First Direct Observation of Neutral Radicals in a Zeolite at Ambient Temperature

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Cyclohexadienyl radicals have been observed in Na-X zeolite at ambient temperature by means of the muon spin rotation technique.

This communication reports the first observation of neutral organic radicals, *viz.* cyclohexadienyl, in a surface adsorbed state in a zeolite (Na-X) at ambient temperature. This has been accomplished by means of the transverse-field muon spin rotation (TF-μSR) technique,[1]† and is especially significant in a number of respects. While radical cations have been studied in zeolites using ESR spectroscopy,[2] and neutral radicals on pure silica surfaces by the muon (avoided level crossing) technique,[3] all previous attempts to observe directly neutral radicals in zeolites at catalytically relevant temperatures have failed.

Neutral radicals have been proposed to mediate the initial C–C bond forming step in the conversion of methanol to

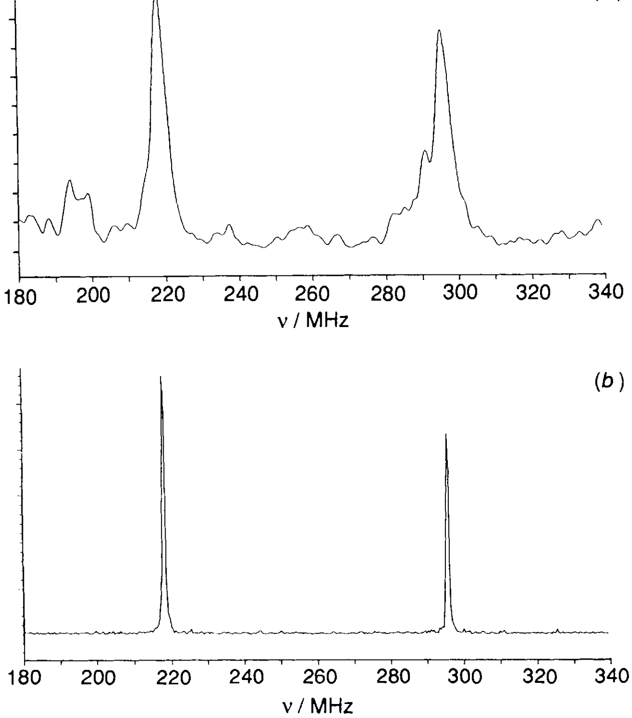

Fig. 1 TF-μSR spectrum recorded at 298 K from cyclohexadienyl radicals (*a*) in Na-X zeolite and (*b*) in liquid benzene. Note greatly increased linewidths in (*a*).

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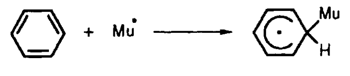
† Full details of the TF-μSR technique have been reported previously,[1] but the following summarises those aspects relevant to the present study. By implantation of positive muons (μ^+) into either liquid or Na-X adsorbed benzene samples (3 molecules per unit cell), association between radiolytically produced electrons and thermal muons occurs to form a bound state (μ^+e^-) which is usually dubbed 'muonium', and is often given the chemical symbol Mu$^•$. Mu$^•$ behaves as an isotope of hydrogen (but with a mass 1/9 that of protium) and will add to unsaturated organic molecules, *e.g.* to benzene to give a cyclohexadienyl radical, eqn. (1). The sample is maintained in a



(1)

transverse magnetic field about which the muon spins undergo precession, being spin $I = ½$ particles. Muons decay to form positrons on a microsecond timescale, and by counting the positrons as a function of time, the muon precession frequencies are revealed. Those muons which find their way into diamagnetic environments undergo precession at the muon Larmor frequency, but two lines are observed in high magnetic fields for each free radical that is formed, corresponding to the population of radical states in which $m_s = +½$ (low-frequency, ν_1) or $m_s = -½$ (high frequency, ν_2), in analogy with the more familiar ENDOR (electron nuclear double resonance) spectroscopy, and the muon-electron hyperfine coupling is obtained as the sum $[A = \nu_2 + \nu_1]$ of the two frequencies, which are of different sign, *i.e.* $A = \nu_2 - (-\nu_1)$. Chemical reactions, or physical processes which modulate anisotropic magnetic interactions, cause line-broadening in the same way as with conventional magnetic resonance methods.

gasoline on H-ZSM-5, but have only been detected indirectly by spin trapping from the gas-stream,[4] and therefore no information is available regarding the behaviour of such radicals within the zeolite network. However, as shown in Fig. 1(*a*), the TF-μSR technique is able to detect cyclohexadienyl radicals formed on the surface of Na-X zeolite, and so is of value to the study of intermediates in real catalysts.

This result is all the more important in that the spectrum was obtained in the presence of a high concentration of reactive substrate (benzene), and at 298 K. This contrasts with both the usual surface-science methods, which require the use of high-vacuum techniques, and normal ESR, which is limited to low-temperature studies in order to suppress radical diffusion and termination with concommitant rapid signal loss.‡ Thus, information on the mobility of transient radicals is not readily available from conventional magnetic resonance methods, but is provided by TF-μSR from the lineshape of the adsorbed radicals. Compared with the spectrum [Fig. 1(*b*)] of cyclohexadienyl in liquid benzene ($\lambda = 1\ \mu s^{-1}$) it is apparent that the lines are broadened appreciably ($\lambda = 8\ \mu s^{-1}$) in the adsorbed state. However, detailed analysis shows that these lines are still Lorentzian and so the situation is not that of a randomly disordered state, nor is there preferential rotation about an axis perpendicular to the ring plane, but a motion that is effectively isotropic since there is no resolution of the lines into a pattern compatible with either rhombic ($A_x \neq A_y \neq A_z$) or axial ($A_x \neq A_y = A_z$) anisotropic hyperfine couplings.

An attractive possibility is that the cyclohexadienyl radicals are diffusing isotropically over the internal surface of the spherical 1.3 nm supercage, but that the motion is partially impeded by virtue of the adsorption. The muon-electron coupling constant is barely increased in the zeolite (514.2 MHz) compared with that in liquid benzene (513.9 MHz), but the enhanced linewidths eliminate the possibility that the radicals are located in local liquid-like phases in the zeolite network.

Detailed temperature and concentration studies are ongoing to reveal further the effect of surface adsorption on reactive radicals in zeolites. However, we feel that the present communication shows the great potential of TF-μSR (and related techniques such as ALC) to the study of the dynamics and reactivity of transient radicals in a range of heterogeneous catalysts, and under conditions of high substrate concentration and temperature that would exclude other methods.

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‡ Particular advantages of TF-μSR over conventional ESR spectroscopy are (*i*) extreme sensitivity, since single-particle counting is employed, and (*ii*) that radicals are generated continuously and so signals can be accumulated over long periods, and at high temperatures of catalytic relevance. The normal approach in ESR is to first generate a concentration of radicals sufficient to give good signal-to-noise, and at low temperature in order to trap them, and then to raise the temperature: unfortunately, efficient radical combination and concomitant signal loss ensues at much lower temperatures than are accessible to μSR, as surface diffusion sets in. The above is true of neutral radicals, but some radical cations are sufficiently stable to be observed by ESR at room temperature,[1] most likely as a result of strong electrostatic surface forces that impede translational diffusion between channels.