the spectrum corresponding to **1a** was observed.

Reaction of 1a with Trifluoromethanesulfonic Acid. To a solution containing **1a** (8 mg) in CD_3OD (0.5 mL) in a NMR tube fitted with a J. Young valve was added trifluoromethanesulfonic acid (2 μL). A complicated ^{31}P NMR spectrum results, which is apparently the result of four phosphorus-containing species (**4a–d**), each of which possess inequivalent BINAP phosphorus atoms: $^{31}P\{^1H\}$ (CD_3OD, −80 °C) δ 82.1 (d, 3%, $J_{PP'}$ = 25 Hz, **4a**), 74.9 (d, 5%, $J_{PP'}$ = 25 Hz, **4a**), 61.9 (d, 27%, $J_{PP'}$ = 44 Hz, **4b**), 61.0 (d, 13%, $J_{PP'}$ = 44 Hz, **4c**), 60.3 (d, 29%, $J_{PP'}$ = 44 Hz, **4b**), 52.3 (d, 13%, $J_{PP'}$ = 42 Hz, **4c**), 52.3 (d, 5%, $J_{PP'}$ = 32 Hz, **4d**), 52.3 (d, 5%, $J_{PP'}$ = 32 Hz, **4d**). The above experiment was repeated three times. The percentages given indicate the relative abundance of **4a–d** for the particular experiment described above. The relative abundance of **4a–d** varied from experiment to experiment; however, **4b** always formed predominantly, followed next by **4c**. Tetrabutylammonium hydroxide and sodium methoxide, in the absence of excess carboxylic acid, react with **4a–d** as they react with **1a**, to give an insoluble orange precipitate. *However, addition of excess tetrabutylammonium acetate converts* ***4a–d*** **to** ***1a***.

Reaction of 1a with Tetrafluoroboric Acid. To a solution containing **1a** (ca. 12 mg) in CD_3OD (0.5 mL) in a NMR tube fitted with a J. Young valve was added tetrafluoroboric acid (5 μL). The resulting ^{31}P NMR spectrum was similar to those obtained when trifluoromethanesulfonic acid was added.

Deuterium Crossover Hydrogenation of Tiglic Acid (2b). A quartz tube fitted with a high-vacuum stopcock and O-ring joint was charged with **1a** (2.0 mg), **2b** (4.5 mg), and CD_3OD (1.5 mL). The resulting solution was freeze–pump–thawed twice on a vacuum line and H_2 (1.5 atm) was introduced to the flask. The solution was stirred *vigorously* with a magnetic stir bar. A 0.5-mL aliquot was removed after 3 h. The ^1H NMR spectrum showed that hydrogenation was complete (Figure 4): ^1H NMR (CD_3OD) δ 2.32 (p, 0.64 H, $^3J_{HH}$ = 6.9 Hz, $OC(CH_3)(\mathit{H})C(H)_2(CH_3)$), 1.62 (m, 0.12 H, $OC(CH_3)(H)C(\mathit{H})_2(CH_3)$), 1.44 (m, 0.74 H, $OC(CH_3)(H)C(\mathit{H})_2(CH_3)$), 1.12 (d, 3.1 H, $^3J_{HH}$ = 6.9 Hz, $OC(C\mathit{H}_3)(H)C(H)_2(CH_3)$), 0.91 (br d, 3.0 H, $^3J_{HH}$ = 6.9 Hz, $OC(CH_3)(H)C(H)_2(C\mathit{H}_3)$).

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Generation, Entrapment, and Spectroscopic Characterization of Radical Cations of α,ω-Diphenyl Polyenes within the Channels of Pentasil Zeolites[†]

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Abstract: Inclusion of *all-trans-α,ω*-diphenyl polyenes (*trans*-stilbene, 1,4-diphenyl-1,3-butadiene, 1,6-diphenyl-1,3,5-hexatriene, 1,8-diphenyl-1,3,5,7-octatetraene) in thermally activated Na-ZSM-5 zeolite leads to the rapid formation of cation radicals of the polyenes. These cation radicals are stabilized within the zeolite host and are conveniently studied by conventional spectroscopic techniques (ESR, UV–vis–NIR diffuse reflectance, emission) enabling us to determine for the first time the steady state fluorescence spectrum of the 1,6-diphenyl-1,3,5-hexatriene and 1,8-diphenyl-1,3,5,7-octatetraene cation radicals. Our method of generation and stabilization of organic cation radicals appears to be both general in scope and simple in practice. While the mechanism of oxidation remains unclear, it appears that the presence of aluminum in the zeolite is a requirement; as the Si/Al ratio decreases the extent of oxidation increases. Using a series of substituted stilbenes of known redox potential leads to an estimated redox potential of 1.65 ± 0.1 eV vs SCE for the zeolite-based oxidant.

Introduction

Although the first stable crystalline cation radical salts were prepared over a century ago, systematic generation and spectroscopic characterization of organic cation radicals has not been routine.[1-3] Conventional methods of generation involve high-intensity photolyses, pulse radiolysis, and treatment with very strong acids.[4,5] Recently, cation radicals have also been generated in fluid solution as intermediates with short lifetimes via photoinduced electron transfer and electrochemical processes.[6-10] Formation of relatively long lived radical cations from aromatics such as anthracene, perylene, etc. on silica–alumina surfaces and on decationized zeolites has been reported previously.[11-25] Radical cations have been generated from zeolite-included saturated and unsaturated hydrocarbons by subjecting them to either X-ray, γ, or UV radiation.[26-29] A study of particular interest to this investigation is a report by Gessner et al.,[30] wherein a color development, possibly due to radical cations, has been observed when *trans*-stilbene was included within silicalite, a pentasil type of zeolite.

In this paper, we present evidence for the generation of stable radical cations from α,ω-diphenyl polyenes (*trans*-stilbene,

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[†] Part of the series Modification of Photochemical Reactivity by Zeolites.

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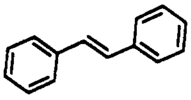
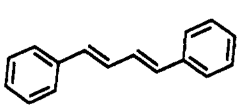
Table I. UV–vis–NIR Absorption Maxima from Room Temperature Diffuse Reflectance Spectra of Radical Cations of α,ω-Diphenyl Polyenes Included in Na-ZSM-5[a]

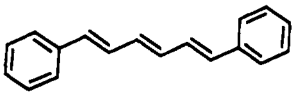
olefin	diffuse reflectance λ_{max} (nm)	color of complex	oxidation potential (eV vs SCE)
trans-4-carbomethoxystilbene	not formed		1.65[d]
trans-stilbene	475, 780	light yellow	1.52[c]
trans-4-methylstilbene	488, 808	light yellow	1.41[c]
trans-4-chlorostilbene	494, 818	light yellow	1.56[c]
trans-4-(dimethylamino)stilbene	456, 478, 739, 817	light yellow	0.58[d]
trans-4,4′-dimethoxystilbene	481, 530, 783, 872	light pink	0.90[e]
trans,trans-1,4-diphenylbutadiene	497, 543, 688, 823	pink	1.07[b]
all-trans-1,6-diphenylhexatriene	540, 597, 766, 802, 879	blue	1.02[f]
all-trans-1,8-diphenyloctatetraene	546, 658, 901, 978	green	0.90[f]

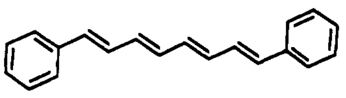
[a] The oxidation potentials of the neutral polyenes in solution and the colors of the zeolite complexes of the cation radicals are also reported. [b] Irreversible, value is E_{pa}.[73] [c] Acetonitrile solution, 0.1 M tetrabutylammonium perchlorate.[74] [d] Potentials were estimated on the basis of measured values for the cis isomers[75] corrected for the empirically determined 35 mV higher oxidation potentials of cis isomers compared to trans.[74] [e] Acetonitrile solution, 0.1 M $LiClO_4$.[76] [f] Acetonitrile solution, 0.1 M $LiClO_4$.[77] [g] Olefin cation radical.

trans,trans-1,4-diphenylbutadiene (DPB), *all-trans*-1,6-diphenylhexatriene (DPHT), and *all-trans*-1,8-diphenyl-1,3,5,7-octatetraene (DPOT)) upon inclusion in the channels of pentasil zeolites. The luminescence spectra of the radical cations of DPHT and DPOT stabilized in pentasil zeolites are also presented. Emission spectra from a few olefinic radical cations have been reported, but only in the gas phase.[31-33] The simplicity of our approach can be readily appreciated when one realizes that fluorescence from radical cations has not attracted much attention due at least in part to the absence of simple methods of preparing and stabilizing the cation radicals of interest. In general either two-photon time-resolved[34] or matrix[35] techniques have been required to carry out such studies.


trans-stilbene


DPB


DPHT


DPOT

Before discussing our approach to the stabilization of polyene cation radicals in zeolites it will be necessary to briefly summarize the properties of the zeolite hosts we will employ as supporting matrices. Zeolites are a large class of crystalline microporous solids with the general formulation $M_x[(AlO_4)_x(SiO_4)_y]\cdot n(H_2O)$ which find wide application as sorbents, ion exchangers, catalysts, and catalyst supports. Their structure is based on a three-dimensional network of AlO_4^- and SiO_4 tetrahedra which are linked to each other via doubly bridging oxygen atoms.[36,37] As each aluminum atom incorporated into the network leads to the presence of one excess negative charge, charge-compensating cations (M^+) must be introduced into the structure. These cations are not covalently bound to the zeolite framework and are readily exchanged. In this paper, we will employ primarily the zeolite Na-ZSM-5 (the Na^+ exchanged form of the zeolite ZSM-5) which has the typical formulation $Na_x[Al_xSi_{96-x}O_{192}]\cdot{\approx}16H_2O$, ($x < 27$; Si/Al > 2.5). X-ray diffraction structural analyses of ZSM-5 reveal that it possesses two types of pore systems.[38] One pore type is sinusoidal with a nearly circular cross-section of about 5.5 Å. The other is straight with an elliptical cross section of 5.2 × 5.5 Å (Figure 1). In general, Na-ZSM-5 zeolite (Si/Al = 22; $x = 4.2$) was used for most of the work reported here; however, ZSM-5 exchanged with other cations (Li, K, Cs, Tl) and with varying Si/Al ratios (22 < Si/Al < 550) were also examined.

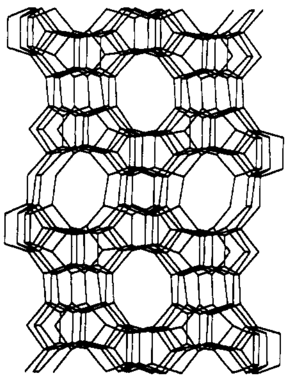


Figure 1. Structure of zeolite ZSM-5. The view is along the direction of the straight channel (crystallographic *b* axis).[38]

Results and Discussion

When activated Na-ZSM-5 (Si/Al = 22) was stirred with α,ω-diphenyl polyenes (*trans*-stilbene, DPB, DPHT, and DPOT) in 2,2,4-trimethylpentane, the initially white zeolite and colorless to pale-yellow olefins were transformed into highly colored solid complexes within a few minutes (see Experimental Section for details of the preparative procedure and method of zeolite activation). A typical experiment consisted of stirring 200 mg of Na-ZSM-5 with 2–5 mg of the olefin in 20 mL of 2,2,4-trimethylpentane at ambient temperature under air. As listed in Table I, the color of the zeolite complexes ranged from light yellow to green depending upon the choice of olefin; λ_{max} of these powders obtained from diffuse reflectance spectra are also provided in Table

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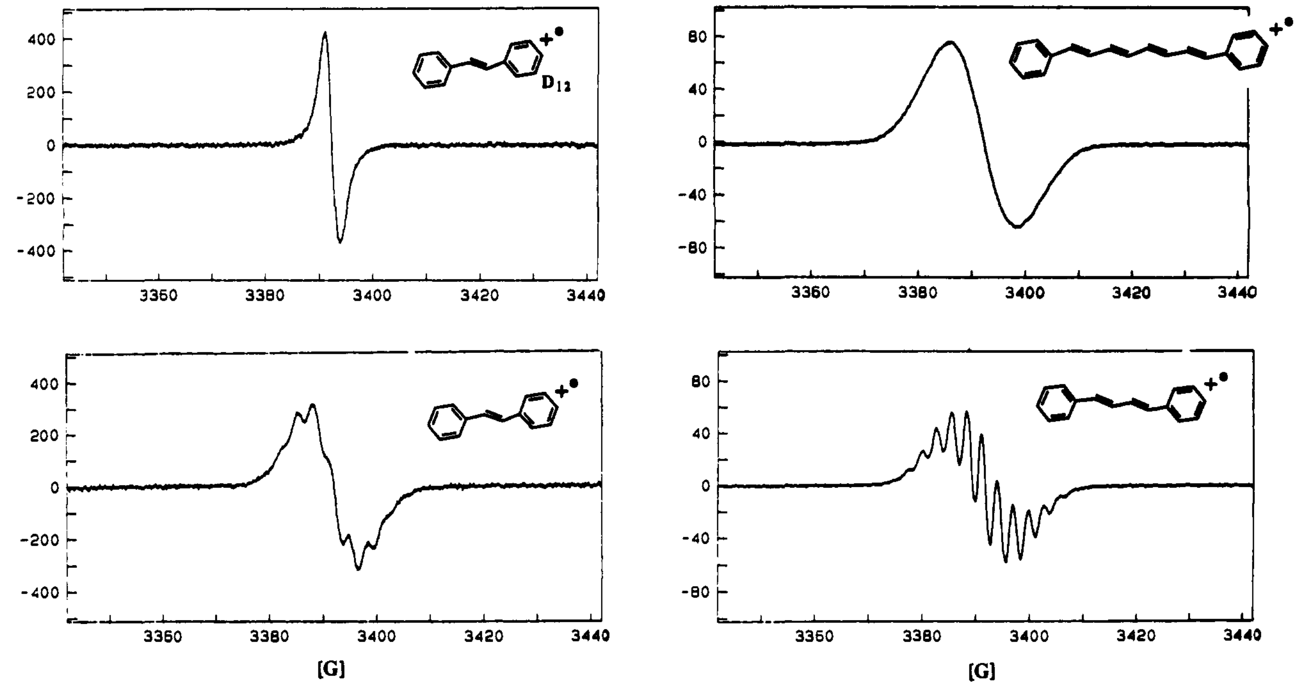

Figure 2. Room temperature ESR spectra of the cation radicals of *trans*-stilbene, *trans*-stilbene-d_{12} DPB, and DPOT included in Na-ZSM-5.

I. In all preparations, the supernatent solvent remained colorless demonstrating that the colored component(s) must be trapped either within the interior or on the external surface of the zeolite crystallites. Lightly colored zeolite complexes were also obtained by mortaring activated Na-ZSM-5 together with α,ω-diphenyl polyenes for a few minutes. However, in all cases the solution method appears to be superior both in ease of use and in the intensity of the color of the complexes. Very palely colored complexes could also be obtained with unactivated zeolite samples. Diffuse reflectance spectra of these complexes showed that the peak positions are identical with those obtained on activated zeolite. It appears that activation leads only to enhanced reactivity and not to a change in the chemical products.

The colored zeolite complexes, collected by filtration and dried under reduced pressure (10^{-4} mm), were demonstrated to contain the radical cations of the corresponding α,ω-diphenyl polyenes trapped within the zeolite channels (vide infra). The samples all exhibited intense ESR signals with g values of 2.0028. No signal was observed for the activated "empty" Na-ZSM-5 control sample. While ESR spectra from *trans*-stilbene and DPB samples were structured, those from DPHT and DPOT were structureless and broad (see Figure 2). No significant improvement in resolution was observed either on cooling to liquid helium temperatures or on heating to 100 °C. While the broad spectra preclude a detailed analysis of line shapes, the observed structure in the case of *trans*-stilbene and DPB is qualitatively as expected for simple cation radicals of the parent neutral molecules. We have demonstrated that in the case of *trans*-stilbene obsreved fine structure is due to proton hyperfine coupling as *trans*-stilbene-d_{12} shows a loss of structure and decrease in line width consistent with the decreased deuterium hyperfine coupling constant (Figure 2).[39] Restriction of motion and strong coupling between the matrix and the long rodlike guest molecules such as DPHT and DPOT within the channels of ZSM-5 are most likely responsible for their broad, featureless ESR spectra. We have observed a similar trend in the appearance of hyperfine structure of ESR signals with chain length in the case of radical cations of thiophene oligomers included in ZSM-5.[40] We conclude on the basis of the above ESR signals that these colored zeolite complexes carry an organic framework possessing an unpaired electron.

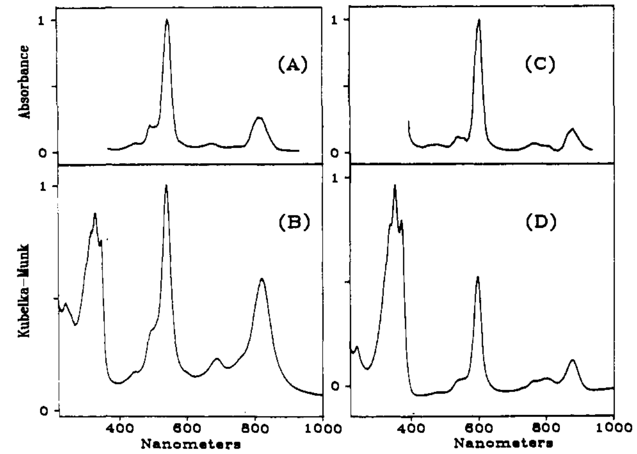

Figure 3. Room temperature diffuse reflectance spectra of the cation radicals of DPB (B) and DPHT (D) generated via inclusion in activated Na-ZSM-5. Spectra of $DPB^{\bullet+}$ (A) and $DPHT^{\bullet+}$ (C) prepared via pulse radiolysis[4] are included for comparison. All spectra have been normalized to unit intensity for clarity.

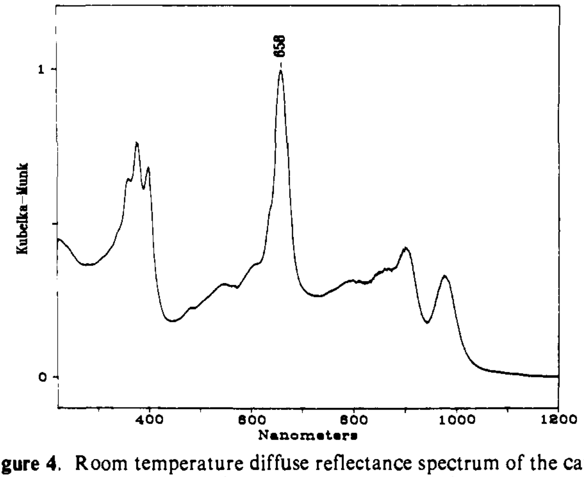

Figure 4. Room temperature diffuse reflectance spectrum of the cation radical of DPOT generated via inclusion in activated Na-ZSM-5. The absorption spectrum of $DPOT^{\bullet+}$ generated by pulse radiolysis is only reported for the range 640–680 nm, with a peak at 658 nm.[43]

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Diffuse reflectance spectra of these powders (Figures 3 and 4) are identical with the spectra of the radical cations of α,ω-diphenyl polyenes reported in the literature. Shida and Hamill have reported the absorption spectra of the radical cations of DPB and DPHT generated via pulse radiolysis techniques.[41,42] The absorption spectrum of the DPOT radical cation has been reported by Yamamoto et al.[43] Absorption spectra of radical cations of several of these olefins have since been reported by other groups under various conditions and all of them confirm the original assignment.[44-48] The match between the diffuse reflectance spectra of Na-ZSM-5–α,ω-diphenyl polyene inclusion complexes shown in Figures 3 and 4 and literature spectra is excellent. Taken together with ESR results this leads us to conclude that the colored species formed upon inclusion of α,ω-diphenyl polyenes in Na-ZSM-5 are radical cations and that they are generated and trapped within the channels of the zeolite.

Our level of understanding of the mechanism of oxidation of the polyenes by Na-ZSM-5 is at a very preliminary stage. With respect to the mechanism, one would like to have answers to at least some of the following questions: Where does the oxidation occur? What is the nature of the site of oxidation? What is the redox potential of the site? What percentage of the included polyenes are oxidized? What functional group within the zeolite is acting as the electron acceptor? Although we have made progress toward finding answers to some of these questions, we are not in a position to offer any concrete mechanism for this oxidation.

Oxidation of the neutral α,ω-diphenyl polyenes to the corresponding radical cations, we believe, occurs within the internal channels of Na-ZSM-5 and not on the exterior surface. This is based on the following observations: (a) The radical cations could not be extracted with diethyl ether (had they been on the outside surface extraction should be possible). (b) The radical cations generated within zeolites were stable in aqueous media. While in general organic radical cations are known to react readily with nucleophiles,[49] α,ω-diphenyl polyene radical cations trapped in Na-ZSM-5 channels were found to be inert even when refluxed in methanol and water. This demonstrates that the radical cations are located in positions that are highly inaccessible to solvent, i.e. within the zeolite interior. (c) Olefins with lower oxidation potentials such as tetraphenylethylene and 1,1,4,4-tetraphenyl-1,3-butadiene which are too large to pass through the narrow channels were not oxidized to the corresponding radical cation in Na-ZSM-5.

The colored α,ω-diphenyl polyene radical cations generated in the channels of Na-ZSM-5 were found to be unusually stable; even after several weeks of storage at ambient temperature in air, the colors persisted and the peak positions of the diffuse reflectance spectra were unchanged. This is to be contrasted with their short lifetimes in solution (μs) and in solid matrices (s).[44-48] In our opinion, the remarkable stability of these radical cations in Na-ZSM-5 derives from the tight fit of the rod-shaped molecules in the narow zeolite channels; the π-orbitals are protected from external reagents by the phenyl rings which fit tightly in the channels at both ends of the radical (Figure 5). Consistent with this proposal is the observation that when the radical cations were released by dissolution of the zeolite framework with aqueous HF, their color was instantly quenched due to reaction. Unfortunately, the quantity of product from this reaction was too small to characterize.

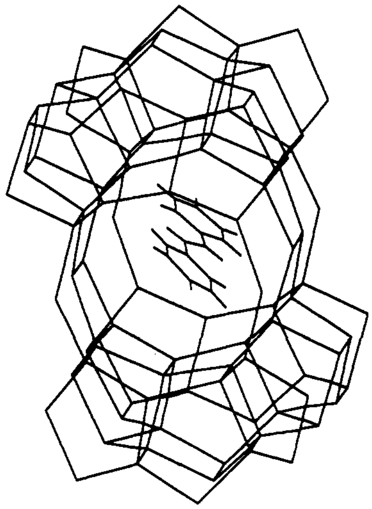

Figure 5. Model showing the structure of *trans*-stilbene included in the channels of ZSM-5. The view is along the direction of the straight channel (crystallographic *b* axis).

Support for the above conclusions about the stability of the radical cations comes from results obtained in another zeolite, Na-β. This zeolite possesses two sets of perpendicular channels with dimensions significantly larger than those in ZSM-5 (one circular with 5.6 Å diameter and one elliptical with dimensions 6.0 × 7.3 Å). The channels intersect to form a three-dimensional array of cages.[50,51] We find that Na-β is also capable of oxidizing included organics such as α,ω-diphenyl polyenes and thiophene oligomers.[52] However, while cation radicals were readily generated and detected spectroscopically within Na-β, the color that developed slowly faded indicating that radical cations formed within these larger channels remained unstable. We believe that instability is the result of channels that are too large to offer effective protection of the radical cations from adventitious impurities such as atmospheric oxygen and moisture. In conclusion, we suggest that the tight fit of the guest α,ω-diphenyl polyenes within the host Na-ZSM-5 is responsible for the remarkable stability of the included radical cations.

The oxidation of *trans*-stilbene proceeded more slowly and to a lesser extent in Na-ZSM-5 than did the oxidation of the more electron rich longer chain polyenes, suggesting to us that the effective redox potential of the unknown zeolite oxidation site might lie near the *trans*-stilbene. We have further refined this estimate of the redox potential of the zeolite's oxidation sites by including a number of *trans*-4-substituted stilbenes with varying oxidation potentials (Table I) within the channels of Na-ZSM-5 (only 4 substitutions at the 4 position were chosen in order to minimize steric interactions with the zeolite channels). Of the five *trans*-4-substituted stilbenes which were included (*trans*-4-methyl-, 4-chloro-, 4-(dimethylamino)-, 4-methoxy-, and 4-carbomethoxystilbenes), all except *trans*-4-carbomethoxystilbene were oxidized. Further, the more easily oxidized, *trans*-4-(dimethylamino)- and 4-methoxystilbenes reacted more readily than did the others. This leads us to conclude that the redox potential of the zeolite oxidation sites must lie close to that of *trans*-4-carbomethoxystilbene (1.65 eV vs SCE). This conclusion is supported by our observations with other types of substrates. While bithiophene and higher oligomers (oxidation potential <1.3 eV vs SCE[53,54]) were readily oxidized, thiophene (1.6 eV vs SCE[55])

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was not.[52] Similarly, neither naphthalene (1.62 eV vs SCE[56]) nor biphenyl (1.80 eV vs SCE[56]) gave rise to radical cations when included in ZSM-5 zeolites. Summarizing, our results indicate an effective redox potential for the zeolite-based oxidant of 1.65 ± 0.1 eV vs SCE.

Direct quantitative determination of the number of available oxidation sites could not be carried out due to both the experimental difficulty in obtaining quantitative optical densities from diffuse reflectance spectra and the absence of reported extinction coefficients for the cation radical absorption bands. However, a crude estimate of the number of oxidizing sites was obtained via dilution studies. The number of radical cations present in the channels was estimated by carrying out the oxidation at various loading levels and determining the loading range at which all of the adsorbed polyenes were oxidized. Through this process, we determined a limiting loading level at which all the olefins included were oxidized and this was taken as an estimate of the number of oxidation sites available within the zeolite. We realize that at low loading levels not all sites will be occupied and at higher levels of loading less accessible sites may be reached. Therefore, the number estimated by this method gives only the lower limit. The relative ratio of the radical cation to the neutral polyenes was estimated from diffuse reflectance spectra. By carrying out several adsorption studies, we found that the maximum amount of DPHT and DPOT which could be adsorbed was about 60 mg ($\sim 2.5 \times 10^{-4}$ M) per g of Na-ZSM-5. Noting that long rod-like molecules such as these are not expected to occupy the zigzag channels, the measured maximum loading is consistent with the available linear channel volume. The limiting loading level at which all the included DPHT and DPOT were oxidized corresponded to about 0.005 mg ($\sim 2 \times 10^{-7}$ M) per g of zeolite. This would correspond to about 0.1% of the total loading capacity and $\sim 2 \times 10^{16}$ oxidizing sites/g (assuming one site oxidizes one molecule only). Although the amount that can be oxidized appears to be small, this is more than sufficient to carry out spectroscopic studies.

With respect to the nature of oxidizing sites we have only limited information. Since several alkali cation (Li, K, Cs, and Tl) exchanged ZSM-5 zeolites (Si/Al ~ 22) were effective as oxidants, the cation is not expected to play any pivotal role in the oxidation process. Trace elemental analysis revealed that the iron content in ZSM-5 was in the range of 0.02%. However, zeolites such as NaY and Na-mordenite which contain much larger amounts of iron impurity[57] did not oxidize included polyenes. Therefore, we believe that iron impurity is not responsible for the oxidation in the case of ZSM-5. By including the above polyenes in ZSM-5 zeolites with different Si/Al ratios (ranging from 22 to 550), we could conclude that the presence of aluminum in the matrix is essential. Purely silicious ZSM-5 (Si/Al ≈ 550) was found to be completely inactive. At lower Si/Al ratios, the extent of oxidation was systematically dependent upon the aluminum content; the greater the aluminum content, the greater the amount of oxidation as monitored by diffuse reflectance spectra. It is not clear at this stage what role aluminum plays in the oxidation process. One possibility is that some type of aluminum containing defect site is acting as the oxidant. We have tried to estimate the generality of this chemistry by surveying a number of common zeolite hosts. We find that oxidation is observed with ZSM-8 and ZSM-11, while no reactivity is detectable for NaX, NaY, M-5, Ω-5, LZ-L, or ZSM-34.

In this context, recent reports[58-60] relating to the oxidation of aromatics in pentasil zeolites and metallocenes in faujasite type zeolites[61] are of interest. Ozin and Godber[61] conclude from their studies on metallocenes in NaY that electron transfer occurs at the α-cage Bronsted acid sites and results in the production of water through a redox-induced dehydroxylation reaction of the zeolite lattice. Such a process is not expected to operate in our systems as all our studies involve the use of alkali ion exchanged forms. Zholobenko et al.[58] as well as Kucherov et al.[59] have identified in H-ZSM-5 two types of sites being responsible for the oxidation of included aromatics. One of these sites is speculated to be Fe^{3+} impurities. For reasons outlined previously we do not believe that Fe^{3+} impurities are the oxidant in our systems. The second site is believed to be lattice Lewis acid sites, and it is estimated that there are $2–4 \times 10^{17}$/g of such sites in H-ZSM-5 (Si/Al ratio of ~20). It is of interest to note that our estimation of the number of α,ω-polyene radical cations in Na-ZSM-5 is in a similar range (see above). Shih[60] has also reported oxidation of 2,3-dimethyl-2-butene in activated H-ZSM-5. He ascribes the oxidation to occur at a defect site with positive holes on oxygen atoms present between the tetrahedral structure of silica–alumina. It is clear from the above studies as well as from ours that the exact nature of the oxidizing sites has not been clearly understood. Further experiments are in progress aimed at obtaining more information about the structure of the oxidation sites and unravelling the mechanism of the reaction.

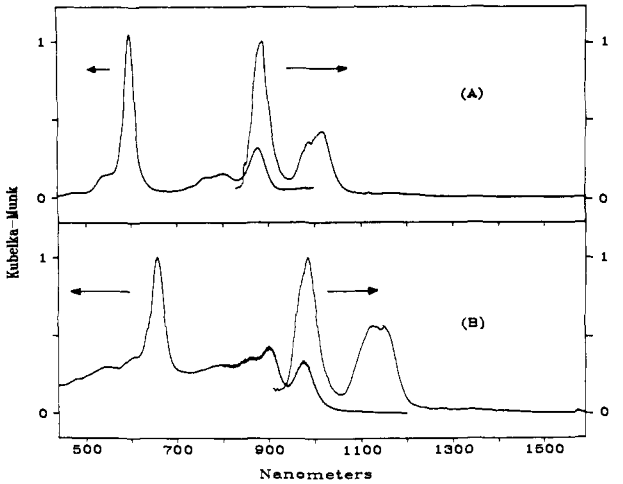

Figure 6. Emission (77 K) and diffuse reflectance (room temperature) spectra of $DPHT^{\bullet+}$ (A) and $DPOT^{\bullet+}$ (B) included in Na-ZSM-5.

The results discussed above demonstrate the radical cations of α,ω-diphenyl polyenes are formed rapidly and trapped within the zeolite channels. These stabilized radical cations are ideally suited to spectroscopic studies, the results of which are described below.

Emission Studies. Emission spectra of $DPHT^{\bullet+}$ included in Na-ZSM-5 are presented in Figure 6. At 77 K with excitation at wavelengths between 350 and 850 nm, readily detectable emission is observed with a clearly resolved vibrational spacing of ca. 1490 cm^{-1} and a poorly resolved shoulder corresponding to a second spacing of ca. 1170 cm^{-1}. Emission is also detectable at room temperature, yielding a broadened spectrum with essentially the same peak positions. For comparison, we also present in Figure 6 the room temperature diffuse reflectance spectrum of $DPHT^{\bullet+}$ included in ZSM-5. The close coincidence of the absorption and emission peaks and their mirror symmetry strongly suggests that emission is originating from the lowest spin-allowed excited state of $DPHT^{\bullet+}$, formally a doublet–doublet transition. To our knowledge, this is the first reported emission spectrum of this species. Support for the assignment of the emission to a spin-allowed doublet–doublet fluorescence comes from the observation that changing the zeolite counterion from Na^+ to Tl^+ has no effect on either the peak positions or (qualitatively) the emission intensity. In previous studies, we have shown that Tl^+-exchanged zeolites yield remarkably large external heavy atom perturbation of spin-forbidden transitions.[62-66] The absence of

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any effect here suggests the observed emission signal is due to a spin-allowed process. Due to the low energy of the emission, we are currently unable to confirm this assignment via lifetime measurements.

In Figure 6, we also present the emission spectrum of DPOT$^{\bullet+}$ at 77 K in Na-ZSM-5. As in the case of DPHT$^{\bullet+}$, we observe a vibrationally structured band with an apparent spacing of 1450 cm^{-1} with a second poorly resolved 1170-cm^{-1} progression. The room temperature diffuse reflectance spectrum exhibits a mirror image relationship to the DPOT$^{\bullet+}$ emission spectrum again arguing for a spin-allowed fluorescence from the lowest doublet–doublet excited state of the cation radical.

Given the ease with which we were able to observe fluorescence from DPHT$^{\bullet+}$ and DPOT$^{\bullet+}$ included in Na-ZSM-5, we expected that the cation radicals of *trans*-stilbene and DPB should also fluoresce in the same spectral region given their similar absorption spectra. However, to our surprise, we have been unable to detect fluorescence from these species. While we cannot offer a detailed explanation for this fact, it is intriguing to note that fluorescence is absent for the only cation radicals for which we have observed hyperfine structure in the ESR. This suggests a possible connection between the extent of free rotation of the cation radical in the zeolite channel and excited state deactivation processes. For the *trans*-stilbene cation radical and DPB$^{\bullet+}$, there is some degree of free rotation leading to structured ESR spectra and to a competing radiationless decay process for the excited state. In the case of DPHT$^{\bullet+}$ and DPOT$^{\bullet+}$, rotation is hindered, ESR are correspondingly structureless, and radiationless decay does not effectively compete with fluorescence. However, we also note that the singlet fluorescence yields of the parent neutrals vary significantly with chain length, increasing in the order *trans*-stilbene < DPOT < DPB < DPHT.[67] In addition, the singlet state photophysics of DPHT and DPOT are complex, characterized by the presence of low-lying excited states which are in thermal equilibrium.[67-70] It is possible that similar complications may arise in the case of the cation radicals.

Our conclusion from these observations is that the cation radicals of the α,ω-diphenylpolyenes can exhibit readily detectable doublet–doublet fluorescence in the near-IR. We note that the coincidental similarity in emission energies between the lowest neutral triplet states and the corresponding cation radicals can impede observation of triplet phosphorescence spectra in these systems. However, triplet phosphorescence and cation radical fluorescence are readily distinguished by their excitation profiles as even in the presence of Tl$^+$ as an external heavy atom perturber the singlet–triplet absorption coefficients remain low and phosphorescence is only observed on UV excitation into the singlet–singlet absorption bands.[62] On the other hand, the cation radical spectra have significant absorption coefficients throughout the visible and near-IR and excitation in this entire region leads to detectable fluorescence.

Conclusion

We have demonstrated that activated Na-ZSM-5 and related zeolites effectively oxidize α,ω-diphenyl polyenes to yield stabilized cation radicals included within the interiors of the zeolites. While the oxidation mechanism is not yet completely determined, it apepars that the zeolite-based oxidant has an effective redox potential near 1.65 ± 0.1 eV vs SCE which is sufficiently positive to effect oxidation of a wide variety of substrates. The resulting cation radicals are protected from adventitious impurities and are held rigidly which effectively inhibits further reactions. The result is that even under ambient conditions the cation radicals are stable indefinitely. The ability to generate these reactive species as stable materials has enabled us to determine the fluorescence spectra of DPHT$^{\bullet+}$ and DPOT$^{\bullet+}$ for the first time.

Given the simplicity and genrality of this approach to the preparation of cation radicals, we are currently extending these studies to a variety of new substrates including thiophenes, acetylenes, and longer chain polyenes including retinals and carotenes. Investigations of the vibrational spectra of stabilized cation radicals are also in progress.

Experimental Section

Materials. *trans*-Stilbene, *trans*-4,4′-dimethoxystilbene, *trans,trans*-1,4-diphenylbutadiene, *all-trans*-1,6-diphenylhexatriene, and *all-trans*-1,8-diphenyloctatetraene were commercial samples and were crystallized from ethanol several times. All other *trans*-4-substituted stilbenes were synthesized following the literature procedure and were recrystallized from ethanol.

Zeolites. Zeolite samples ZSM-5 and Na-β were prepared as described below following literature procedures and were characterized by ICP elemental analysis[57] and powder X-ray diffraction. Analyses results are also summarized.

ZSM-5: Samples of Na, TPA-ZSM-5 with Si/Al varying from 20 to 550 were prepared by slight modification of Rollman and Volyocski's procedure.[71] Samples were calcined in flowing air at 60 °C/h to 550 °C and then held at 550 °C for 10 h to give Na-ZSM-5. The samples were then exchanged by conventional methods to give Li-ZSM-5, K-ZSM-5, Cs-ZSM-5, and Tl-ZSM-5. These samples were stored under ambient conditions.

Na-β: Samples of Na-β were prepared by literature methods,[72] calcined in flowing air at 60 °C/h to 550 °C, and then held at 550 °C for 10 h to give Na-β.

Na-X, Na-Y, and Na-mordenite were commercial Linde samples.

Activation of Zeolites. In general, ca. 250 mg of zeolite was placed in a silica crucible and heated at 500 °C for about 12 h. The freshly activated zeolites were rapidly cooled in air to ca. 50 °C and added to solutions of the polyenes of interest. Activated zeolites were used immediately after activation. In general, we have found that the time required for these activated zeolites to readsorb water to their full capacity is about 10 h under our laboratory conditions. This is easily monitored by keeping the activated zeolites on the pan of an analytical balance and watching the weight change. It should also be noted that unactivated zeolites were also found to be capable of generating radical cations of the polyenes, although to a much lesser degree than the activated zeolites.

Preparation of Complexes. Weighed amounts of α,ω-polyenes and activated zeolite (as above) were stirred together in 20 mL of trimethylpentane for about 2 h. In a typical preparation 250 mg of the zeolite and 5 mg of the α,ω-polyene were stirred in 20 mL of the solvent. During this process, the zeolite developed color which varied depending upon the olefin. The colored zeolite complexes were collected by filtration, washed with hexane several times to remove any material adsorbed on the external surface for crystallites, dried under nitrogen, and finally thoroughly degassed (10^{-4} mm) in either Pyrex or quartz cells fitted with Teflon stopcocks. These cells were used for recording absorption, emission, and ESR spectra.

Diffuse Reflectance Spectra. Diffuse reflectance spectra of the above zeolite solid samples were measured in 2 mm path length quartz cells using a Varian 2400 spectrometer equipped with either an integrating sphere (Varian) or a "Praying Mantis" all reflective light collection system (Harrick Scientific) in both cases with barium sulfate (Kodak, White Reflectance Standard) as the reference. Sample packing densities were not determined nor were they specifically controlled. Spectra were recorded between 220 and 2000 nm. For comparison, spectra of the empty zeolites were also recorded. Data were recorded digitally, and

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appropriate background corrections were carried out with the computer program SpectraCalc (Galactic Industries).

ESR Spectra. ESR spectra were recorded at 9.52 GHz on a Bruker Model ER200D spectrometer equipped with an ESP1620 data system. Samples were thoroughly degassed under vacuum and flame sealed in quartz tubes.

Emission Spectra. Near-IR emission spectra of the cation radicals were determined with a SPEX 212 Fluorimeter (Spex Industries) modified to accept a high-sensitivity germanium detector (North Coast Model EO-817L, useful wavelength range ≈750–1750 nm). Spectra were corrected for detector and optical system response by using curves determined with a NBS traceable calibrated tungsten lamp (Optronics Laboratories). Signal to noise was improved via lock-in detection (Stanford Instruments with the chopper located at the entrace slit of the emission monochrometer). Scattered light was removed by use of either short wave pass or narrow band pass interference filters (Corion Corp.) placed between the excitation monochrometer and the sample and by use of long wave pass interference filters (Corion Corp.) placed between the sample and the emission monochrometer. Background scans of both as prepared and activated zeolite samples showed no detectable emission in this wavelength region.

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Preparation and Spectroscopic Characterization of Polarons and Bipolarons of Thiophene Oligomers within the Channels of Pentasil Zeolites: The Evolution of Organic Radical Ions into Conducting Polymers[†]

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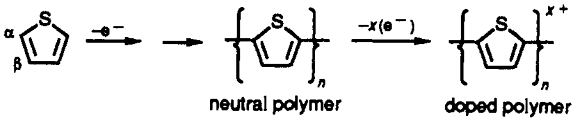
Abstract: Pentasil zeolites such as ZSM-5 and Na-β can be used as supporting matrices in which short-chain oligomers of polythiophene can be prepared, oxidatively doped to the conducting state, stabilized, and finally spectroscopically characterized. For the first time the evolution of the electronic structure of doped polythiophene from monomer to polymer has been observed directly for chain lengths between two and nine. Plots of the electronic absorption band energies for the polaron and bipolaron are found to be linear functions of inverse chain length. These results are extrapolated to infinite chain length to predict the positions of heretofore unobserved electronic transitions of bulk polythiophene. These extrapolations suggest that the lowest energy polaron and bipolaron levels of doped polythiophene are remarkably close in energy, implying that transient formation of polarons from bipolarons is energetically feasible and that this process could play a role in interchain charge hopping in this material.

Introduction

We recently reported that following activation at modestly high temperatures certain types of pentasil zeolites such as ZSM-5 and Na-β can effect the room temperature oxidation of included α,ω-diphenyl polyenes to yield stabilized cation radicals of the parent olefins. These cation radicals, which are protected within the zeolite channels, persist for months even in the presence of air and water and can be characterized via conventional spectroscopic techniques.[1] While we were unable to determine the precise nature of the zeolite-based oxidant, we were able to demonstrate that its effective redox potential is near 1.6 ± 0.1 eV vs SCE and that the presence of aluminum in the zeolite framework is essential to observe oxidation. Precedent for this type of one-electron-oxidation of guests in zeolites also comes from the work of both Ozin et al., who observed oxidation of metallocenes in zeolite Y,[2] and Bauld et al., who have inferred cation radical formation in Diels–Alder reactions catalyzed by zeolites.[3,4]

These observations suggested to us a simple method by which isolated conducting polymer strands and/or oligomers might be prepared and doped to their conducting state within the confines of a zeolite channel. It is well-known that one-electron oxidation of thiophene leads to rapid formation of polythiophene resulting from linking monomers in the α-position. The neutral polymer can be doped electrochemically to yield electronically conducting polythiophene.[5]



Given the oxidation potentials of oligomeric thiophenes (<1.3 eV vs SCE for $n \geq 2$), we expected that the zeolite-based oxidant would be capable of oxidizing them, leading to oligomerization/polymerization within the zeolite interior as outlined above. In this paper we demonstrate that this oligomerization does occur and that the zeolite-based oxidant can be used to prepare and stabilize cationically doped thiophene oligomers which can then be characterized by conventional spectroscopic techniques. The zeolite encapsulation has the added advantage of yielding oligomers that are well-isolated from one another so that effects due to interchain contacts are eliminated.

The evolution of electronic structure of organic conducting polymers with chain length remains an intriguing unresolved problem. In principle the problem is easily addressed simply by determining the spectroscopic properties of short-chain oligomers

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[†] Part of the series Modification of Photochemical Reactivity by Zeolites.

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