Oxidation and dehydrogenation of a phenol ether in a pentasil zeolite (Na ZSM-5): an EPR study

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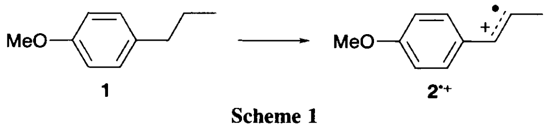
Incorporation of *p*-propylanisole 1 onto a pentasil zeolite (Na ZSM-5) gives rise to the EPR spectrum of anethole radical cation $2^{\cdot+}$; this conversion requires three separate oxidation steps alternating with two deprotonations, a reaction sequence of remarkable complexity for a room temperature reaction, albeit on the internal surfaces of a zeolite.

During the past thirty years the structures and catalytic properties of zeolites have been extensively investigated and many chemical reactions on the surface and in the micropores have been studied.[1–3] Recently, a method for the generation of π-type radical cations within the channels of pentasil zeolite at ambient temperatures has been reported, which appears to be general in scope and simple in practice.[4,5] The resulting radical cations have very long lifetimes and, hence, can be studied by conventional spectroscopic techniques.

Recently, we extended the scope of this method to the generation of σ-type neutral radicals (iminoxyls) from oximes.[6,7] In the formation of these free radicals the zeolite played the dual role of one-electron oxidant and proton acceptor. Here we describe the extension of zeolite-induced oxidation to phenol ethers and report the conversion of *p*-propylanisole **1** to the radical cation $\mathbf{2}^{\cdot+}$ of anethole (Scheme 1).

Incorporation of phenol ethers into the channels of Na ZSM-5 zeolite[8,9] causes light colorations in the sample. After washing and evaporation of the solvent the zeolite samples loaded in this fashion show strong and persistent EPR spectra characteristic of organic free radicals with line widths of $\leqslant 2$ G. Anethole **2** is oxidized with particular ease; upon addition of this substrate to a suspension of the zeolite in dry 2,2,4-trimethylpentane the sample immediately turned light blue. The EPR spectrum of the dried zeolite measured after washing and evaporation of the solvent indicates the presence of an organic free radical (g = 2.0032 ± 0.0002) with four strongly coupled nuclei ($A \sim 11$ G; Fig. 1). The central portion of the EPR spectrum is well resolved, showing hyperfine couplings as small as 2 G. The line width increases upfield or downfield from the centre, indicating that the hyperfine and g factor anisotropies are not completely averaged. This finding is compatible with a radical ion whose motion in the cavities of the zeolite is somewhat restricted.

The persistent radicals appear to be sequestered in the channels of the zeolite, since any radicals formed on the external surface of the zeolite are expected to either decay or be removed by washing. Indeed, the light blue coloration observed upon mixing the reagents is very likely due to free radicals or radical ions on the external surface of the zeolite. These radicals, and the corresponding coloration, are removed (or reduced) by washing.



1 $\mathbf{2}^{\cdot+}$

Scheme 1

Surprisingly, we observed the identical EPR spectrum upon addition of *p*-methoxypropylbenzene **1** to the zeolite. A comparison of this EPR spectrum with those of *p*-methylanisole (quartet of quartets; A = 15.0, 3.9 G)[9,10] or *p*-ethoxytoluene radical cations (quartet of triplets; A_{3H} = 15.0 G, A_{2H} = 4.7 G)[9] shows that it is incompatible with the simple one-electron oxidation of the phenol ether **1**. Instead, it suggests that **1** is converted on the internal surfaces of the zeolite to the radical cation $\mathbf{2}^{\cdot+}$ of anethole. This conversion can be explained by three separate oxidation steps alternating with two deprotonations, a reaction sequence of remarkable complexity for a room temperature reaction on the internal surfaces of the zeolite. Alternatively, the initially formed radical cation $\mathbf{1}^{\cdot+}$ may be dehydrogenated by an active site of the zeolite.

To the best of our knowledge, the radical cation $\mathbf{2}^{\cdot+}$ has not been observed by EPR spectroscopy before; however, it has been generated and characterized in solution by photo-induced electron transfer to triplet quinones.[11,12] Schilling and Roth found strong CIDNP emission for the allylic methyl signal and strongly enhanced absorption for the alkenic β- signal, demonstrating a large positive hyperfine coupling (HFC) for the allylic nuclei and a sizeable negative HFC for the β-proton.[11] Eckert and Goez showed that anethole cation–semiquinone anion pairs undergo back electron transfer in the triplet manifold, giving rise to triplet 1,4-biradicals and, ultimately, to Paterno–Büchi-type oxetane products.[12] AM1 calculations showed significant hyperfine coupling constants for the α- (+2.3 G) and β-protons (−5.5 G), and for the allylic methyl group (+4.9 G).[12] In agreement with the CIDNP results, we identify the four strongly coupled nuclei as those of the allylic methyl group and the alkenic β-proton. The calculations also indicate these nuclei as the most strongly coupled; however, the coupling constants measured in the zeolite are twice as large as the calculated ones.[12] In addition, the EPR spectrum documents the presence of at least two nuclei with smaller HFCs.

The magnitude of the major HFC determined for $\mathbf{2}^{\cdot+}$ is compatible with known experimental splittings of more or less

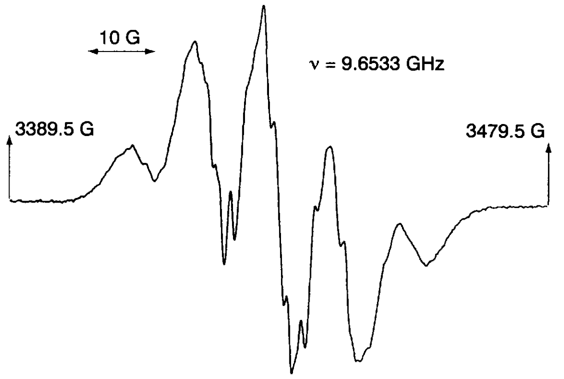


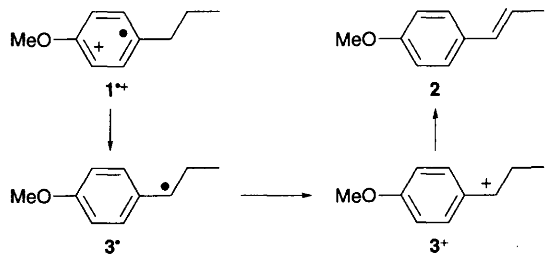
Fig. 1 X-Band EPR spectrum of anethole radical cation $\mathbf{2}^{\cdot+}$, sequestered in pentasil zeolite (Na ZSM-5). The four strongly coupled ^{1}H nuclei in the radical cation ($A \sim 11$ G) are assigned as the alkenic β- proton and those of the allylic methyl group.

closely related radical cations. For example, the styrene radical cation has splittings of 11.0 G for the alkenic β proton;[13] this value was reproduced well by INDO calculations ($A_\beta = -11.1$ G).[13] Similarly, the methyl groups of 1,1-diphenyl-2-methylpropene radical cation shows splittings of 14.7 G.[13]

The conversion of **1** to **2**$^{\cdot+}$ amounts to a three-electron oxidation plus a double deprotonation. Since the detailed nature of the redox-active site in the zeolite is subject to speculation and debate,[14–18] the detailed mechanism leading to **2**$^{\cdot+}$ poses similar questions. The conversion can be rationalized *via* the initial generation of **1**$^{\cdot+}$ by one-electron transfer (Scheme 2) followed by deprotonation of the primary radical cation to the benzyl radical **3**$^{\cdot}$. Both steps are well documented and have precedent in the formation of iminoxyl[6,7] or phenoxyl radicals.[9] Oxidation of the benzyl radical **3**$^{\cdot}$ to the cation **3**$^{+}$ should proceed readily, given the established oxidation strength of the zeolite ($E_{\text{ox}} \sim +1.65$ V *vs.* SCE)[4,5] and the relatively low oxidation potentials of benzylic free radicals.[19] The second deprotonation, forming the styrene derivative **2**, has ample precedent for a wide variety of carbocations, and the final oxidation has been demonstrated independently (*vide supra*).

Three of the potential individual steps are known to occur in the zeolite; the remaining two are expected to occur readily. It is an interesting question whether this reaction sequence can be accomplished on a single active site in the zeolite, or whether it involves the cumulative action of several sites, *i.e.* migration of an intermediate to another site in the zeolite. In order to elucidate this question, we compared the approximate yield of **2**$^{\cdot+}$ obtained from the two precursors. The zeolite has a 'capacity' of *ca.* 2×10^{-4} mol g^{-1} and an 'activity' of *ca.* 2×10^{-7} mol g^{-1}.[4] At the level of maximum loading, comparable quantities of **1** and **2** generated comparable EPR intensities for **2**$^{\cdot+}$, supporting the view that the entire conversion of **1** to **2**$^{\cdot+}$ is achieved on one reactive site of the zeolite.

While π-type radicals have been previously generated in zeolites, the experiments descibed here document an interesting unprecedented reaction, the equivalent of a five-step reaction sequence, in this medium under mild conditions. We are currently exploring the expansion of our findings to the generation of additional σ- as well as π-type radicals.



Scheme 2

Support of this work by the National Science Foundation through grant NSF CHE-9414271 and an equipment grant NSF CHE-8912238 is gratefully acknowledged. We are indebted to Drs D. Corbin and V. Ramamurthy of the DuPont Company and Tulane University for a generous sample of Na ZSM-5.

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Received, 24th June 1996; Com. 6/04481F