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Spontaneous oxidation of a sulfide in zeolite CaY: the unprecedented reaction of a sulfide radical cation with oxygen

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Addition of 1,5-dithiacyclooctane (1,5-DTCO) to CaY resulted in electron transfer formation of the corresponding radical cation, which was characterized by EPR and diffuse reflectance UV–VIS spectrometry and which undergoes an unprecedented reaction with molecular oxygen to give mono- and bis-sulfoxide products.

The spontaneous formation of radical cations in zeolites has been extensively investigated with the realization that electron transfer is pivotal to many processes promoted by these important catalysts.[1] The lifetimes of radical cations are often dramatically extended in the interior of the zeolite allowing spectroscopic characterization, however, these species are not inert[2] and dimerizations,[3] rearrangements,[4] ring contractions,[5] and loss of protons[6,7] have all been observed. We report here the first example of the formation of a 2σ–1σ* radical cation[8] in the interior of CaY and the ability of the zeolite to promote a reaction of this radical cation that is not observed in homogeneous solution.

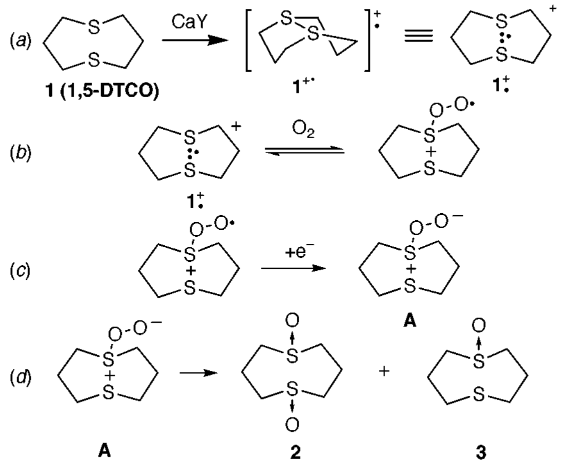
The substrate chosen for examination was 1,5-dithiacyclooctane (1,5-DTCO). 1,5-DTCO adopts a boat chair conformation in which lone pairs on the two sulfur atoms point in towards one another.[9] Its molecular volume is 193 Å^3 and it can conveniently fit in a 6 × 6 × 6 Å box.[10] Consequently, it can diffuse readily though the 7.4 Å windows into the 13 Å diameter supercages of CaY.

The oxidation of 1,5-DTCO has been extensively examined, and both its radical cation $\mathbf{1}^{+\cdot}$ and dication $\mathbf{1}^{2+}$ have been characterized.[8] The radical cation is conveniently synthesized by one-electron oxidation of 1,5-DTCO or by treatment of the corresponding 1-oxide with acid. The unique stability of $\mathbf{1}^{+\cdot}$ has been attributed to a transannular interaction between the two sulfur atoms to form a three electron bond species. Asmus[11] has described this unique bonding situation as an overlap of the p-orbitals on each sulfur to form a bond consisting of a filled σ and a half-filled σ* orbital. The suggestion, from electrochemical data, that the second oxidation of 1,5-DTCO is 20 mV easier that the first provides a dramatic confirmation of this bonding picture.[12]

Addition of 5 ml of a 0.04 M 1,5-dithiacyclooctane (1,5-DTCO) hexane solution to 0.3 g of a freshly prepared sample of CaY[13] under an argon atmosphere followed by GC monitoring of the hexane revealed a rapid and nearly quantitative (> 96% in all cases) adsorption of the sulfide by the zeolite. Immediate evidence for successful formation of $\mathbf{1}^{+\cdot}$ was provided by the fact that the hexane remained colorless during the absorption process while the zeolite immediately changed color from white to bright yellow.[14] An EPR spectrum of the yellow solid/hexane slurry confirmed this suggestion by exhibiting five lines (g = 2.0123; a_H = 14.50 G) indicative of an unpaired electron on sulfur interacting with four equivalent hydrogens. This EPR and the three line spectra generated by introducing 2,2,8,8-tetradeutero-1,5-dithiacyclooctane into the zeolite (g = 2.0121; a_H = 14.43 G) are nearly identical to those assigned to $\mathbf{1}^{+\cdot}$ by Hirschon and Musker for the solution oxidation of 1,5-DTCO.[15] In addition, the diffuse reflectance UV–VIS spectrum of the yellow zeolite exhibited a λ_{max} at 420 nm identical to that reported for $\mathbf{1}^{+\cdot}$ in MeCN.

The zeolite encapsulated radical cation has a lifetime in excess of 8 h in an argon atmosphere, but the diagnostic yellow color and the EPR signal disappear after approximately 2 h when air is introduced into the reaction mixture. Samples which had been purged with oxygen until the yellow color faded were extracted with THF and the products analyzed by GC or GC/MS. The products were identified by comparison to authentic samples as 1,5-dithiacyclooctane 1,5-dioxide **2** and 1,5-dithiacyclooctane 1-oxide **3**, and were formed in > 90 and < 7% yields, respectively (Scheme 1). This extractive workup procedure resulted in material balances in excess of 80% in all cases, consisting primarily of the products accompanied by only traces of 1,5-DTCO and an unidentified material.

Monitoring of the reaction in air by diffuse reflectance UV-VIS spectrometry (Fig. 1) for more than three half-lives demonstrated that the yellow color (λ_{max} = 420 nm band)



Scheme 1

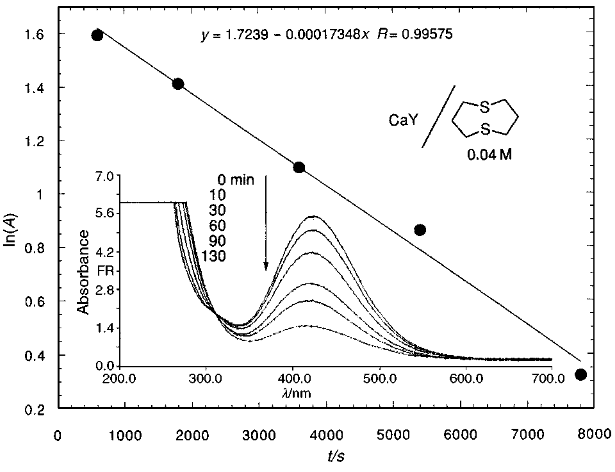


Fig. 1 Plot of the first order decay of the 420 nm band generated by encapsulation of 1,5-DTCO in CaY. Insert: diffuse reflectance UV–VIS spectra of the 1,5-DTCO/CaY sample in the presence of air showing the decrease in the 420 nm band and the isobestic point at 310 nm.

disappears in a strictly first order process. The presence of an isobestic point at 310 nm suggests a simple process, as shown in Scheme 1.

The overall process is initiated by a spontaneous formation of the 2σ–1σ* radical cation. Reported examples of spontaneous formation of sulfur-centered radical cations in the interior of zeolites are rare. Nevertheless, Roth and co-workers[4,5] have reported formation of both diphenyl disulfide and 2-phenyl-1,3-dithiane radical cations in ZSM-5. Electron transfer oxidations of encapsulate substrates [Scheme 1(*a*)] have often been discussed in terms of electron transfer to a Lewis acid or defect site formed during zeolite pretreatment or as an oxidation by absorbed oxygen.[1] The formation of $\mathbf{1}^{+\cdot}$ in CaY is clearly a function of its ease of oxidation. Radical cations were not formed in CaY calcined at 100 or 500 °C upon adsorption of 1,5-dithiacyclononane **4**, 1,4-dithiacycloheptane **5**, 1,3-dithiacyclohexane **6** or 1,4-dithiacyclohexane **7**. All of these bis(sulfides) are more difficult to oxidize than 1,5-DTCO as demonstrated by their oxidation potentials *vs.* Ag/0.01 M $AgNO_3$ in MeCN, shown in Fig. 2.

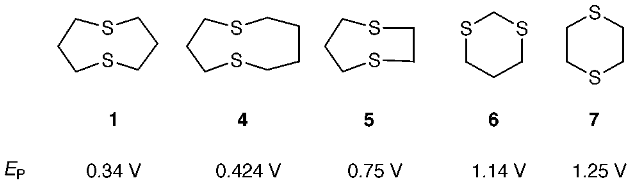


Fig. 2 Oxidation potentials of **1** and **4**–**7**.

The addition of O_2 to $\mathbf{1}^{+\cdot}$ [Scheme 1(*b*)] is unprecedented and is not observed in solution.[16] Asmus has attributed the lack of reactivity of oxygen with 2σ–1σ* sulfur centered radicals to an orbital mismatch between the LUMO on oxygen and the highly energetic antibonding electron in the σ* orbital on sulfur.[11] Consequently, oxidations of sulfur centered radical cations with molecular oxygen have only been accomplished at high O_2 pressures.[17,18] We suggest that the successful oxidation in the interior of the zeolite can be attributed to the proximity of the reducing agent, which traps the oxygen adduct [Scheme 1(*c*)] prior to its reversion to $\mathbf{1}^{+\cdot}$ and O_2. This reduction produces a persulfoxide which is a well established intermediate in the reactions of singlet oxygen with sulfides. The persulfoxide **A** (Scheme 1) has been independently produced by addition of singlet oxygen to 1,5-DTCO in acetone and is known to give predominately the bis(sulfoxide) **2**, identical to the result observed in the interior of the zeolite.[19]

In conclusion, we have demonstrated that CaY is limited in its ability to spontaneously produce sulfur-centered radical cations to easily oxidized sulfides. We further conclude that the reduction potential of the acceptor in CaY is approximately 0.4 V or less *vs.* Ag/0.01 M $AgNO_3$. In addition the minor amount of monosulfoxide **3**, which would be the expected product from reaction of the 1,5-DTCO dication with the residual water in CaY, reveals that the zeolite overwhelmingly functions as a one- rather than as a two-electron oxidizing agent. It is likely that 1,5-DTCO, once oxidized to the radical cation, is restricted in its ability to diffuse to a second oxidizing site to be converted to the dication.

The unprecedented discovery that CaY can promote oxidation at sulfur with only molecular oxygen as an oxidant has far reaching environmental and economic implications. A great need exists for an economical means of selectively oxidizing waste thioethers.[17,18] Further work with other zeolites to extend the generality of this important discovery will be reported in due course.

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