkenes than for **6**.

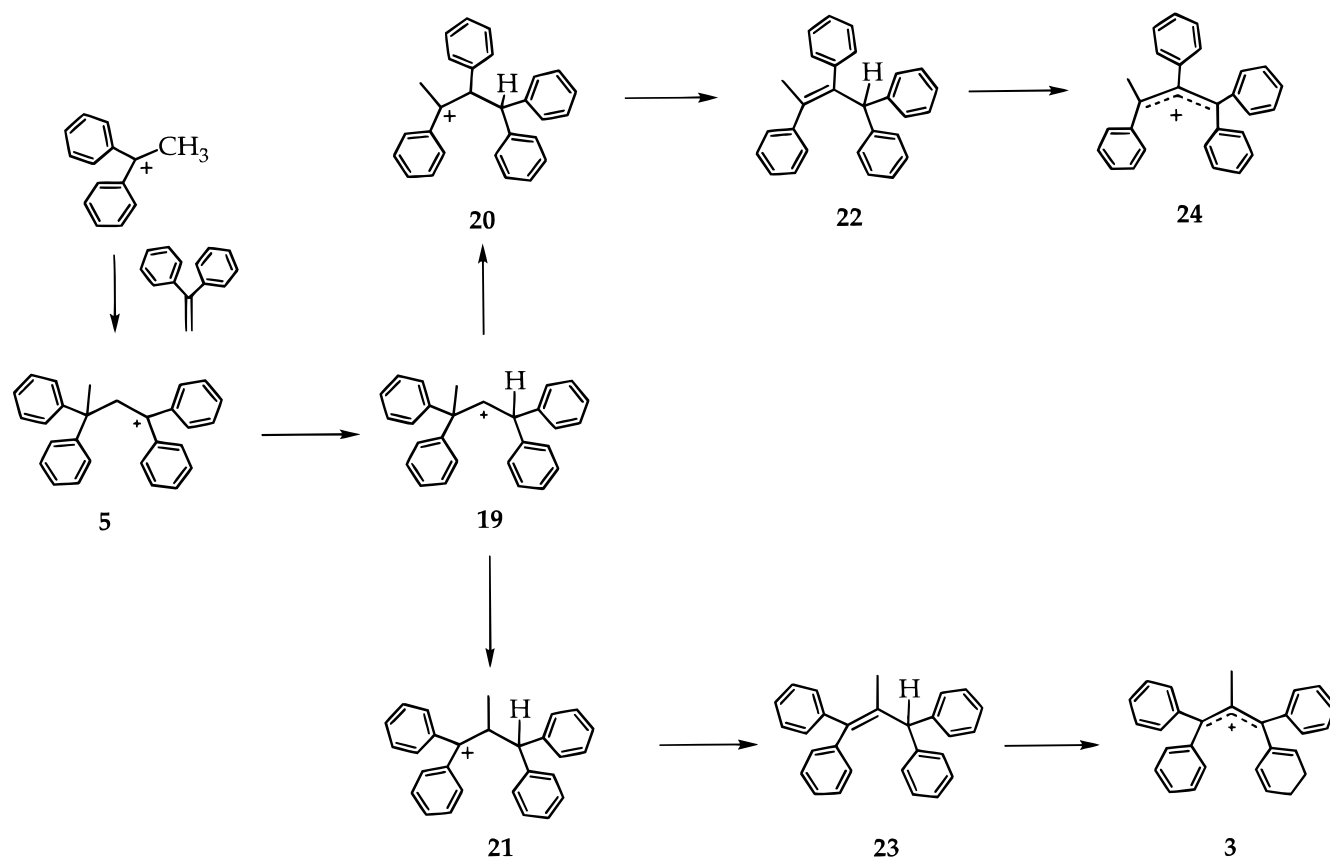
The spectra obtained for the *p*-methoxy substituted diphenylethylene radical cations show a similar absorption in the 400 nm region. However, there is an additional absorption at approximately 600 nm that clearly also belongs to the radical cation. Note that this is in agreement with recent studies of $\mathbf{9}^+$ in a matrix, although the 600 nm absorption had not previously been reported in solution studies of related systems.²⁰ The fact that $\mathbf{10}^+$ and $\mathbf{11}^+$ can also be generated in NaY zeolite and show very similar spectra under these conditions confirms that the zeolite does not significantly modify their spectral characteristics. The transient results again confirm that the long wavelength absorption (680 nm) generated by inclusion of **9** in CaY is not the radical cation. It is interesting to note that the spectra for the bis (4-methoxyphenyl) ethylene radical cations are all quite similar to those of the *t*-anethole radical cation which has λ_{max} at 380 and 600 nm; by contrast, the spectra for the diphenylethylene radical cations do not exhibit the 600 nm absorption that is observed for related styrenes, although they do have a weak band at considerably longer wavelengths.²² Examination of spectra shown in Figures 1 and 2 reveals the absence of absorption in the region near 400 nm which is characteristic of radical cations of diarylethylenes. This conclusively rules out radical cation as the species responsible for the blue color when diphenylethylene is introduced within activated CaY.

Having ruled out the radical cation as the species responsible for the long wavelength absorption in CaY, we turned our attention to the dimer cation **5**. This cation was generated from

SCHEME 5



SCHEME 6



the two precursors shown in Scheme 4. The observed absorption maximum (430 nm) is consistent with that expected for a diphenylalkyl cation.¹⁶ We conclude that the absorption recorded soon after the inclusion of olefin 15 and alcohol 16 in activated HY is due to the dimer cation 5 and it does not have significant absorption above 500 nm.

Having excluded monomer cation radical 2 and dimer cation 5, we next explored the possibility of a dimeric allylic cation similar to the ones obtained from indene and vinyl anisole as the intermediate responsible for blue color (Scheme 5). Formation of allylic dimer cations within CaY is well established in the case of vinylanisole and indene. As illustrated in Scheme 6 the allylic dimer cation is believed to be formed through a series of acid–base reactions. An important difference between vinyl anisole, indene and diphenylethylene is the fact that while the former two can readily yield an alkene containing an allylic hydrogen (structures 17 and 18 in Scheme 5) as the precursor for the allylic cation, a similar reaction cannot take place easily for diphenylethylene (compare Schemes 5 and 6). One could

visualize the dimer allylic cations 3 and 24 as possible candidates for the absorption at 615 nm. Both structures require the formation of alkenes with allylic hydrogen (22 in the case of 24 and 23 in the case of 3). The most unusual step in the mechanistic scheme outlined in Scheme 6 is the formation of 19 from 5. Once 19 is formed it may undergo rearrangement via migration of either a methyl group or a phenyl group (Scheme 6) to 21 and 20 respectively. Both are likely. We believe that the driving force for the rearrangement of 5 to 19 is the fact that the latter should be viewed as a nonclassical cation stabilized by adjacent phenyl and methyl groups.²⁸ Such stabilization ultimately leads to migration of either methyl or phenyl group to produce olefins 23 and 22 (Scheme 6). The formation of dimer allylic cations 3 and 24 from the precursor alkenes 23 and 22 would be anticipated based on the behavior of vinylanisole and indene within CaY.^{9a–c} We suggest that the blue color of CaY is due to these persistent cations. Both structures would be expected to absorb above 550 nm.²⁹

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