PERKIN 2 COMMUNICATION

Extended radical cation of diphenyl disulfide and oxidative cyclization on a pentasil zeolite: an EPR study

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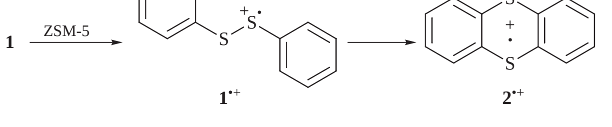
Incorporation of diphenyl disulfide (1) into a pentasil zeolite (Na-ZSM5) results in the formation of the extended radical cation, $\mathbf{1}^{\cdot+}$, as well as thianthrenium radical cation ($\mathbf{2}^{\cdot+}$) formed by oxidative cyclization. The stabilization of $\mathbf{1}^{\cdot+}$ on the internal surfaces of the zeolite is unprecedented because in solution it is converted spontaneously into $\mathbf{2}^{\cdot+}$. A mechanism for the conversion of $\mathbf{1}^{\cdot+}$ to $\mathbf{2}^{\cdot+}$ consistent with processes observed on the internal surfaces of the zeolite is proposed.

During the past 30 years the structures and catalytic properties of zeolites have been investigated extensively and many chemical reactions on the surface and in the micropores have been studied.[1–6] The generation of π-type radical cations and their stabilization in the channels of pentasil zeolite at ambient temperatures is an attractive application of zeolites.[7,8] The resulting radical cations have long lifetimes and, hence, can be investigated by conventional spectroscopic techniques. The technique may also generate σ-type neutral radicals; for example, oximes were converted to iminoxyls *via* one-electron oxidation followed by deprotonation.[9,10] Further, selected substrates undergo oxidative dehydrogenation, as exemplified by the generation of anethole radical cation from *p*-propylanisole.[11] In this communication, we report the utility of zeolites in stabilizing 'extended' radical cations that, in solution, undergo spontaneous intramolecular cyclization reactions. Diaryl disulfide radical cations have not been observed in solution because they rapidly cyclize with dehydrogenation, forming thianthrenium ions. For example, Giordan and Bock observed substituted thianthrenium ions upon oxidation of *para*-substituted diphenyl disulfides.[12]

Incorporation of **1** into the channels of pentasil zeolite (Na-ZSM5)[13] gave rise to an EPR powder pattern characteristic for organic free radicals containing heteroatoms. The observed spectrum is quite complex (Fig. 1, top); its interpretation was aided significantly by comparison with the EPR spectrum of a zeolite sample into which an authentic sample of thianthrene (**2**) had been sequestered (Fig. 1, bottom). The comparison suggests that introduction of **1** into the zeolite produces two distinct radical species. The EPR powder pattern at high field (Fig. 1, top) closely matches that observed for $\mathbf{2}^{\cdot+}$ in the zeolite (Fig. 1, bottom). The spectrum shows an orthorhombic powder pattern with $g_{11} = 2.0136$, $g_{22} = 2.0081$ and $g_{33} = 2.0024$; the average of the three principal g values, $g_{avg} = 2.0080$, is in good agreement with the isotropic g value ($g_{iso} = 2.0084$) measured for $\mathbf{2}^{\cdot+}$ in solution,[12] particularly when considering possible minor g-factor changes due to host–guest interactions in the zeolite. This feature is ascribed to $\mathbf{2}^{\cdot+}$.



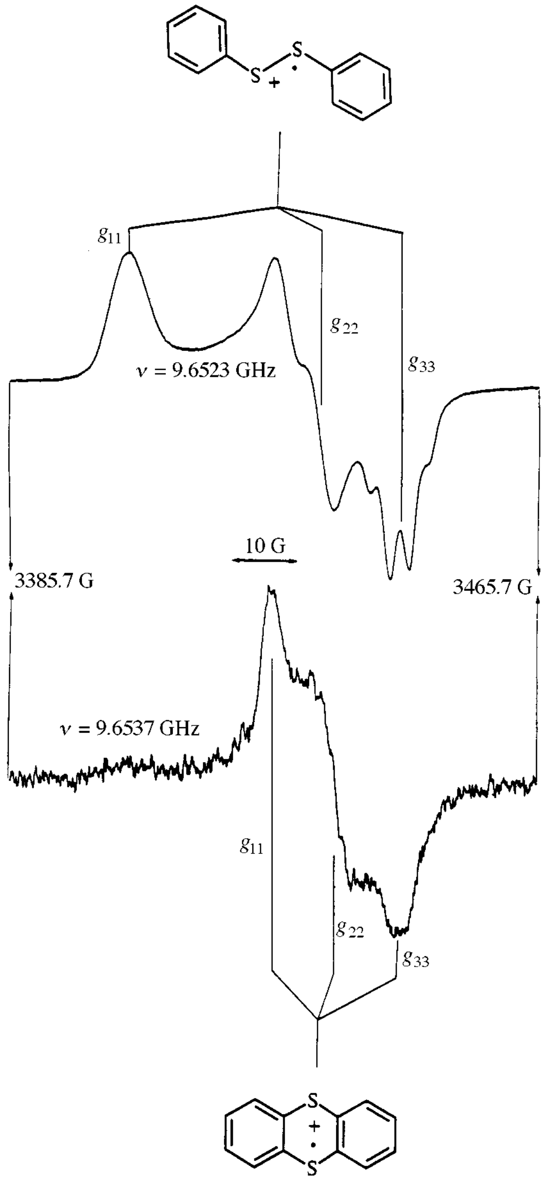
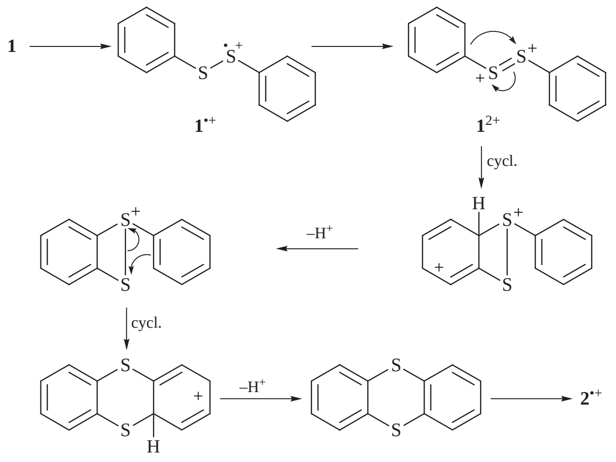


Fig. 1 X-Band powder EPR spectra obtained upon sequestering diphenyl disulfide (**1**; top) or thianthrene (**2**; bottom) into Na-ZSM5. The features assigned to the radical cations $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ are indicated above the top and below the bottom spectrum, respectively.

A second orthorhombic powder pattern ($g_{11} = 2.0263$, $g_{22} = 2.0090$, $g_{33} = 2.0022$; $g_{avg} = 2.0125$), characteristic for a free radical (ion) with spin on sulfur, is assigned to the extended radical cation, $\mathbf{1}^{\cdot+}$, of the precursor, a species not previously reported. The observed g_{avg} is in good agreement with the isotropic g factor, $g_{iso} = 2.0112$, of 2,2′-biphenyl disulfide radical cation.[14] The apparent resolution in the high field region of the

EPR spectrum (Fig. 1, top) could arise from either of two sources: different linewidths for the two overlapping powder patterns, or hyperfine splitting of the phenyl hydrogens of $\mathbf{1}^{\bullet+}$. Couplings from phenyl hydrogens have been reported for radical cations of α,ω-diphenylpolyenes.[7]

A mechanism for the complex conversion of **1** to $\mathbf{2}^{\bullet+}$ has not been suggested. We propose a mechanism that appears to be consistent with the constrained geometry within the zeolite and with processes (oxidation, deprotonation) previously established in this medium. We have excluded bimolecular processes from consideration, as molecules and intermediates most likely assume extended conformations and have limited mobility. We propose a mechanism involving two successive, intramolecular, electrophilic aromatic substitutions of diphenyl disulfide dication ($\mathbf{1}^{2+}$) as shown in Scheme 1. This mechanism is consistent with oxidation and deprotonation processes observed for **1** in solution and established for other substrates in the zeolite. Some of the key intermediates deserve comment.

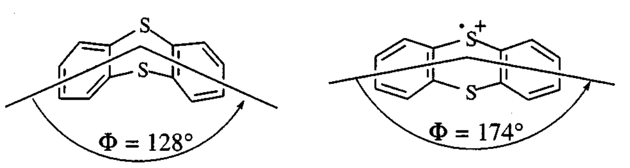


Scheme 1

The disulfide radical cation, $\mathbf{1}^{\bullet+}$, is the logical first intermediate in any oxidation of **1**, however elusive it may be in solution. The fact that its EPR spectrum is observed along with the cyclized species, requires that some zeolite sites sequester this intermediate without the possibility of further reaction. This suggests the existence of sites with a range of reactivities. Pentasil zeolites have two kinds of pore systems, either straight elliptical channels (5.2 × 5.7 Å) or sinusoidal ones, with nearly circular diameter (*ca.* 5.5 Å). It is not clear what factors promote or prevent the cyclization of $\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$. The existence of zeolite sites with varied reactivities is also supported by other observations. For example, we have evidence for as many as three distinct species in the oxidative aromatization of 2-methoxy-5,6,7,8-tetrahydronaphthalene.[15]

Concerning $\mathbf{1}^{2+}$, two-electron oxidations in zeolites have precedent. Dialkyl disulfide dications have been observed previously by optical spectroscopy and conductivity measurements following pulse radiolysis; these experiments were interpreted as evidence that disulfide radical cations disproportionate, at an essentially diffusion controlled rate, to disulfide and dication.[12] The disproportionation of $\mathbf{1}^{\bullet+}$ is favored by the formation of a sulfur–sulfur double bond in $\mathbf{1}^{2+}$. An intermediate of this type is consistent with the failure of bis(*p*-nitrophenyl) disulfide to undergo oxidative cyclization;[16,17] the strong electron withdrawing nature of the *p*-nitro moiety can hardly be expected to support either the dication or electrophilic aromatic substitution. In essence, the net conversion of **1** to $\mathbf{2}^{\bullet+}$ involves the loss of three electrons and two protons, a net conversion equivalent to the generation of anethole radical cation from *p*-propyl anisole.[11]

It is interesting to note that the EPR spectrum of $\mathbf{2}^{\bullet+}$ generated by incorporating **1** into ZSM-5 (Fig. 1, top) is significantly stronger than that generated by incorporating **2** (Fig. 1, bottom). We attribute this discrepancy to the fact that the two precursors have different shapes and, therefore, are incorporated into the zeolite with different degrees of ease. An X-ray diffraction analysis showed **2** to be a rigid non-planar molecule with a flap angle of *ca.* 128°.[18] On the other hand, **1** is flexible, can adopt an extended conformation and, hence, is readily sequestered into the zeolite. The thianthrene radical cation, $\mathbf{2}^{\bullet+}$, is nearly planar with a flap angle of 174°.[19] Once formed, this species is readily accommodated in the zeolite. We note, however, that more intense EPR spectra of $\mathbf{2}^{\bullet+}$ have been obtained by incorporating **2** into H-ZSM-5 at elevated temperatures or into zeolites with larger pore sizes (H-mordenite).[20,21]



In conclusion, we have demonstrated that a radical cation ($\mathbf{1}^{\bullet+}$), that is known to undergo spontaneous intramolecular cyclization with dehydrogenation in solution, can be stabilized in pentasil zeolite. However, the oxidative cyclization of **1** to $\mathbf{2}^{\bullet+}$ is not completely suppressed on the internal surfaces of a pentasil zeolite, suggesting the existence of sites with different reactivities in ZSM-5. We propose an intramolecular mechanism for the cyclization process, that is consistent with processes previously observed in the zeolite. We are extending these investigations to additional disulfides as well as diselenides.

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13 EPR samples were prepared by stirring 2–3 mg of the substrate with 70 mg of zeolite (Na-ZSM5, thermally activated by calcination at 500 °C for 12 h, and stored under argon) in 10 ml of 2,2,4-trimethylpentane for 2 h. The loaded zeolite is collected by filtration, washed with hexane and dried under vacuum (0.001 Torr).

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