Oxidative ring contraction of 2-phenyl-1,3-dithiane in ZSM-5: restricted mobility of 1,2-dithiolane radical cations in zeolite channels

Heinz D. Roth,*[a] Kui Shen,[a] Prasad S. Lakkaraju*[b] and Lorenzo Fernández[c]

[a] *Department of Chemistry, Rutgers University, Wright-Rieman Laboratories, New Brunswick, NJ 08854-8087, USA. E-mail: roth@rutchem.rutgers.edu*
[b] *Department of Chemistry, Georgian Court College, Lakewood, NJ 08701, USA. E-mail: lakkaraju@georgian.edu*
[c] *Instituto de Tecnología Química CSIC-UPV, Universidad Politécnica de Valencia, Apartado 22012, 46071 Valencia, Spain*

Received (in Corvallis, OR, USA) 17th June 1998, Accepted 7th October 1998

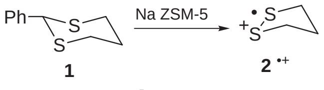
Incorporation of 2-phenyl-1,3-dithiane 1 into ZSM-5 generated 1,2-dithiolane radical cation $\mathbf{2}^{\cdot+}$, the EPR spectrum of which shows an orthorhombic powder pattern ($g_1 = 2.0293$, $g_2 = 2.0193$, $g_3 = 2.0030$); each g component showed a 1:4:6:4:1 pattern ($a_1 = 10.5$, $a_2 = 9.3$ and $a_3 = 9.2$ G) due to coupling to four equivalent ^{1}H nuclei, suggesting that the pseudo-axial and −equatorial α-protons undergo conformational equilibration whereas the sulfur centers are held stationary on the EPR time scale.

In the past three decades the structures and properties of zeolites have been extensively studied as prototypes of acidic industrial catalysts.[1–3] In addition, a wide range of organic radical cations have been generated, either spontaneously or upon inclusion of appropriate precursors into zeolites.[4–8] Radical cations generated by this method typically have extended lifetimes and can be studied by conventional spectroscopic techniques. We are interested in zeolite-induced radical cation reactions; our contributions to intra-zeolite chemistry include oxidative deprotonation,[9] dehydrogenation[10] and cyclization.[11]

In a recent study of diphenyl disulfide **3** we observed the EPR spectrum of the 'extended' radical cation $\mathbf{3}^{\cdot+}$,[11] even though this species undergoes rapid conversion to thianthrenium ion $\mathbf{4}^{\cdot+}$ in solution. In an attempt to observe the EPR spectrum of a similarly elusive species, 2-phenyl-1,3-dithiane radical cation $\mathbf{1}^{\cdot+}$, we incorporated **1** into ZSM-5 (Scheme 1). The resulting EPR spectrum supports the conversion of $\mathbf{1}^{\cdot+}$ to $\mathbf{2}^{\cdot+}$ and offers unique insights into the mobility of this radical cation in the zeolite channels.

Incorporation of 2-phenyl-1,3-dithiane **1** into Na-ZSM-5 at room temperature produced an EPR spectrum that can be interpreted as an orthorhombic powder pattern with $g_1 = 2.0293$, $g_2 = 2.0193$ and $g_3 = 2.0030$; each g component showed hyperfine coupling (hfc) due to four equivalent protons (1:4:6:4:1 pattern, $a_1 = 10.5$, $a_2 = 9.3$ and $a_3 = 9.2$ G; Fig. 1). The average g value, $g_{\text{avg}} = 2.0172$, is in reasonable agreement with the isotropic g value, $g_{\text{iso}} = 2.0183$, reported for the radical cation of 1,2-dithiolane, $\mathbf{2}^{\cdot+}$, in solution.[12,13] Likewise, the average hfc observed in the zeolite, $a_{\text{avg}} = 9.7$ G, agrees well with the isotropic coupling constant of 9.75 G reported for $\mathbf{2}^{\cdot+}$ in solution.[12,13] The identity of the species was confirmed by an essentially identical EPR spectrum obtained upon incorporation of an independently synthesized[14] sample of **2** into ZSM-5.

The generation of $\mathbf{2}^{\cdot+}$ by oxidative ring contraction of **1** has precedent in solution; either chemical or electrochemical oxidation of **1** led to the debenzylated, ring-contracted species, $\mathbf{2}^{\cdot+}$.[15–17] In fact, anodic oxidation of dithioacetals has been used to remove the dithiane protecting group of carbonyl compounds. The mechanism for the ring-contraction of dithiane radical cations appears to be understood in general terms.[15–17] This conversion has two principal elements, the formation of an S–S bond and the detachment of the benzyl group. This conversion is formulated typically *via* a disulfide dication.



Scheme 1

1,2-Disulfide dications have been observed by fast time-resolved spectroscopy in solution[18] and have been invoked recently in zeolite media.[11] The formation of the S–S bond in the 1,3-dithiane radical cation may favor the second oxidation step. The benzyl function may be removed by two consecutive nucleophilic displacements at the dication.[15–17] In view of the limited diameter of the ZSM-5 channels and the dimensions of **1** and its radical cation and dication, these species should not be accessible to external nucleophiles. Instead, Lewis base sites within the zeolite framework are the likely reagents.

The dynamic behaviour of $\mathbf{2}^{\cdot+}$ in the internal voids of the zeolite is also unusual. The g factor anisotropy of $\mathbf{2}^{\cdot+}$ at room temperature indicates that this species is not tumbling or rotating rapidly on the EPR time-scale. On the other hand, the conformational re-orientations ('flickering') of the methylene group (C_4) is still fast, based on the equivalence of the pseudo-axial and −equatorial α-protons at C_3 and C_5. This implies that one or both sulfur centers bearing spin and charge are held rigidly in a potential well or are 'attached' covalently to the zeolite network, whereas the mobility of the trimethylene segment is unaffected by the 'anchoring' of the sulfur centers (Scheme 2). This observation establishes an interesting differ-

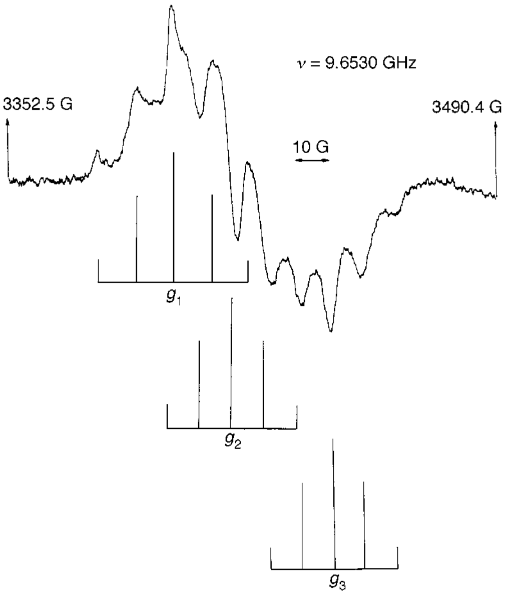
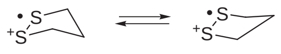


Fig. 1 Room temperature EPR spectrum obtained upon sequestering **1** into ZSM-5. The spectrum is interpreted as an orthorhombic powder pattern with g factors $g_1 = 2.0293$, $g_2 = 2.0193$ and $g_3 = 2.0030$, split into 1:4:6:4:1 patterns ($a_1 = 10.5$, $a_2 = 9.3$ and $a_3 = 9.2$ G) due to coupling with four equivalent ^{1}H nuclei. The spectrum is assigned to radical cation $\mathbf{2}^{\cdot+}$.



Scheme 2

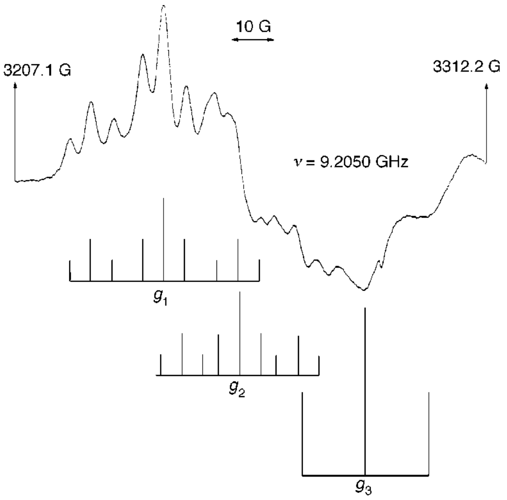


Fig. 2 Low-temperature (77 K) EPR spectrum of $\mathbf{2}^{\cdot+}$, an orthorhombic powder pattern with $g_1 = 2.0298$, $g_2 = 2.0190$ and $g_3 = 2.0023$. Each g component is split into triplet of triplets (interaction with two non-equivalent groups of two ^{1}H nuclei), $a_1 = 16.2$ and 4.9, $a_2 = 13.3$ and 4.6 and $a_3 = 14.7$ G, unresolved.

ence between the dynamicas of $\mathbf{2}^{\cdot+}$ in the zeolite and in solution. In solution, the flickering can be arrested without causing g factor anisotropy;[12,13] in contrast, the zeolite spectrum shows significant g factor anisotropy even when flickering rapidly.

The dynamics of **2** and its radical cation are well-documented in fluid solutions as a function of temperature. The five-membered ring of **2** is slightly twisted around the S–S bond; the sulfur lone pairs are aligned at a dihedral angle of *ca.* 30°.[19] Oxidation of **2** results in a subtle structure change; the sulfur lone pairs (and the S–CH_2 bonds) in $\mathbf{2}^{\cdot+}$ become eclipsed, facilitating the delocalization of spin and charge between the sulfur centers. The planar arrangement of the CH_2–S–S–CH_2 segment forces the bridging methylene group out of plane; a planar structure is a low-lying transition state between two equivalent 'envelope' conformers. At room temperature, the conformers equilibrate rapidly causing the four α-protons to be equivalent ($a = 9.75$ G, 4H). The inversion slows down with decreasing temperature; the pseudo-axial and −equatorial ^{1}Hs become non-equivalent at 180 K ($a = 16.25$ G, 2H; $a = 3.9$ G, 2H).

The low temperature dynamic behavior of $\mathbf{2}^{\cdot+}$ in the zeolite is similar. At 77 K, the flickering of the methylene group is sufficiently slowed to render the α-protons non-equivalent; each g component shows a triplet of triplets (Fig. 2). As in the room temperature spectrum, the splitting is well resolved in the downfield component. However, the g tensor of $\mathbf{2}^{\cdot+}$ remains orthorhombic, similar to that at room temperature.

The severely restricted mobility of $\mathbf{2}^{\cdot+}$ in the zeolite channels was unexpected. Because of its relatively small size (Fig. 3), we had expected $\mathbf{2}^{\cdot+}$ to tumble freely in the zeolite channels. Several radical cations of comparable size showed essentially isotropic spectra; for example, the sharp lines observed for 2,3-dimethylbut-2-ene radical cation in silicalite ($a = 11.8$ G; 11 of 13 lines are detected) are compatible with essentially free rotation of this radical cation.[20,21] In pentasil zeolites, the corresponding spectra have considerably greater linewidths, apparently due to interaction with the zeolite host and the resulting reduced mobility. Of course, the rotation of bulkier molecules is expected to be hindered; this is confirmed, for example, by the broad(ened) lines observed for anethol radical cation[10] or by the anisotropic (powder type) spectra of iminoxyls in ZSM-5.[9]

Concerning the question of whether the radical cation, $\mathbf{2}^{\cdot+}$, is 'held' in a potential well or covalently linked to the zeolite network, we can exclude the second possibility. The covalent link would most likely involve bonding of one sulfur atom to the zeolite. The resulting aggregate would be unsymmetrical; its spin density would be localized at the unattached sulfur center, creating a species in which only one CH_2 group is coupled. This is clearly incompatible with the EPR spectrum.

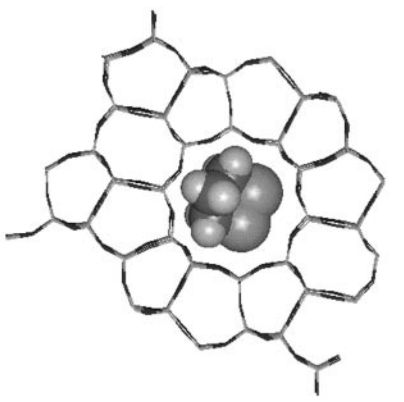


Fig. 3 Molecular modeling visualizing the docking of 1,2-dithiolane radical cation, $\mathbf{2}^{\cdot+}$, optimized at the UHF/6-31G* level of theory, inside the straight channels of ZSM-5.

In summary, the formation of 1,2-dithiolane radical cation, $\mathbf{2}^{\cdot+}$, upon inclusion of 2-phenyl-1,3-dithiane, **1**, into Na-ZSM-5 shows several interesting features. The removal of the benzyl function requires nucleophilic displacement; since the intermediate is not accessible to an external nucleophile, Lewis base sites within the zeolite framework are the likely reagent. The orthorhombic g tensor of $\mathbf{2}^{\cdot+}$ in the zeolite indicates that the radical cation is held in a coulombic well within the network of oxygen centers; however, intramolecular processes, such as the ring inversion of the β-methylene group, are unaffected.

Support of this work through grant NSF CHE–9714850 and two NSF equipment grants is gratefully acknowledged.

Notes and references

1 *Zeolite Microporous Solids: Synthesis, Structure, and Reactivity*, ed. E. G. Derouane, F. Lemos, C. Naccache and F. R. Rebeiro, Kluwer, Dordrecht, 1991.
2 Y. Izumi, K. Urabe and M. Onaka, *Zeolite, Clay, and Heteropoly Acid in Organic Reactions*, Verlag Chemie, Weinheim, 1992.
3 *Radicals on Surfaces*, ed. A. Lund and C. J. Rhodes, Kluwer, Dordrecht, 1995.
4 V. Ramamurthy, C. V. Casper and D. R. Corbin, *J. Am. Chem. Soc.*, 1991, **113**, 594.
5 F. R. Chen and J. J. Fripiat, *J. Phys. Chem.*, 1992, **96**, 819.
6 C. J. Rhodes, I. D. Reid and E. Roduner, *J. Chem. Soc., Chem. Commun.*, 1993, 512.
7 E. Roduner, R. Crockett and L. M. Wu, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 2101.
8 F. R. Chen and J. J. Fripiat, *J. Phys. Chem.*, 1993, **97**, 5796.
9 P. S. Lakkaraju, J. Zhang and H. D. Roth, *J. Phys. Chem.*, 1994, **98**, 2722.
10 P. S. Lakkaraju, D. Zhou and H. D. Roth, *Chem. Commun.*, 1996, 2605.
11 P. S. Lakkaraju, D. Zhou and H. D. Roth, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1119.
12 H. Bock and U. Stein, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 834.
13 H. Bock, U. Stein and A. Semkow, *Chem. Ber.*, 1980, **113**, 3208.
14 D. N. Harpp and J. G. Gleason, *J. Org. Chem.*, 1970, **35**, 3259.
15 J.-G. Gourcy, G. Jeminet and J. Simonet, *J. Chem. Soc., Chem. Commun.*, 1974, 634.
16 Q. N. Porter and J. H. P. Utley, *J. Chem. Soc., Chem. Commun.*, 1978, 255.
17 J.-G. Gourcy, P. Martigny, J. Simonet and G. Jeminet, *Tetrahedron*, 1981, **37**, 1495.
18 M. Bonifacic, K. Schafer, H. Mockel and K.-D. Asmus, *J. Phys. Chem.*, 1975, **79**, 1496.
19 T. Schaefer, J. P. Kunkel, R. W. Schurko and G. M. Bernard, *Can. J. Chem.*, 1994, **72**, 1722.
20 P. L. Corio and S. Shih, *J. Phys. Chem.*, 1971, **75**, 3475.
21 M. V. Barnabas and A. D. Trifunac, *Chem. Phys. Lett.*, 1992, **193**, 298.

Communication 8/04593C