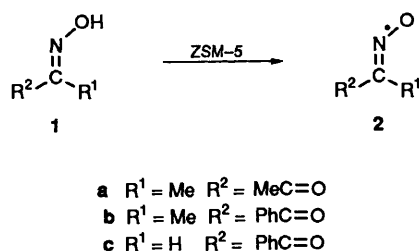# Generation and EPR Spectra of Iminoxyl Radicals in a Pentasil Zeolite

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Incorporation of acetyl or benzoyl oximes into the channels of a pentasil zeolite (ZSM-5) gives rise to iminoxyl radicals which show characteristic solid state EPR powder patterns.

During the past 30 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 pi-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 life times and, hence, can be studied by conventional spectroscopic techniques. We have extended the scope of this method to the generation of sigma-type neutral radicals derived from oximes 1.

a R^1 = Me R^2 = MeC=O
b R^1 = Me R^2 = PhC=O
c R^1 = H R^2 = PhC=O

The iminoxyl radicals 2 so generated have been investigated by electron paramagnetic resonance (EPR) spectroscopy and their identity established by comparison with EPR data obtained in benzene solutions. Iminoxyl radicals are sigma-type radicals, whose spin density is essentially confined to the sp^2 hybrid orbital on the nitrogen and a p-orbital on oxygen. They are characterized by large isotropic ^{14}N hyperfine coupling constants in the range 25–35 G.[6-11]

We have investigated the oxidative deprotonation of acetyl and benzoyl oximes, viz., butane-2,3-dione monoxime (1a), 1-phenylpropane-1,2-dione 2-oxime (1b), and phenylglyoxaldoxime (1c). For example, incorporation of 1a into the channels of a zeolite (Na ZSM-5)† gives rise to an EPR spectrum with a powder pattern characteristic of a free radical with axially symmetric g and hyperfine tensors (Fig. 1). The $g_{\parallel}$ and $g_{\perp}$ components are split into 1:1:1 triplets due to the hyperfine interaction with a ^{14}N nucleus ($I = 1$; $A_{\parallel} = 45.7$, $A_{\perp} = 26.7$ G). The central portion of the spectrum shows a three-proton hyperfine interaction ($I = \frac{1}{2}$, $A_{iso} = 1.9$ G). A comparison of the EPR powder spectrum of (3-oxobut-2-ylidene)aminoxyl (2a) in the zeolite with the spectrum observed in frozen solution‡ shows an excellent match between the parallel components. We interpret this finding as evidence that
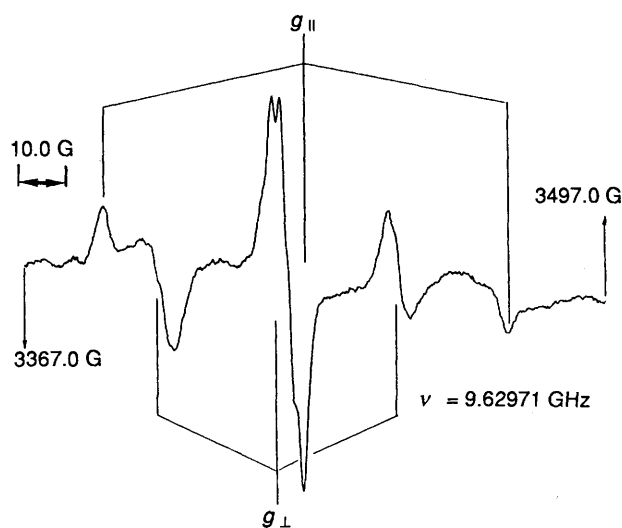
† EPR samples were prepared by stirring 3–5 mg of the oxime with 70 mg of zeolite (Na-ZSM-5, thermally activated by calcination at 500 °C for 12 h, and stored under Ar) in 10 cm³ of 2,2,4-trimethylpentane for 2 h. The loaded zeolite was collected by filtration, washed with hexane, and dried in vacuo [0.001 Torr (1 Torr = 133 Pa)].
‡ Iminoxyl radicals were prepared by condensing thoroughly degassed benzene onto a solid mixture of oxime and lead tetraacetate at −78 °C. After warming the sample to room temp. to allow the formation of the iminoxyl radicals, the EPR spectrum was recorded at room temp. or 77 K.

Fig. 1 X-Band EPR spectrum of iminoxyl 2a, sequestered in pentasil zeolite (Na ZSM-5). The spectral features assigned to the parallel and perpendicular components, $A_{\parallel} = 45.7$ and $A_{\perp} = 26.7$ G, respectively, are indicated.

the radicals generated in the zeolite are not undergoing motion which would cause an averaging of the spin Hamiltonian parameters. On the other hand, an exact comparison between the perpendicular EPR components in zeolite and frozen solution is difficult, because the spectrum in frozen solution is complicated by the presence of aminoxyl radicals and possibly, dimers.[12] The isotropic parameters calculated from the powder spectrum observed in the zeolite match the corresponding parameters measured in solution reasonably well (Table 1).

Very similar spectral patterns are obtained for (1-oxo-1-phenylprop-2-ylidene)aminoxyl (2b). The (2-oxo-2-phenyleth-2-ylidene)aminoxyl (2c) shows an additional splitting due to the azomethine hydrogen ($A_{\parallel} = 8.8$, $A_{\perp} = 2.9$ G). The maximum hyperfine coupling component (A_{zz}) for this hydrogen is oriented nearly perpendicular to the direction of maximum coupling for the ^{14}N nucleus.

The lifetime of the iminoxyl radicals generated in pentasil zeolite is about 2–3 days in contrast to tens of minutes in benzene solutions. We propose that the radicals are sequestered in the channels of the zeolite, since any radicals formed on the external surface of the zeolite would either decay or be removed by washing. The generation of iminoxyl radicals from oximes requires one-electron oxidation as well as proton loss. The presence of oxidation centres in the channels of pentasil zeolite has been established,[4,5] but the detailed mechanism of the oxidation–deprotonation is, as yet, unclear. Our attempts to obtain iminoxyl radicals were successful only for oximes with a carbonyl group on the azomethine carbon.

While pi-type radicals have been previously generated in zeolites, our experiments are the first to succeed in the generation of sigma-type radicals; in these species the spin is

Table 1 Magnetic parameters of iminoxyl radicals in ZSM-5 and benzene solution

Radical	$g_{\parallel}$	$g_{\perp}$	$g_{avg}{}^{b}$	$g_{iso}{}^{c}$	^{14}N hfc/G				^{1}H hfc/G^{a}			
					$A_{\parallel}$	$A_{\perp}$	$A_{avg}{}^{b}$	$A_{iso}{}^{c}$	$A_{\parallel}$	$A_{\perp}$	$A_{avg}{}^{b}$	$A_{iso}{}^{c}$
2a	2.0022	2.0056	2.0045	2.0048	45.7	26.7	33.0	30.7	—	—	—	—
2b	2.0023	2.0053	2.0042	2.0045	47.3	28.2	34.5	32.6	—	—	—	—
2c	2.0030	2.0068	2.0053	2.0046	44.1	29.1	34.1	29.1	8.8	2.9	4.9	5.8

^{a} Azomethine–^{1}H coupling. ^{b} $g_{avg} = (g_{\parallel} + 2g_{\perp})/3$; $A_{avg} = (A_{\parallel} + 2A_{\perp})/3$. ^{c} Prepared by lead tetraacetate oxidation in benzene.^{i}

localized in one function of the molecule and is not stabilized by conjugation. The radicals appear to be held rigidly in the channels of the zeolite; this may account for their increased stability. We are currently exploring the generation of other sigma- or pi-type radicals in pentasil zeolite by incorporating substrates with functional groups containing nitrogen, sulfur or phosphorus.

Acknowledgements

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