REVIEW

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Muonium—the second radioisotope of hydrogen—and its contribution to free radical chemistry

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1 Overview

Muonium (Mu)—a radioactive hydrogen atom with a positive muon as its nucleus—is formed in a range of media when these are irradiated with positive muons. This exotic hydrogen isotope may be thought of as a second radioisotope of hydrogen—*after tritium*. Addition of this light atom to unsaturated organic molecules forms *free radicals*, in which the muon serves as a radioactive probe of their kinetic and structural properties. Suitable examples are chosen to illustrate the very large functionality of organic radicals which have been measured using muons; the techniques employed, collectively termed μSR (MuSR), are outlined from a *chemical* point of view. Particular applications of the MuSR methods are described, including the mechanisms for radical formation, the measurement of radical stabilisation energies, kinetics of reactions of free muonium atoms and of free radicals, and the structural and mechanistic interpretation of reaction rates. It is further shown that MuSR is most useful in measuring radical reaction rates in non-aqueous media, to provide information of relevance to cell membrane damage and repair. Muonium may further be used as a mechanistic probe since it determines a true pattern of H-atom reactivity in molecules, against which results from similar radiolysed materials may be compared. The application of MuSR in studying the reorientation of reactive radicals on reactive surfaces forms the subsequent part of the review: considered specifically are radicals in zeolites, in clays and in silica particles, and in porous carbons, in their role as intermediates in catalytic systems (hydrocarbon cracking and oxidation), and in atmospheric aerosol chemistry.

2 Introduction

The involvement of free-radicals in Nature is so widespread that they have entered not only the scientific but the public consciousness. Nonetheless, studying radicals, especially reactive radicals, as they frequently are, is rather difficult. Most physical-organic chemists are familiar with ESR (electron spin resonance)—now often dubbed E*P*R (electron *p*aramagnetic resonance)—as a principal means for detecting radicals, but even this powerful method often lacks the sensitivity required to accomplish the task. There are, however, methods available for the detection of radicals with enormous sensitivity and specificity which are given the collective acronym μSR (MuSR). All the MuSR methods involve a radiolabelling strategy, since they rely upon the addition of the light hydrogen atom "muonium"—a radioactive hydrogen atom with a positive muon as its nucleus, having a mass $\frac{1}{9}$th that of a protium atom—to an organic substrate. Muonium may be considered, therefore, to be a *second* radioisotope of hydrogen, after tritium, but it is much shorter-lived (tritium has a mean lifetime of 17.7 *years*, but muonium lives for just 2.2 *microseconds*!).

In addition to its property of radioactive decay, the muon also has spin, and therefore experiments akin to those of conventional magnetic resonance may be undertaken. However, the experiments which are rendered possible by muons are *unique*, and have no practicable counterpart in more conventional techniques. In particular, the feature of single-particle-counting methods being used in combination with nuclear spins which are 100% polarised (*i.e.* vastly in excess of the Boltzmann factor!) permits unparalleled sensitivity regarding reactive radicals. Through the incisiveness of these methods, knowledge in the field of free radical chemistry has been gained that would be unachievable using the more established methods of EPR and its relatives.

In order to do such experiments, it is necessary to obtain access to one of the several muon facilities which are distributed around the world, particularly the Paul Scherrer Institute (PSI; Switzerland); the ISIS facility at the Rutherford Appleton

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Laboratory (RAL; UK); TRIUMF (Canada) and KEK (Japan). My group works mainly at PSI and RAL. As is usual with sophisticated techniques, we have borrowed MuSR from the physicists, and it is they who remain by far the greatest in number as muon users. Nonetheless, muon *chemistry* has been active for over two decades, and much has been accomplished through its agency, as this review aims to show. Before I began writing this article, it was impressed upon me that I should focus on the *physical-organic* aspects of MuSR; consequently, the review material is chosen in an attempt to trace the essential development of this area. There is some arbitrary element of selection in this, but the coverage begins in the mid-1980's, when free-radical kinetics and structural studies of radicals were of paramount focus. They remain important topics, but have developed, in hand with prevailing technology, into unique investigations of free-radical processes on reactive surfaces, in efforts to comprehend the involvement of radicals as reactive intermediates in zeolites catalysis and in reactions of pollutants on solid atmospheric aerosols. Due to the power of MuSR methods, although my own background is in EPR, my research group has become increasingly involved in the techniques of MuSR, especially in regard to catalytic systems and in heterogeneous environmental processes, and for the measurement of free radical reaction rates pertinent to biological membrane damage and repair. These are all topics whose investigation we could not have attempted without muons.

I have tried to minimise the duplication of re-reviewing material which already exists in the detailed and lucid critiques referred to and I invite the reader to consult these for more specific details of many of the techniques employed using muons. Important examples are further reinforced, however. This article is intended to provide a broad overview of the many possibilities offered by MuSR to chemists in general.

3 Background to MuSR

3.1 Muonium as a radiolabel

Muonium, a radioactive hydrogen atom with a positive muon as its nucleus, is formed *in situ* in materials when they are irradiated with positive muons (μ^+). Thus the method is one of radiolabelling, and is used extensively in mechanistic and kinetic studies of molecular processes.[1,2] As an isotopic *hydrogen* label, tritium (^3H) is often used, since its nucleus has spin ($I = \frac{1}{2}$) so NMR experiments are feasible, and being also radioactive, may be detected by scintillation counting of the β-particles (electrons) produced in its decay [eqn. (1)]. Indeed, ^3H is usually considered *the* radioisotope of hydrogen. Since the muon is radioactive, also being a β-emitter [eqn. (2)], muonium atoms, either free or bound in molecules, may similarly be detected by scintillation counting; it is, however, a positively charged electron (*positron*) which is produced, since μ^+ is "anti-matter"!

The muon has a *half life* of 1.52×10^{-6} s, and a *radioactive decay constant* of $0.455 \times 10^6\ s^{-1}$, so setting a "microsecond" timescale over which kinetic processes may be studied using muons.

$$ {}_1^3H \longrightarrow {}_2^3He + e^- \tag{1}$$

$$ \mu^+ \longrightarrow e^+ + \nu_e + \bar{\nu}_\mu \tag{2}$$

$$ \pi^+ \longrightarrow \mu^+ + \nu_\mu \tag{3}$$

In eqns. (2) and (3), ν_e is an electron-neutrino, ν_μ is a muon-neutrino, $\bar{\nu}_\mu$ is a muon *anti*-neutrino and π^+ is a pion.

$$ \mu^+ + e^- \longrightarrow Mu^\bullet \tag{4}$$

Though they are present in cosmic radiation, muons are needed in high fluxes for research purposes, and are produced using a particle accelerator, by which means a beam of energised protons is caused to impinge on a beryllium or a carbon target. Among the products of the ensuing nuclear reactions are pions (binding components of nuclei), which decay on a nanosecond timescale to form muons [eqn. (3)]. Depending on the charge of the pion, either positive or negative muons are formed in their decay: negative muons find application, *inter alia*, in the promotion of nuclear fusion, while their positive counterparts can be applied particularly to chemistry, biology, materials and catalysis research.[3]

Muonium atoms (μ^+e^-; $Mu^\bullet$) may be formed *in situ* in a range of liquid, solid and gas phase samples, according to eqn. (4), where e^- is a radiolytic electron. Muonium is equivalent to a normal protium atom (p^+e^-) and indeed shows the chemical properties of a *light* hydrogen atom; if the sample contains unsaturated organic molecules, Mu can undergo an addition reaction. The method is highly specific for the study of free radicals, of which many types may be so formed, as is described in the section on structural studies of radicals. Some examples are shown in eqns. (5)–(7):

$$ R_2C{=}CR_2 + Mu^\bullet \longrightarrow R_2C(Mu)CR_2^\bullet \tag{5}$$

$$ R_2C{=}CR{-}CR{=}CR_2 + Mu^\bullet \longrightarrow R_2C(Mu){-}C(R)^\bullet{-}CR{=}CR_2 \tag{6}$$

$$ R_2C{=}O + Mu^\bullet \longrightarrow R_2C^\bullet{-}OMu \tag{7}$$

Since Mu is a "hydrogen" atom, it is expected that abstraction reactions will also occur, *e.g.* $Mu^\bullet + RH \longrightarrow MuH + R^\bullet$; however, the muon is then "lost" as muonic dihydrogen and does not contribute to the regions of the MuSR spectrum associated with free radicals, but instead, appears along with all other *non-radical* muons in the intense signal detected at the muon Larmor frequency (13.55 kHz G^{-1}).

4 The magnetic muon

4.1 Transverse-field muon spin rotation spectroscopy (TF-MuSR)[1,2]

Though the process outlined above may be viewed in connection with other isotopic labelling techniques, information akin to that obtainable from magnetic resonance experiments[4] is also available, since magnetic spectroscopic (hyperfine) interactions (couplings) are revealed through their influence on the positron count rate in designated detectors. The following is a description, specifically, of the transverse field muon spin rotation technique (TF-MuSR), in which each radical is characterised by a single pair of lines in its TF-MuSR spectrum (in high magnetic fields, applied transverse (at 90°) to the muon beam direction; Fig. 1), which represent the $-\frac{1}{2}, +\frac{1}{2}\ m_s$ electron spin combination with the muon (m_μ) states: these occur at the precession frequencies from muons which experience the sum of the applied and ($-\frac{1}{2},+\frac{1}{2}\ m_s$) hyperfine magnetic fields. [One can imagine the muon spin *rotating* around the axis of the applied magnetic field (Fig. 1), as the spin of a similar magnetic nucleus, following a 90° pulse of radiofrequency radiation in an "FT-NMR" experiment.][5] The muon–electron hyperfine coupling constant is obtained from

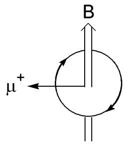


Fig. 1 μ^+ spin "rotating" under the influence of a magnetic field (*B*), applied *transverse* to the muon beam direction.

the difference between the high (ν_2) and low (ν_1) frequencies for each radical: $A_\mu = \nu_2 - \nu_1$; as the coupling increases, for a given magnetic field, the frequency ν_2 increases, while concomitantly ν_1 first decreases, reaches zero and then increases due to a sign change in the transition: in the latter limit the coupling is obtained from the sum of the frequencies: $A_\mu = \nu_1 - (-\nu_2)$. A representative example of an *actual* such TF-MuSR spectrum is that of PhCH$^\bullet$–OMu radicals, derived from benzaldehyde (Fig. 2). Given that *single-particle counting* methods are employed, and the muon spins are nearly 100% polarised (as compared with the Boltzmann factor, on which EPR and NMR depend), techniques involving muons are extremely sensitive (one *single* molecular radical is detected at a time by TF-MuSR).

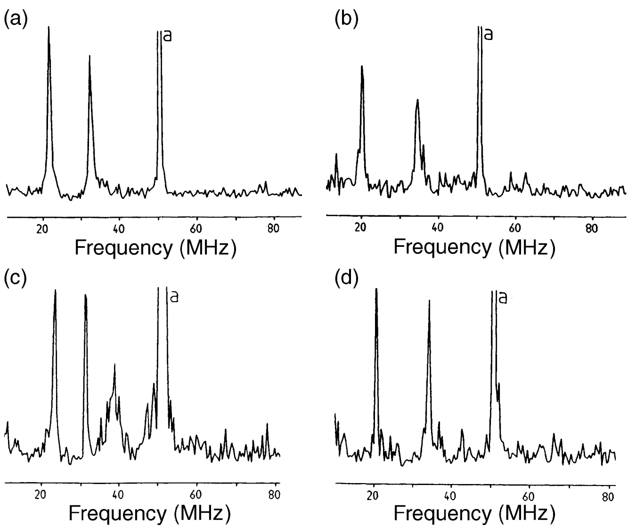


Fig. 2 TF-MuSR spectra recorded from radicals (a) *m*-Cl–C$_6$H$_4$CH$^\bullet$–OMu, (b) *p*-MeO–C$_6$H$_4$CH$^\bullet$–OMu, (c) PhCH$^\bullet$–OMu in ethanol and (d) PhCH$^\bullet$–OMu in cyclohexane; the signal "a" is the cyclotron frequency.

4.2 Avoided level crossing (ALC-MuSR) spectroscopy[6,7]

This is a quite different approach from TF-MuSR, since it uses a magnetic field applied in a direction longitudinal to that of the muon beam. In this case, the muon spins do not *rotate*, but "sit" along the magnetic field axis: what may be observed is the relaxation (change of spin orientation) of the muons, caused by resonant energy transfer with another magnetic nucleus ($\Delta m = 0$; "flip–flop" transition), or pure flips of the muon spins ($\Delta m = 1$), induced by anisotropic muon–electron magnetic dipolar couplings. Applications of ALC-MuSR have been reviewed by Roduner, both in the general context,[6] and as concerned specifically with studies of radicals sorbed on surfaces.[7] The reader is directed to these reviews and to the papers cited therein for details of the method, whose advantages, in structural determinations of muonated radicals, include the determination of hyperfine coupling constants of magnetic nuclei in the radical, other than the muon itself, and their sign relative to that of the muon hyperfine coupling.

4.3 Longitudinal-field muon spin relaxation measurements (LF-MuSRx)

This is a relatively new approach, but is a technique which shows promise in the study of the reorientational rates of sorbed radicals, which so far include: radicals sorbed in zeolites,[8–10] in activated carbon,[11,12] in silica[13] and in clays[10,13] and on a highly dispersed ice-surface.[14] Though it does not (certainly in its present simple form) approach the level of detail regarding determining molecular reorientation that is possible with ALC-MuSR, the method can provide an estimate of motional correlation times and so the activation energy associated with a particular kind of motion. The underlying theory appears fairly well understood,[15,16] and we note that studies have also been made of the intramolecular dynamics of radicals formed by muonium addition to Ph$_4$X (X = C, Si, Ge, Pb),[17,18] and to some metallocenes and benzene–metal π-complexes,[17,18] in which the muon acts as a spin-probe of torsional motion of the phenyl groups and of the overall motion of the cyclopentadienyl or benzene ring, about the metal atom. Similar torsional dynamics have been measured in samples of solid dipeptides.[19] The restricted overall molecular reorientation of the muonium adduct of the C$_{60}$ fullerene has also been measured by its LF-MuSRx.[20]

The physical basis of the method is one of resonance. In general, when the frequency of a particular molecular motion approaches that of the dominant spectral transition (ω) in the muon-electron coupled system,[15,16,20] there is an increase in the relaxation rate (λ) of the muon spins, as measured in a longitudinal magnetic field (LF). This reaches a maximum when the frequencies are equal, as shown in Fig. 3. Different motional regimes may be identified, and in some cases two maxima are measured (Fig. 4), corresponding to two distinct sorbed fractions, each with its own motional characteristics. Motional correlation times (τ) are extracted from the LF-relaxation rates (λ) *via* eqn. (8):

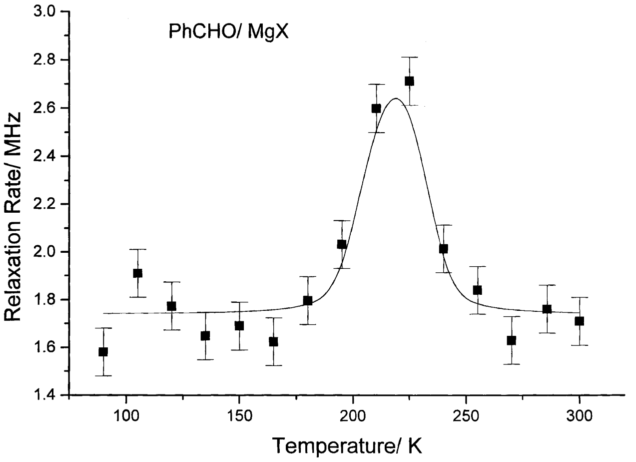


Fig. 3 LF-MuSRx plot for muonium adduct radicals formed from benzaldehyde sorbed in zeolite MgX, at a 20 wt% loading of benzaldehyde, showing a single maximum (see text).

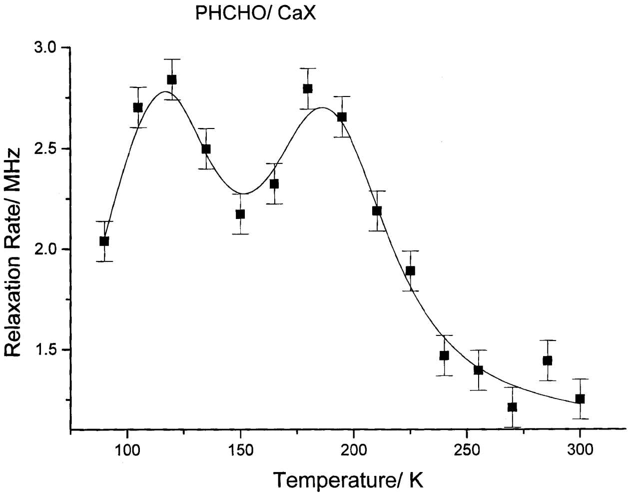


Fig. 4 LF-MuSRx plot for muonium adduct radicals formed from benzaldehyde sorbed in zeolite CaX, at a 20 wt% loading of benzaldehyde, showing 2 maxima (see text).

$$\lambda = (2\pi\delta A)^2\tau/(1 + \omega^2\tau^2) \qquad (8)$$

Here, δA is the variation in the hyperfine frequency during the motional event, and represents the anisotropy in the hyperfine interaction, the modulation of which relaxes the muon spin; ω is generally taken as the frequency of the $\langle 1| \leftrightarrow |2\rangle$ transition, which is strongly induced by this mechanism.[15,16,20] Since $\lambda = 1/T_1$, the maximum in the relaxation rate corresponds to a "T_1 minimum" familiar[4,5] in NMR and EPR spectroscopy.

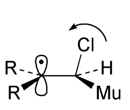
5 Structural studies of radicals

Other than muonium itself, the simplest radical so far detected using muons is "ethyl". This has been formed in its various isotopomeric forms by adding muonium to liquid samples of ethene and of deuterium substituted ethenes.[21,22] By analysing the temperature dependence of the muon hyperfine couplings in these radicals, estimates of the energy barriers for torsion about the C–C bonds were made (all were *ca.* 3 kJ mol^{-1}). They were interpreted in terms of pairwise interactions between the substituents, being smallest for a D–D, and largest for an Mu–H interaction, in accord with the view that the lighter isotope experiences a higher and the heavier isotope a lower degree of steric hindrance; the lighter isotope has in effect a larger interaction radius than the heavier isotope. The vibrational properties of the bound muonium atom in excited vibrational states of the $MuCH_2CH_2^{\bullet}$ radical were later studied theoretically, in which profound anharmonicity of the C–Mu bond was indicated.

There are many examples of hydrocarbon radicals which have been formed by muonium addition to alkenes, dienes and aromatic compounds,[1,2] from which some general trends emerge. In all cases, of which ethyl is the fundamental example, for conformationally unconstrained radicals, there is a hyperfine isotope effect[23] in which the muon has a coupling increased by a factor of *ca.* 1.4 from that for an equivalent proton, even after allowing for the fact that the magnetic moment of the muon is greater by 3.1833 than that of a proton. [This is usually referred to as the *hyperfine isotope ratio* (a_μ'/a_H), in which a_μ' is the muon coupling divided by 3.1833, in order to make a direct comparison with proton couplings]. The properties of muonated radicals appear overall very similar to those determined for normal hydrocarbon radicals by EPR techniques; the essential difference is that the bound muonium atom interacts more strongly with the unpaired-electron orbital: the coupling is increased both intrinsically, and by an increased weighting of conformations in which the C–Mu bond eclipses the orbital. In many cyclic systems, structural constraints prevent the conformational advantage and the hyperfine isotope ratio falls nearer to *ca.* 1.2; calculations[24a] indicate that a C–Mu bond is, on average, 5% longer than a C–H bond and so the intrinsic increase in the coupling may be viewed in terms of an increase in the limiting valence-bond structure: $Mu^{\bullet}$ C=C, compared with $H^{\bullet}$ C=C. The origin of the effect has been shown to be that of differential vibrational zero-point energy for the bound muon.[24b]

5.1 Substituent effects

In an effort to probe the effects of silicon, phosphorus and chlorine substituents on muonated radicals, the compounds $H_2C{=}CHSiMe_3$,[25] $H_2C{=}CHSi(OMe)_3$,[25] $H_2C{=}CHP(O)(OEt)_2$[26] and $Me_2C{=}CHCl$[25] were irradiated with positive muons. Although there are, in principle, two distinct radicals that might be formed when an asymmetrically substituted double bond is present, often the regioselectivity is such that only one radical is detected, according to the normal order of radical stability: tertiary > secondary > primary. This was the case for $Me_2C{=}CHCl$, which displayed a single radical with the relatively low muon coupling of 8.7 G. Since it is well known from EPR studies[27] that β-Cl substituents interact strongly with the unpaired-electron orbital, in the manner of an incipient bridging structure, the radical is $Me_2C^{\bullet}$–CH(Mu)Cl; the "bridging" effect distorts the structure displacing the β-"hydrogens" from efficient overlap with the unpaired-electron orbital and reduces their coupling (**1**). The greater stabilisation of this radical renders the absence of the alternative isomer. In contrast, both radical isomers were detected in each of the other compounds. It is suggested that, although $H_2C^{\bullet}$–$CH(Mu)SiMe_3$, $H_2C^{\bullet}$–$CH(Mu)Si(OMe)_3$ and $H_2C^{\bullet}$–$CH(Mu)P(O)(OEt)_2$, are formally "primary" radicals, the stabilising effect of the second-row substituent is sufficient to increase their relative yields to detectable limits. The muon couplings are all reduced from the value in ethyl,[21,22] $H_2C^{\bullet}$–CH_2Mu, indeed indicating a stabilising interaction, and a minimum energy conformation (**2**) in which the second-row substituent (X) eclipses the unpaired-electron orbital, preferentially over the muonium atom. $^{35/37}$Cl and ^{1}H couplings, to the unpaired electron, have been determined for the radicals $MuCH_2CH^{\bullet}$–CH_2Cl, $^{\bullet}CH_2CH(Mu)CH_2Cl$ and $MuCH_2C^{\bullet}(Me)$–CH_2Cl, using ALC-MuSR.[28] From the temperature dependences of the muon and ^{1}H couplings, rotational barriers all in the region of 2 kJ mol^{-1} were determined for the $MuCH_2$– and $MuCH(CH_2Cl)$– groups in these radicals; it is concluded that the presence of the muon is the major factor in determining the low energy conformation and not the type of substituents involved.



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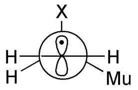

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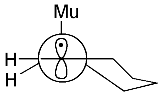

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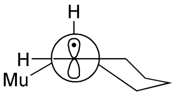

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5.2 Cyclic systems

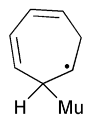
The hyperfine isotope ratio (a_μ'/a_H) is close to 1.2 for all cyclic radicals,[23] other than the cycloheptyl radical, formed by muonium addition in liquid cycloheptene, which shows a ratio of 1.38. Indeed, cycloheptyl appears unique in the considerable conformational freedom permitted within its ring-structure, such that conformations in which the C–Mu bond eclipses the unpaired-electron orbital may be achieved with little steric strain; thus the value is close to those measured for open-chain radicals.

Cyclopentyl has a more rigid structure. The parent cylopentyl radical has been studied by EPR,[29] in which the four β-hydrogens form a pseudo-axial and a pseudo-equatorial pair with distinct couplings; these are resolved below 102 K, but undergo dynamic averaging such that they appear equivalent above 216 K. The muonated cyclopentyl radical has been studied by TF-MuSR[24,25] and by ALC.[24] The results show that the muonium substitution makes only small changes to the overall ring conformation, but that an energy difference of 1.4 kJ mol^{-1} exists between those conformers in which the muon occupies either an axial or an equatorial site.

The muonated cyclohexyl radical is undetectable at ambient temperatures.[23,24a] EPR spectra of the parent cyclohexyl radical show pronounced line-broadening at ambient temperatures,[30] arising from modulation of the axial and equatorial β-proton couplings, which are resolved separately only below 186 K. Since the muon magnetic moment is larger than that of a proton by 3.1833, the difference in axial and equatorial couplings (frequencies) for the muonated species **3**/**4** is correspondingly greater than for the proton case. Assumption of an equal activation energy and frequency factor for the ring-inversion of cyclohexyl and its muonated version suggests that in order to observe the radicals **3** and **4** in slow-exchange, a further reduction in the temperature of 30 K would be required. At 153 K, two sets of signals were recorded[31] corresponding to muon couplings $a_\mu' = 48.8$ G and $a_\mu' = 6.4$ G, which are, therefore from the axial **3** and equatorial **4** isomers, respectively; comparison of these couplings with those for the parent cyclohexyl radical[30] leads to a hyperfine isotope ratio close to 1.2 for both conformers, suggesting that the radical exists in (and converts between) rigid chair forms, and cannot easily weight other conformations where the muon is more strongly coupled; an activation energy of 19 kJ mol^{-1} was deduced for the ring-inversion process, in good agreement with that obtained by EPR.[30]

A single form of the muonated 9-octalinyl radical was detected in a TF-MuSR study of liquid 9-octalin (1,2,3,4,5,6,7,8-octahydronaphthalene).[32] This was surprising since Lloyd and Williams had reported from an EPR study that the 9-octalinyl radical existed in distinct *cis* and *trans* forms, as formed by hydrogen atom abstraction from *cis* or *trans*-decalin (decahydronaphthalene).[33] The MuSR result shows that the radical centre is in fact planar, otherwise both isomers would be detected. This was confirmed by Roberts[34] who observed by EPR that the identical bridgehead radical is formed from either *cis* or *trans*-9-chlorodecalin; it appears that the radicals observed by Lloyd and Williams do not arise by direct abstraction of bridgehead hydrogen atoms from the decalin isomers, but have other causes.

A more complex case is that of cycloheptatriene, which can in principle form three radicals **5**–**7**, and indeed three pairs of signals are observed below 240 K, although a single species only is detected at 373 K.[35] The lines from the single radical broaden on cooling from 373 K, indicating it to be in the fast-exchange limit; it is assigned to the spin-localised radical **5** (the couplings quoted however, do not agree with the values indicated by the published spectrum, which appear similar to those measured previously for allyl-type radicals). One would expect to observe the allyl-type species **6**, yet it is concluded that this is unobservable due to dynamic (ring-inversion) effects. The lines from the two additional radical species detected below 240 K are observed to sharpen on cooling, and so are in the limit of slow exchange: they are assigned to the Mu-axial and Mu-equatorial forms of the dienyl-type radical **7**. Activation parameters are deduced for the exchange processes in these systems, which for **7** are very similar to those measured for the parent cycloheptatriene.



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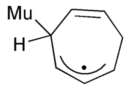

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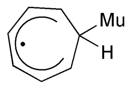

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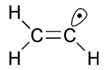
5.3 Acetylenes, allenes and butadienes

The first observation of radical formation by muonium addition to a triple bond was from phenylacetylene,[36] yielding principally $\mathrm{PhC^{\bullet}{=}CH(Mu)}$ along with minor amounts of its ring-adducts. This result contrasts with a similar experience with ethyne from which nothing was detected. An explanation for this is that the radical centre in the resulting vinyl radical $\mathrm{Mu(H)C{=}C^{\bullet}{-}H}$ behaves like that in the parent radical $\mathrm{H_2C{=}C^{\bullet}{-}H}$,[37] which executes a vibrational mode in which the unique hydrogen atom flips between the two sides of the molecule defined by its bent geometry **8**.[38] The coupling constants are approximately 64 G and 34 G respectively for the *trans* and *cis* β-protons in the fixed geometry of the vinyl molecule **8**, and are modulated between these limits by the dynamic process; this results in a line-broadening effect which broadens the TF-MuSR features beyond detection. Conjugation with the phenyl substituent in $\mathrm{PhC^{\bullet}{=}CH(Mu)}$ eliminates this effect by fixing the radical centre into an essentially linear geometry. Appreciable bonding character has been deduced between silicon substituents and first-row atoms, since they exert a dramatic influence on the bond-lengths and bond-angles in siloxanes and silylamines, and delocalise spin-density from the nitrogen centre in silylamine radical cations.[39] It seemed possible, therefore, that muonium addition to $\mathrm{Me_3SiC{\equiv}CH}$ might lead to the radical $\mathrm{Me_3SiC^{\bullet}{=}CH(Mu)}$ in which the $\mathrm{Me_3Si}$ group acts similarly to a phenyl substituent, *vide supra*, thus rendering it detectable. This was indeed the case,[40] while the alternative isomer $\mathrm{Me_3Si(Mu)C{=}C^{\bullet}{-}H}$, in which this effect is absent, remained invisible. EPR studies on the radicals $\mathrm{PhC^{\bullet}{=}CH_2}$[41] and $\mathrm{Me_3SiC^{\bullet}{=}CH_2}$[42] confirm that the radical centre is linear in both cases. A rare vinyl radical measured using MuSR, in which the radical centre is bent, is $\mathrm{Me_3SiC^{\bullet}{=}C(Mu)SiMe_3}$, since the muon coupling (a_μ') is a massive 82.2 G,[40] pointing to a strongly coupled *trans* configuration for the muon. As in the parent $\mathrm{Me_3SiC^{\bullet}{=}C(H)SiMe_3}$ radical,[43] this reflects an appreciable steric interaction between the two $\mathrm{Me_3Si}$ substituents which is minimised in their *trans* orientation; thus no inversion of the radical centre occurs.



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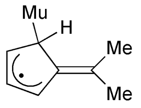
This chemistry was next extended to diacetylenes,[44,45] namely the compounds $\mathrm{MeC{\equiv}C{-}C{\equiv}CMe}$, $\mathrm{Me_3SiC{\equiv}C{-}C{\equiv}CSiMe_3}$ and $\mathrm{PhC{\equiv}C{-}C{\equiv}CPh}$. It is concluded that the major radical produced in each case is the C-1 adduct, *i.e.* the radicals, $\mathrm{Me(Mu)C{=}C^{\bullet}{-}C{\equiv}CMe}$, $\mathrm{Me_3Si(Mu)C{=}C^{\bullet}{-}C{\equiv}CSiMe_3}$ and $\mathrm{Ph(Mu)C{=}C^{\bullet}{-}C{\equiv}CPh}$. The muon coupling appears particularly large in $\mathrm{Me_3Si(Mu)C{=}C^{\bullet}{-}C{\equiv}CSiMe_3}$ (54.6 G), compared with 44.2 G in $\mathrm{Me(Mu)C{=}C^{\bullet}{-}C{\equiv}CMe}$, which led to its original ascription[44] as the alternative "localised" structure $\mathrm{Me_3SiC^{\bullet}{=}C(Mu){-}C{\equiv}CSiMe_3}$, but the new assignment is compelled by MO calculations[45] of both energies and coupling constants for these radicals. $\mathrm{PhC{\equiv}C{-}C{\equiv}Ph}$ forms additionally the C-2 adduct, $\mathrm{PhC^{\bullet}{=}C(Mu){-}C{\equiv}CPh}$, and a ring-adduct which is probably the *ortho* isomer.

One example of muonium addition to an allene derivative is known,[46] *viz.* $\mathrm{Me_2C{=}C{=}CH_2}$, which yields the radicals $\mathrm{Me_2C{=}C^{\bullet}{-}CH_2Mu}$ and $\mathrm{Me_2C{=}C(Mu){-}CH_2^{\bullet}}$. Both are structurally unique: in the former case, although the vinyl radical centre must undergo rapid inversion, the muon is placed in a position where it is invulnerable to the resulting relaxation effect for β-nuclei, so the radical is detected; the second species, an allyl radical, was the first example in which a muon occupies a position which is nodal to the π-system. A very small hyperfine isotope ratio of 1.04 was deduced, since the muon is subject to completely different hyperfine coupling mechanisms and dynamic effects than are muons in β-positions; a similar value[47] was reported by Percival *et al.* for the radical $\mathrm{Me_3SiCH(Mu)^{\bullet}}$ in comparison with its isotopomer $\mathrm{Me_3SiCH_2^{\bullet}}$.

A series of allyl radicals is known from muonium addition to a range of dienes, in which the muon again occupies a position β to the π-system, $\mathrm{R_2C(Mu){-}CR^{\bullet}{-}C(R){=}CR_2}$. These include some of the first radicals detected using TF-MuSR, and depending on the substitutional symmetry about the diene system, various isomeric species could be detected in some samples.[48] As is discussed later, heats of formation were calculated for these radicals and were used in an attempt to rationalise the mechanism by which they were formed; it was concluded that the muonium atom was the probable precursor, though a mechanism involving initial muon addition followed by electron capture at the resulting carbocations could not be disqualified.[48]

Muonium addition to 6,6-dimethylfulvene formed two radicals, which were deduced to be the C-1 adduct **9**, a dienyl radical, and the C-2 adduct **10**, an allyl radical, on the basis of ALC measurements.[49] This is a nice example of the utility of the ALC method since its evaluation of the proton couplings present in these radicals enabled their selection from the four possible candidates in this system. The muon couplings measured from 6,6-diphenylfulvene suggest that the C-1 and C-2 adducts are also formed, but are reduced from those in the 6,6-dimethylfulvene adducts, each by about 40%, because of additional spin delocalisation onto the phenyl substituents.[49]



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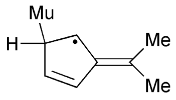

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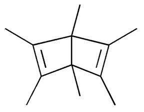

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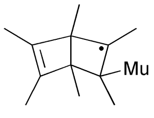

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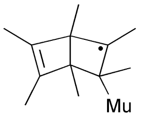

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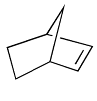

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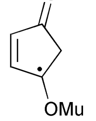
5.4 Cyclohexadienyl and bicyclic radicals

As with the other hydrogen isotopes, when muonium adds to benzene a cyclohexadienyl radical is formed. Due to the Whiffen effect,[50] which is the quantum mechanical reinforcement of the hyperfine interaction from a nucleus when it interacts with two positions of high spin-density, a large muon coupling a_μ' in the region of 58 G is found.[51] Additionally, the ^{1}H[6,7] and ^{13}C[52] coupling constants for cyclohexadienyl have been determined from ALC measurements, which indicate that substitution of protium by the muon causes little perturbation of the spin density distribution. Since cyclohexadienyl radicals are formed in high yield, and have been thoroughly characterised, they are frequently employed as molecular probes. For example, substituted benzenes may be used to evaluate substituent effects, both on the spin-density distribution in radicals[2] and in determining the relative yields of isomeric radicals,[51] which reveal the influence of substituents on the regioselectivity of the parent molecules toward radical addition. Additionally, cyclohexadienyl radicals, used in connection with the techniques of TF-MuSR, ALC and LF-MuSRx, provide unique information about the reorientational diffusion of radicals sorbed on reactive surfaces, *e.g.* those of zeolites, clays, silica, porous carbon and ice. More will be made later of these matters under their relevant headings.

Fulvene is an isomer of benzene, and so the fulvene–muonium adducts **9** and **10** might be thought of as isomers of the cyclohexadienyl radical. Dewar benzene also falls into this category, and muonium adducts of hexamethyl(Dewar)benzene (HMD) **11** have been characterised.[53] The dominant process is addition to the *exo* face of HMD **12** which occurs at four times the rate for the formation of the *endo* isomer **13**. The muon coupling is also largest for the *exo* isomer. TF-MuSR results for norbornene (bicyclo[2.2.1]hepta-2,5-diene) **14**[54] show that both *exo* and *endo* muonium adducts are similarly formed: the latter in greatest yield and with the larger of the two coupling constants. There are, therefore, parallels between both the reactivities of norbornene and HMD toward muonium, and the coupling constants of the radicals so formed. One possible explanation of the preferential muonium atom addition to the *exo* site in these systems is steric hindrance: approach to the *exo* site is less hindered than that to the *endo*, particularly in HMD.

5.5 Muonium adducts of C=O, C=S, C=N, N=N and NO$_2$ compounds

The C=O compound most often studied by MuSR is acetone, which yields the "muoxy-isopropyl" radical, $Me_2C^{\bullet}$–OMu, by addition to the oxygen atom of the C=O group.[55–66] Assuming that the relative order of bond energies for species X–Mu is approximately the same as that for X–H, it might reasonably be concluded that the driving force for this is the formation of an O–Mu bond, which might be 80 kJ mol^{-1} stronger than a C–Mu bond. Compared with most of the radicals so far considered, the muon coupling is very small, in the region of 2.8 G, its precise value depending both on solvation effects and temperature. $R_2C^{\bullet}$–OMu adducts cannot be thought of as effectively "localised", since *ca.* 20% of the spin-density lies on the oxygen atom:[56] this is a consequence of π-overlap between carbon and oxygen 2p$_z$ orbitals, which introduces partial C=O bonding character to the system. It is mainly this effect which causes the low coupling constant, since the bound muonium atom is thereby confined to a region of poor overlap with the spin-bearing atomic orbital on the carbon atom, and so receives little *positive* spin-density; additionally, there is a cancellation of this from *negative* spin-density arising from the spin on the oxygen atom, which polarises the O–Mu σ-bonding electrons. If the latter effect dominates, the coupling is of negative sign; it becomes increasingly positive as the out-of-plane vibrational amplitude of the muon increases, and so passes through zero, and becomes actually of positive sign for large enough amplitudes. This results in a strong temperature dependence of the muon coupling in $R_2C^{\bullet}$–OMu radicals which may be used to determine the sign of the muon coupling: according to the above argument, a steady increase in the coupling as the temperature increases means that its sign is positive, while a similar reduction shows that it is negative. In all examples bar one, the muon coupling is positive; the exception is **15**, in which the electronic "push–pull" effect within the MuO–$C^{\bullet}$–C=C–C=O unit increases the C=O π-bonding character of the MuO–C group so as to confine the muon to the region of negative coupling[67] (most likely, the sign would become positive if a high enough temperature could be achieved). It is noteworthy that the "push–pull" effect in this more extended π-system is stronger than in MuO–C(Me)$^{\bullet}$–C(Me)=O, derived from muonium addition to biacetyl,[55] since the coupling in the latter case, though very small, remains positive. Muonium addition to benzaldehyde results mainly in the radical $PhCH^{\bullet}$–OMu, which shows promise as a probe both of electronic substituent effects[65,66] and of molecule–cation interactions in cation exchanged zeolites.[10,65] The utility of $PhCH^{\bullet}$–OMu as a probe depends on variations in the muon coupling of similar origins to those just described; indeed, the muon coupling in $PhCH^{\bullet}$–OMu is acutely sensitive both to medium (solvation) effects and to the electronic demand of the aromatic ring.[65,66] Representative TF-MuSR spectra are shown in Fig. 2. The absolute value of the coupling varies from 0.88 G in ethanol to 1.51 G in cyclohexane, an increase of 73%; in a similar study, instead measuring the ^{14}N coupling in an aminoxyl by EPR, the difference was only 6%.[68] The effect of substituents in the aromatic ring is almost as dramatic, since the coupling varies from 1.19 G in the muonium adduct of *m*-chlorobenzaldehyde to 1.71 G in the *p*-methoxy derivative. A simple explanation can be provided in terms of the relative contribution of the canonical structures: $ArCH^{\bullet}$–OMu (I) ↔ $ArCH^{-}$–$O^{+\bullet}$–Mu (II), which is one description of the C=O π-bonding in the C–OMu unit. Hydroxylic solvents will tend to stabilise II, as will electron withdrawing substituents in the ring; electron releasing substituents will increase the weighting of structure I, so the coupling rises over that for the unsubstituted $PhCH^{\bullet}$–OMu radical (1.41 G). A detailed study has been made of the related radical, $Ph_2C^{\bullet}$–OMu, formed in a single crystal of benzophenone, in which all components of the muon hyperfine tensor have been determined: this is found to be dominated by the spin-density on the oxygen atom.[69]



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An attempt was made to extend the series to C=S adducts, which were expected to have fairly similar properties to $R_2C^{\bullet}$–Mu radicals. In fact, the results were surprising since couplings in the region of 50 G were found, but there was nothing in the low frequency region where signals from $R_2C^•$–OMu radicals had been detected.[70] Such large couplings led to the proposal that these were thiyl radicals, R_2(Mu)C–$S^•$ rather then the expected $R_2C^•$–SMu analogues; the single exception was the adduct of thiobenzophenone, with a coupling of *ca.* 7 G, which was ascribed as $Ph_2C^•$–SMu, an expectedly highly delocalised and stabilised radical. Kinetic studies[71] of these species have been made which, if they are indeed thiyl radicals, are of considerable biological importance; a caveat is appropriate, however, since a recent theoretical study indicates that, despite the large muon coupling, they are all S–Mu adducts.[72] This proposal awaits definitive experimental evaluation using ALC-MuSR, since it is necessary to measure the couplings from nuclei other than the muon to prove the case either way, but to be correct an unparalleled substituent effect must operate in $R_2C^•$–SMu radicals; unfortunately, there is almost no EPR data for $R_2C^•$–S*H* radicals with which to compare.

Some C=N adducts have been measured,[73] and the small couplings found are very similar to those for C=O adducts, as expected for a functional group, $R_2C^•$–N(R)Mu, which is structurally equivalent to $R_2C^•$–OMu in terms of π-overlap between the carbon and nitrogen $2p_z$ orbitals. The couplings are highly sensitive to hydrogen-bonding effects. Adducts of N=N bonds (*hydrazyl* radicals) $RN^•$–N(Mu)R,[74] form a related category, again showing small couplings limited by π-bonding within the N–N unit. Adducts of nitroalkanes, RN($O^•$)OMu, have also been characterised, and the temperature dependences of the *positive* muon couplings were rationalised in terms of calculated N–OMu torsional barriers.[75]

6 Mechanisms of radical formation

We have mainly used the term “muonium addition” to describe the formation of radicals in materials which are irradiated with positive muons, which implies that the act of forming a muonated radical involves the initial scavenging of an electron by a positive muon at near thermal energies, and the resulting muonium atom then adds to an unsaturated substrate molecule forming a radical. As we are reminded shortly by a comparison of MuSR results with those from related EPR studies, however, neutral radicals may also be formed in materials by the charge-neutralisation of initial (radical) ionic species; therefore, these routes should also be considered, *e.g.* for acetone [eqns. (9)–(12)]:

$$Me_2CO + \mu^+ \longrightarrow Me_2COMu^+ \qquad (9)$$

$$Me_2COMu^+ + e^- \longrightarrow Me_2C^•\text{–}OMu \qquad (10)$$

$$Me_2CO + e^- \longrightarrow Me_2CO^{-•} \qquad (11)$$

$$Me_2CO^{-•} + \mu^+ \longrightarrow Me_2C^•\text{–}OMu \qquad (12)$$

When the MuSR signal from free muonium can be detected in a (usually dilute, aqueous) medium, the concentration dependence of its linewidth can be used to determine reaction rates for actual Mu atoms with confidence, as is described subsequently. In terms of reactivity, Mu lies between H-atoms (protium) and hydrated electrons. Examples where Mu and H appear to react by different mechanisms[76] in their addition to (aza)benzenes,[77,78] and where Mu adds to the oxygen atom of a carbonyl group, but H instead abstracts a hydrogen atom from an adjacent alkyl group. It is difficult to be sure, in some cases, what path is taken by H, since product radicals detected by EPR are often not formed by a genuine H-atom reaction,[79] or the pH is strongly acidic,[80] as compared with a MuSR study made in a near neutral medium. The rate constants measured by Neta and Schuler[80] for radiolytically produced H-atoms in acidic solutions of substituted benzene show negative ρ in a Hammett plot of k_H *vs.* σ, whereas that for Mu addition to the neutral materials is positive,[76] indicating mildly nucleophilic character for Mu, whereas H is electrophilic to a similar degree.[80]

Walker has proposed that Mu adds to the carbon sites in pyrazine (1,4-diazabenzene),[77,78] but EPR studies are reported[79] which instead identify the N–H adduct, and this is taken to imply that the difference in *philicity* of the two isotopes leads to a different mechanism, the “electron releasing” Mu being directed to the nitrogen atoms. The problem is that like is not being compared with like, since the N–H radicals were in fact generated by a photochemical reaction,[79] involving electron-transfer to the base, followed by protonation, with no free H-atoms being formed; so any difference in mechanism is hardly surprising. We note that Gelabert *et al.*[81] have made a theoretical study of protium and muonium atom addition to pyrazine, which suggests that formation of the C–Mu adduct is more favourable than the N–Mu adduct, in agreement with experimental MuSR studies;[77] the C–H adduct is also predicted to be formed in preference to the N–H adduct. A similar scenario has been envisaged for pyridine,[78] but again, the N–H adduct radical, though detected by EPR in a number of studies,[82–84] is not formed by direct H-atom addition, but rather by charge-neutralisation of an initial ionic precursor.[85]

6.1 Muonium addition to imidazoles

The mechanism of muonated radical formation in purely organic media has been probed in several studies, the most recent being one of Mu–imidazole adducts.[73] For example, 1-methylimidazole shows the formation of 3 radicals, representing Mu addition to the 3 distinct carbon sites (no N-3–Mu adduct was detected): the ratio of the yields of these radicals (P_{Ri}/P_{Rmin}) represents the ratio of the rate constants for their formation, where P_{Rmin} refers to the minor radical formed in each system, and these are found to follow very closely the differences in the (PM3) calculated heats of formation ($\Delta\Delta H_f$) for the product radical isomers. For the series studied, a reasonable correlation ($r = 0.95$; Fig. 5) is found between ln (P_{Ri}/P_{Rmin}) and $\Delta\Delta H_f$, the exception being the Mu–CH_2CH– adduct of *N*-vinylimidazole, inclusion of which reduced r to 0.72. One might argue that this is due partly to a difference in the nature of the transition-state for “overall” Mu addition to the exocyclic C-atom compared with that for addition to the ring, but moreover, it is likely that the calculated heat of formation is too negative, as was the case for the Mu adduct of styrene

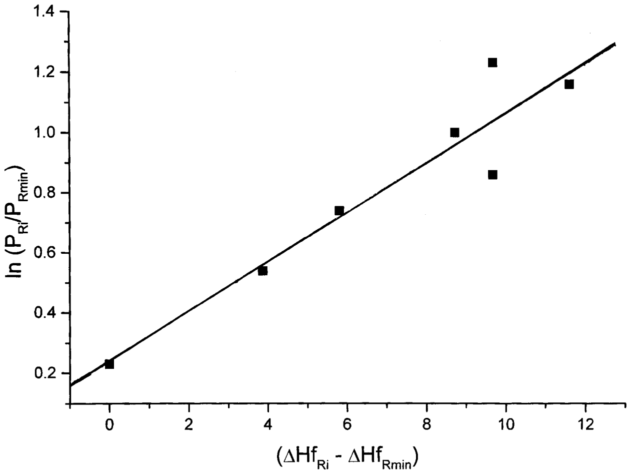


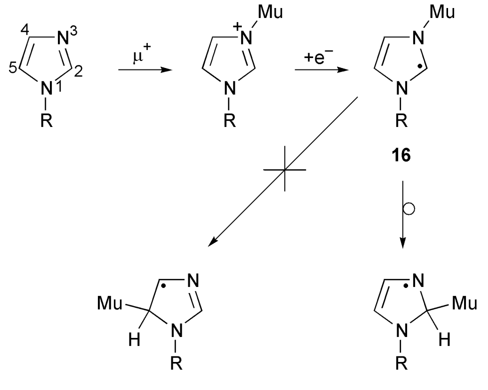
Fig. 5 Plot of (ln) yields of radicals in imidazole derivatives, relative to the yield of the minor isomer in each compound, ln (P_{Ri}/P_{Rmin}) *vs.* the differences in the PM3 calculated enthalpies of formation ($\Delta H_{f,Ri} - \Delta H_{f,Rmin}$) for these radicals. The straight line represents the fit: ln (P_{Ri}/P_{Rmin}) = 0.239($\Delta H_{f,Ri} - \Delta H_{f,Rmin}$) + 0.083; $r = 0.95$.

(vinylbenzene).[86] Arnold and his co-workers[87–89] concluded that the stability, and hence the relative rate of formation, of a π-conjugated radical, with varying substituents, follows the delocalisation of spin-density in the system. Although this premise seems to hold for the benzyl radical,[87,88] there is no evidence for it here [a plot of ln ($P_{R_i}/P_{R\min}$) *vs.* $A_{R\max} - A_R$ giving a correlation coefficient of $r = 0.11$]; the relative stability of each radical within its isomeric group relating to the muon coupling constants (A/MHz) in no clearly quantifiable way, although the radical formed in smallest yield does, in each case, have the largest coupling constant ($A_{R\max}$). Similarly, there is no compelling relationship to be found for the coupling constants measured for the distribution of radicals formed in monosubstituted benzene derivatives with their relative yields.[2,51]

As discussed previously for acetone,[90] when the substrate is polar and could readily accept either radiolytically produced electrons or muons, the actual radical precursor may not necessarily be Mu itself, since ionic routes could be important [*cf.* eqns. (9)–(12)]. Imidazole is known from pulse-radiolysis experiments to add electrons to form the radical anion,[91] and will also easily protonate (and therefore add a positive muon) given its pK_a.[92] Hence, in the preceding discussion, we have used the term "overall" Mu addition merely to identify that Mu-labelled radicals are formed.

To explore conceptually the possibility of ionic routes, we need to consider what is likely to happen when a high-momentum (85 MeV/*c*) muon interacts with the medium: clearly, in the transfer and dissipation of so much energy, there will be extensive ionization along the muon track—those events most relevant to chemistry will occur close to the end of the track, when all reactive species have achieved *near* thermal energies. The muon must then find itself surrounded by electrons; if it *binds* with one of these, *actual* Mu will be formed; if the electron is already associated with one particular molecule (radical anion), muon addition will lead to an *overall* Mu-adduct—this is a more favourable process than electron abstraction by the muon *from* the radical anion to yield Mu. An alternative is for the muon to add first to a substrate molecule ("protonate"), which must then capture an electron to form the free radical.

We first consider the possible outcomes of these ionic routes (Scheme 1). Primary muon addition to an imidazole, followed



Scheme 1

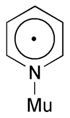
by electron addition, would give the nitrogen adduct **16**; in order for this adduct to form the radical **17**, which is predominant, it would need to rearrange on a 10^{-10} s timescale, and *via* a 1,3-shift, which would be unprecedented. Were rearrangement to occur, it is the 2-isomer **18** that would be formed, in analogy with the apparent behaviour of anionic centres in imidazole single crystals, according to EPR measurements;[93–95] EPR and MuSR differ, however, in that the latter is critically dependent on the final radical being formed very rapidly[1,2,90] (*vide supra*) a restriction that does not apply to EPR; similarly, electron addition followed by muon addition would also lead to the radical **18**.

The good correlation of calculated heats of formation (Fig. 5) with the observed yields of the radicals is significant, since it points to all 3 isomers originating *via* a common mechanism, *i.e.* approach of the Mu atom to the imidazole ring, from which the distribution of product radicals is dictated by their relative energies. This is further supported by the behaviour of 1-methylimidazole and 1,2-dimethylimidazole; in the latter compound, addition to the 2-position is strongly disfavoured. If the 2-isomer arose from an independent route involving, say, rearrangement of an ionic precursor, it is reasonable that its formation could also be inhibited; however, since we have already argued that the 5-Mu adduct could not, thereby, be formed on the necessary rapid MuSR timescale, probably *no* radical would arise *via* this route—what happens though is that the yield of the 5-Mu adduct almost doubles, which is in accord with the above model where Mu approaches the imidazole and, not being able to attack the 2-position, is instead directed mainly at C-5, with a lesser attack on C-4.

6.2 Further "organic" media

The case of imidazoles has been given exacting coverage, as it appears to be so definitive, and a comparison with some additional purely "organic" systems should prove fruitful. A plot of $\Delta\Delta H_f$ *vs.* k/k_o (similar to that in Fig. 5) was made by Roduner and Webster[48] for the formation of Mu-adduct radicals in a series of substituted dienes, from which they concluded that thermal Mu was the probable radical precursor, but left the caveat that a similar distribution of radical yields would be expected if the mechanism was that of electron addition to initially formed μ^+ adducts (allylic carbocations). The results for imidazoles enable the rejection of this possibility, because the free thermal muon (μ^+) would surely add to the N-3 nitrogen atom, and certainly on the fast timescale required to observe them, the radical distributions could not be explained by subsequent electron addition and rearrangement of the initially formed radicals **16**. In accord with this conceptual view, Roduner has presented compelling evidence that thermal Mu is the direct muonic precursor of the cyclohexadienyl radical:[96] in neat benzene, it has a lifetime of 10 ps and disappears by addition to the aromatic ring; Mu is formed within *ca.* 1 ps by the combination of μ^+ with an electron near to the end of the radiation track of the (near thermal) positive muon. Walker's group have also concluded that thermal Mu is the dominant radical precursor in liquid mixtures of benzene and styrene.[97] In a study of radical formation in liquid acetone,[90] though Mu was found to be the major reacting muonic species, an alternative channel (possibly involving charge-neutralization of ionic precursors) was also implicated.

In a sample of liquid pyridine, a mixture of three radicals is formed: the N–Mu adduct and two (aza)cyclohexadienyl radicals from overall muonium addition to the "*ortho*" and "*meta*" positions; the "*para*" adduct is undetectable.[85] It is concluded that free Mu is the precursor of these radicals. In complete contrast, EPR studies of radiolysed pyridine in an alcohol glass at 77 K show only the N–H adduct,[83,84] which is believed to arise from protonation of the initially formed pyridine radical anion. Protonation of pyridine to form the pyridinium cation changes its behaviour appreciably: in particular, significant reactivity toward Mu now appears at the *para* position; additionally, the radical **19** is formed very dominantly.[85] The formation of a radical by a "hydrogen" (Mu) atom addition to the N(H$^+$) atom is unexpected, since it has been proposed[83] that protonation of the pyridine N-atom serves to "block" it against addition of an H-atom. However, the evidence is compelling, and the most probable mechanism involves addition of muonium to the N(H$^+$) atom, followed by deprotonation.



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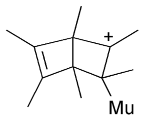

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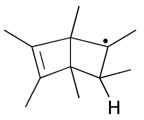


21

Our final example is hexamethyl(Dewar)benzene **11**, from which Mu-adducts were detected, in a diethyl ether solution, and EPR was used to identify radicals produced by radiolysis of the pure compound at 77 K. Overall Mu addition was found to yield a mixture of the *exo* and *endo* isomers **12** and **13**, in the ratio 4 : 1. It is concluded that the precursor is also free Mu, on the grounds that protonation of **11** occurs predominantly at the electron-rich *endo* face, and so an equivalent initial muon addition **20** should lead almost exclusively to **13** by electron capture, yet this is the minority product. In contrast, a majority "overall" H-atom *endo* adduct **21** was measured by EPR, in support of the alternative mechanism involving electron addition to the initial *endo* carbocation.[53]

In conclusion, knowing that Mu is the true radical precursor in a diversity of organic materials enables its use as a mechanistic probe, since it reveals a true pattern of hydrogen atom selectivity; when very different product distributions are found in similar compounds, alternative mechanisms are implicated. It would appear that formal H-atom adducts detected in materials which have been exposed to ionising radiation generally do not involve free H atoms, but arise *via* charge-neutralisation of initially formed ions.

7 Kinetic studies of Mu atoms

The TF-MuSR method may be used to study the kinetics of reactions of free Mu atoms,[1,2,76] but because the muon hyperfine coupling in Mu is very large (*ca.* 4.5 GHz) it is not normally feasible to measure the ν_1 and ν_2 frequencies directly as is normally done for radical species (with typical hyperfine couplings of *ca.* 200–500 MHz). In contrast, a low ($B < 20$ G) magnetic field is often applied, which reveals the ν_{12}/ν_{23} transitions in the muon hyperfine diagram[1,2] in a single resonance whose linewidth (λ) may be measured as a function of substrate concentration [S], thus yielding the direct rate constant k from a plot of λ *vs.* [S] according to eqn. (13).

Muonium and protium atoms differ by only 0.43% in their reduced mass, but by a factor of 8.8 in atomic mass: therefore, they provide an excellent pair of atoms with which to probe kinetic isotope effects. This topic is the subject of an excellent recent review by Walker.[76] When these atoms react with various solutes in water, the ratio of rate constants ($k_{\mathrm{Mu}}/k_{\mathrm{H}}$) was found to vary in the range 10^3–10^{-2}, and in the main, these can be explained in terms of differences in diffusion rate, differing zero-point energies, quantum mechanical tunnelling and steric hindrance, at least when there is a single reaction mechanism involved.

8 Kinetics of radical reactions

As we have seen, the relative yields of radicals formed in mixtures represents their relative rates of formation. We now turn to direct means for measuring rate constants for reactions of radicals, which are actually similar to those used for free muonium atoms. For kinetic studies of reactive radicals, the classical method is pulse-radiolysis,[91] but generally this necessitates using aqueous media, since the radicals are generated *via* the radiolysis products of water, *e.g.* hydroxyl radicals. This should provide no difficulty when it is desired to model processes that occur in aqueous regions of cells, but is surely a potential limitation in understanding radical reactions in cell membranes, since these are non-aqueous, and it is known that the rates of radical reactions can vary according to the hydrophilic or hydrophobic character of their medium.[71]

The TF-MuSR method requires only that the medium should contain an appropriate substrate for muonium addition, and so both aqueous and non-aqueous media can readily be studied. In one recent example, non-aqueous solutions of the appropriate thiocarbonyl compounds (in "super-dried" ethanol and in tetrahydrofuran) were used. The widths of TF-MuSR spectral lines (λ) are measured for a given radical, as a function of concentration of a reacting substrate [S], as is done for muonium:

$$\lambda = \lambda_o + k[\mathrm{S}] \qquad (13)$$

k, the second order rate constant for the reaction of a given (thiyl) radical with a given substrate (S), was determined from a plot of λ *vs.* [S] (Fig. 6). Beyond the acknowledged sophistication of the overall accelerator and related technology employed, this is a very straightforward approach to experimental rate constants. There are very many examples known in which radical reaction kinetics have been so determined, and we have already alluded to some of their results.

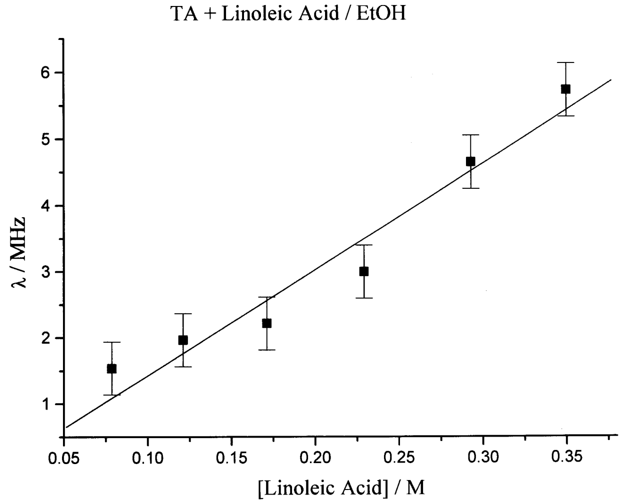


Fig. 6 Plot of linewidth (λ) as a function of linoleic acid concentration for MeC(NH$_2$)=S/Mu$^\bullet$ radicals in diethyl ether solution, leading to the second order rate constant (k), according to eqn. (13).

9 Radical stabilisation

9.1 Captodative stabilisation in radicals

An extension of the concept of "radical stabilisation" is that of "captodative stabilisation" of radicals; seeking proof for the existence of which has formed the basis of a number of studies.[98–102] In essence, if the combined effect of a donor (*e.g.* NH$_2$ or OMe) and an acceptor (*e.g.* CN, COMe) group on the stability of a radical is greater than the sum of their individual effects, then it may be taken that there is some "captodative" stabilisation present. At the present time, opinion seems to be divided: the results of different kinetic measurements may be taken to either support or oppose the concept, whereas measurements of the spin delocalising abilities of substituents in benzyl,[98–100] cyclohexadienyl[101] and propargyl (prop-2-ynyl)[102] radicals show there is an enhanced spin-delocalisation when both a donor and an acceptor substituent are present. Interestingly, an "antagonistic" effect is often found when two substituents of the same kind (*i.e.* both electron releasing, or both electron withdrawing) are present, each reducing the spin-delocalising efficiency of the other. Results[101] obtained using TF-MuSR from disubstituted benzene derivatives are shown in Table 1. A typical spectrum from a mixture of isomeric radicals, so produced, is shown in Fig. 7.

Assuming only a cumulative effect of the substituents, eqn. (14) is expected to hold, where A_μ is the muon coupling in

Table 1 Parameters (Δ_{XY}) for the interaction of two substituents in the cyclohexadienyl radical in units of 100 Δ_{XY} (eqn. 15)

Position of X, Y	X = Me Y = Me	F F	Cl Cl	OMe OMe	OMe CN	CN OMe
1,5	−0.13	−1.93		−2.62	+2.62	+2.62
1,2	−1.81	−1.62	−0.46	−7.07	+0.72	−2.60
1,4	+0.36	+1.12		+4.44	−1.20	−2.96
1,3	−0.45	−0.71	+0.04	−3.37	+5.17	+6.98
2,4	+0.01	−0.90		−1.45	−1.18	−1.18
2,3	−0.99	+1.53	+0.08	−2.53	−2.59	−1.37

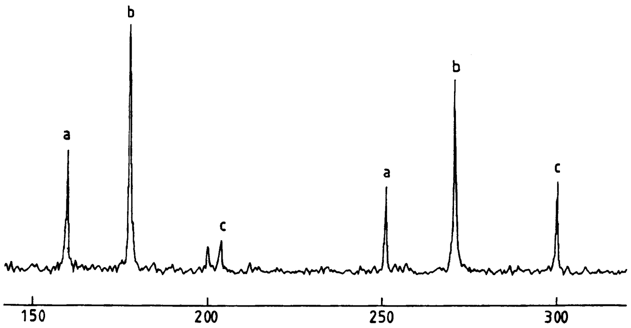
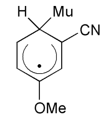
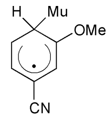
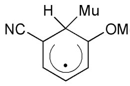
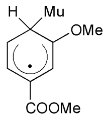


Fig. 7 TF-MuSR spectrum of isomeric radicals recorded during the irradiation of liquid 1,3-dimethoxybenzene with positive muons: (a) 1,5-isomer, (b) 1,3-isomer, (c) 2,4-isomer.

Table 2 MuSR data [muon hyperfine couplings (in MHz)] for captodatively substituted cyclohexadienyl radicals

				
	387.65[a]	417.79[a]	432.93[a]	390.07[a]
Δ_{XY}	6.98%	5.17%	2.62%	5.27%
	386.87[b]	416.31[b]	430.14[b]	388.69[b]
Δ_{XY}	7.14%	5.51%	3.25%	6.10%

[a] In diethyl ether solvent. [b] In formamide (+10% methanol). Δ_{xy} are the substituent interaction parameters used in eqn. (15).

the substituted cyclohexadienyl radical, while $A_\mu{}'$ is that for the unsubstituted case (derived from benzene itself), and Δ_X is a delocalisation parameter similar to that (σ) derived by Arnold for benzyl radicals:

$$A_\mu = A_\mu{}'\Pi(1 - \Delta_X) \qquad (14)$$

Better agreement is obtained, however, if eqn. (14) is modified by the addition of a substituent interaction parameter Δ_{XY}, as in eqn. (15):

$$A_\mu = A_\mu{}'\Pi(1 - \Delta_X)\Pi(1 - \Delta_{XY}) \qquad (15)$$

Clearly, if Δ_{XY} is positive, then there is a synergetic interaction between the substituents, and if it is negative, then the interaction is antagonistic. We see that for the cases in which a direct conjugation is possible between the 2 substituents and the "radical centre" (*i.e.* 1,3- and 1,5-substitution) the "captodative" proposal is borne out. (For all other arrangements of substituents, the signs scatter, illustrating the complexity of the effect of substituents on spin-delocalisation.) On the basis that there is a direct relationship between the degree of spin delocalisation and the component of energy that is associated with this (Arnold),[87–89] these spectroscopic measurements have been taken as evidence for the existence of captodative stabilisation.

The results of theoretical calculations as to the reality of the effect appear to vary according to the method and the radical system chosen,[103,104] but one study predicts that while there should be no effect in the ground state of an isolated radical bearing both a donor and an acceptor substituent, a very large stabilisation would be induced in the system by a medium of high relative permittivity.[105] Following a previous study[101] by TF-MuSR of pairwise radical substituent effects in cyclohexadienyl radicals (yielding the results given in Table 1), the radicals shown in Table 2 were produced in diethyl ether and in formamide–10% methanol solution.[106] The advantage of TF-MuSR is that the spectra of even complex mixtures of radicals (Fig. 7) are quite straightforward to interpret, because (as noted before) each radical gives only a single pair of lines. The corresponding EPR spectrum of such a mixture of cyclohexadienyl radicals would be extremely complex, and precise measurements of their individual coupling constants would be accordingly difficult. Essentially, there is only a very minor enhancement in the apparent (Table 2) degree of spin delocalisation even in a strongly polar medium (formamide + 10% methanol), and so the results argue against the prediction that a highly polar medium has a significant promoting influence on the captodative phenomenon. We note that the results from a kinetic study also failed to provide any support for this proposed solvent effect.[107]

9.2 Unimolecular isomerisation of radicals

There are a small number of EPR studies reported which have identified geometric isomers of delocalised radicals, and which were able to monitor their rate of interconversion by rotation about a partially multiple bond.[108,109] Such information can provide relative energies against which theoretical models may be tested, and on a pragmatic level, can provide insight into the so called "radical stabilisation energies" (resonance energies)[87–89] which arise from the effect on the *overall* electronic structure incurred by delocalisation of the unpaired electron. We have already noted that Arnold was able to show good correlations between rates of formation of substituted benzyl radicals and the α-CH_2 coupling constants,[87,88] which measure the degree of delocalisation of the unpaired electron from the exocyclic carbon atom. Comparisons can also be made with thermochemical data, such as bond dissociation energies,[110] which are usually taken as being indicative of the relative stability of a free radical (*i.e.* the weaker a given C–H bond is in a series of compounds R_3C–H, the more stable is the radical $R_3C^\bullet$, which is formed in the step $R_3C\text{–}H \longrightarrow R_3C^\bullet + H^\bullet$). An alternative to measuring bond energies is the determination of the activation energy for isomerisation of a conjugated radical,[108,109] *e.g.* benzyl, or allyl, since in the act of isomerisation it must pass through an orthogonal "deconjugated" state, which may, therefore, be taken as the resonance energy.

Though this has been accomplished for relatively simple cases,[108,109] it is not always an easy feat, because the EPR spectra of many conjugated, and structurally extensive, radicals are made very complex by interaction of the unpaired electron with many magnetic nuclei, and since the structure must be unsymmetrical, to render distinct isomers, the spectra are more complex still. A very appropriate example of this is the 2-pyridylmethyl radical, which has a fairly complicated EPR spectrum,[111] and in the limit of the steady-state concentration

Table 3 Arrhenius parameters for *cis–trans* isomerizations of radicals: (24) $\rightleftharpoons$ (25)

		Forward step		Backward step		
R^1	R^2	log (A/s)	E/kJ mol^{-1}	log (A/s)	E/kJ mol^{-1}	Technique
H	CH_3	10.6(2)	27(2)	10.7(9)	31(6)	MuSR
		10.4(5)	23(3)	10.4(5)	25(3)	EPR
H	OC_2H_5	13.9(6)	44(4)	b)	b)	MuSR
		14.0(5)	$\approx$45	14.0(5)	47(2)	EPR
H	$N(CH_3)_2$	12.7(1.1)	48(8)	b)	b)	MuSR
CH_3	OC_2H_5	13.2(2)	45(1)	13.2(2)	45(1)	MuSR

of these radicals achievable in fluid solution, is too weak for normal analysis (by "eye"), though it may be solved using powerful computational analysis methods of "correlation".[111,112]

MuSR comes into its own, here, since the closely related radical 1-(2-pyridyl)ethyl **22**–**23**, is formed by Mu addition to 2-vinylpyridine,[113] and just 2 lines are observed for each radical isomer (Fig. 8), which are found to broaden with increasing temperature, as the rate of interconversion of the 2 isomers increases into the observational (microsecond) timescale of the experiment. The rate of interconversion is the absolute rate constant (k),[108] directly, in the equation, $\lambda = \lambda_o + k$ (where λ is the observed linewidth, and λ_o is the linewidth in the absence of a reaction), and since this is related to the temperature through the activation energy (E_a) and frequency factor (A), $k = A\exp(-E_a/RT)$, the latter parameters can be extracted from a plot of ln k *vs.* $1/T$.

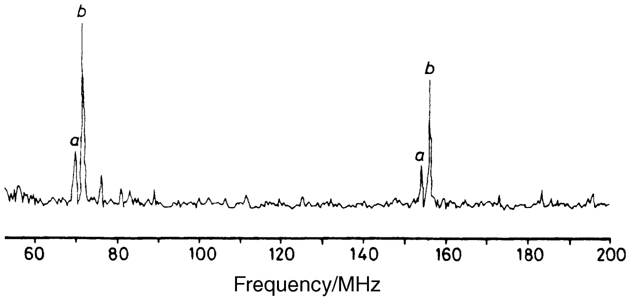
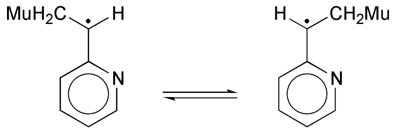


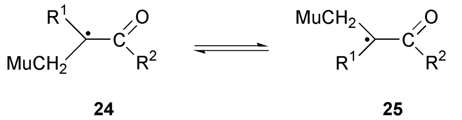
Fig. 8 TF-MuSR spectrum of isomeric radicals recorded during the irradiation of 2-vinylpyridine with positive muons: (a) is isomer **22**, (b) is isomer **23**.



22 **23**

Within the experimental error, the activation energies for the two processes (*cis* ⟶ *trans*; *trans* ⟶ *cis*) are the same, at 56.4 ± 4.2 kcal mol^{-1}, which is very similar to that determined by EPR for the isomerisation of 1-phenylethyl radicals. The A factors are the same too, and suggest that the entropy of activation ($\Delta S^{\ddagger}$) is close to zero.

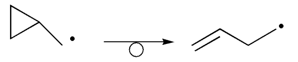
Roduner and his co-workers have used this method to study the isomerisation kinetics for carbonyl-conjugated radicals[108] **24**–**25**, where R^1 = H or Me, R^2 = CH_3, OEt or NMe_2. Since related radicals have also been studied by EPR, it is possible to make comparisons between the two methods (Table 3), and it is clear that the A factors and activation energies obtained by MuSR and by EPR agree well with each other. In the context of radical stabilisation, all results confirm that the $C^{\bullet}$–C(=O) C–C bonds contain considerable "double-bond" character, but compared with the allyl radical $H_2C^{\bullet}$–CH=CH_2, the carbonyl group imposes less C–C(=O) "double bond character", hence the smaller barrier to internal rotation. As with the 1-(2-pyridyl)ethyl radical **22**–**23**, the log A values are *ca.* 13, in accord with a near zero $\Delta S^{\ddagger}$ for the process.



24 **25**

9.3 Radical rearrangements ("kinetic clocks")

The rationale and application of "kinetic clocks" has been discussed by Griller and Ingold,[114] where rates of radical-molecule reactions are studied in competition with a unimolecular radical rearrangement, whose rate is known. Therefore the product distributions arising from rearranged or unrearranged initial radicals serve to "time" the latter reactions, the rearrangement providing an internal free radical "clock". Much effort has therefore been made in calibrating these clocks, often by means of measurements made relative to other processes; as noted earlier, the MuSR method yields absolute rate constants,[1,2] and a number of studies have been made[115] on systems whose mechanism is well understood, involving ring fission of cyclopropylmethyl radicals (**26**), and cyclisation of substituted hex-5-enyl radicals (**27**). The data obtained for a representative range of such processes is listed in Table 4.



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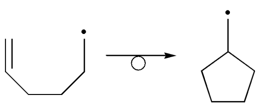


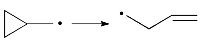
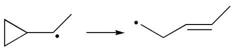
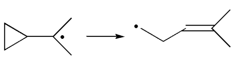
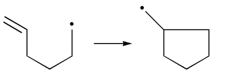
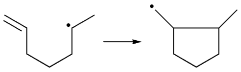
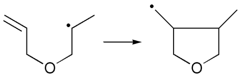
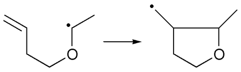
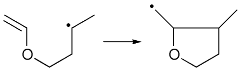
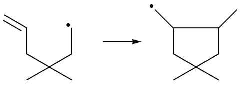
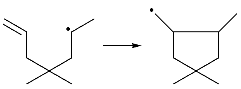
27

10 Biological systems

From the early days of MuSR, information relevant to "biological systems" has been sought using its methods. Its successes include the measurement of rate constants for the reaction of Mu with DNA[116] and some isolated "base" analogues,[116] and the identification of the product radicals formed in the latter, simpler cases,[117,118] and in imidazoles.[73] In radiation biology[119–121] it is of some matter to know the outcome of H-atom reactions with organic bases, such as are present in DNA, and indeed those with protein constituents. We acknowledge that trying to study actual DNA, or an intact protein would not be feasible due to the large number of reaction sites and the complex mixture of product radicals expected.

To illustrate the procedure for measuring the kinetics of free radical reactions using TF-MuSR, we have already mentioned a study of radicals proposed to be of the thiyl type, $RS^{\bullet}$. β-Carotene has received considerable attention as a dietary supplement supposed to protect against developing cancer, and to alleviate the effects of ageing: the rates are indeed very large for the scavenging of thiyl radicals by this agent, and accords that such a protective role might contribute in these conditions, though the effect of this agent on the incidence of lung cancer in smokers has proved highly contentious.[127,128]

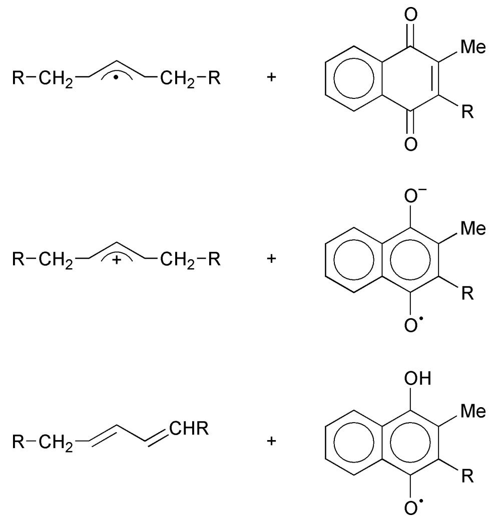
Table 4 Rate parameters for cyclopropyl ring fission and 1,5-cyclization reactions[115]

Reaction	k/s^{-1} (T/K)	E/kJ mol^{-1}	log (A/s^{-1})	Method
	5.6×10^7 (273)	24.8 ± 2.5	12.5 ± 0.9	Conv.[a]
	5.6×10^6 (273) 7.0×10^6 (273)	22.2 ± 3.0	11.0 ± 0.6	MuSR Conv.
	1.5×10^6 (273)	43.5 ± 2.7	14.5 ± 0.4	MuSR
	9.4×10^5 (338)	28.7 ± 1.8	10.4 ± 0.3	Conv.
	4.7×10^5 (338) 6.4×10^5 (338) 7.5×10^5 (338)	22.2 ± 2.5 26.8 ± 1.3	9.1 ± 0.3 9.8 ± 0.3	MuSR Conv.
	8.2×10^6 (338) 8.6×10^6 (338)	16.7 ± 1.9	9.5 ± 0.3	MuSR Conv.
	1.4×10^6 (338)	18.4 ± 3.0	9.0 ± 0.4	MuSR
	1.8×10^5 (338)	26.4 ± 5.0	9.3 ± 0.7	MuSR
	1.6×10^7 (338)	21.3	10.5	Conv.
	1.9×10^6 (338)	24.7 ± 1.9	10.1 ± 0.3	MuSR

[a] Conv.: Conventional product kinetic analysis.

Table 5 Second order rate constants (M^{-1} s^{-1}) for the reactions described in the text

	Vitamin E	Vitamin K$_1$
Me(MuCH$_2$)C$^•$–C(Me)=CH$_2$	9.38×10^6	3.54×10^7
MuCH$_2$CH$^•$CH$_2$OC(O)Me	1.76×10^8	2.03×10^6



Scheme 2

10.1 Vitamin K as a potential antioxidant

It has been proposed[129] that oxidative damage to membrane lipids might involve the formation of C-2 glyceryl radicals, in addition to main chain allylic radicals, which are generally thought important.[130] Since it is known that vitamin E and Vitamin K are lipophilic, and tend to accumulate in cell membranes, the kinetics of their potential "repair" reactions with 1,1,2-trimethylallyl [Me(MuCH$_2$)C=C(Me)–CH$_2^•$] and 1-acetoxy-2-propyl [MuCH$_2$CH$^•$CH$_2$OC(O)Me] radicals were measured.[131] These radicals are intended as models of, respectively, main-chain and glyceryl type radicals (damage sites), and were formed by Mu addition to 2,3-dimethylbuta-1,3-diene and to allyl acetate.

The second order rate constants for these reactions are shown in Table 5. The results suggest that direct scavenging of glyceryl radicals by vitamin E could be an efficient process, and of main-chain allylic radicals fairly so; additionally, it appears that vitamin K$_1$ can act directly as a "radical repair agent", given its relatively high reactivity with allylic radicals (4× faster than with vitamin E), so prior reduction to the quinol form[132,133] may be unnecessary. The interceptive role of vitamin K toward allylic radicals is proposed in Scheme 2, in which the conjugation of the initial ene is increased by one C=C unit. Squalene is central to biology since it is a key intermediate in the biosynthesis of steroids,[134] and like β-carotene and vitamin E is proposed to possess antioxidant properties.[135] There are no EPR studies reported of radicals formed from squalene, and in *neat* squalene no radicals could be observed using TF-MuSR.[136] However, when the squalene was diluted 50 : 50 by volume with diethyl ether, the spectrum shown in Fig. 9 was obtained. The spectrum shows two signals only, with unusually broad lines, which are confirmed to be from a single type of radical species. Inspection of the molecular structure of squalene (**28**) shows that it contains 6 C=C double bonds, and so there are potentially 12 sites at which a Mu atom could add. In such additions, tertiary radicals are normally formed in preference to secondary radicals, and so addition at the 3, 7 and 11 positions is expected, in each case giving a radical of the type: RCH$_2$C$^•$(Me)CH(Mu)CH$_2$R′. R′ is, in each case a "large" hydrocarbon group, and the spin-delocalising properties of the RCH$_2$CMeCH units are expected to be all very similar; therefore, because there is no reason to expect that addition at positions 3 or 7 or 11 (equivalent by symmetry with positions

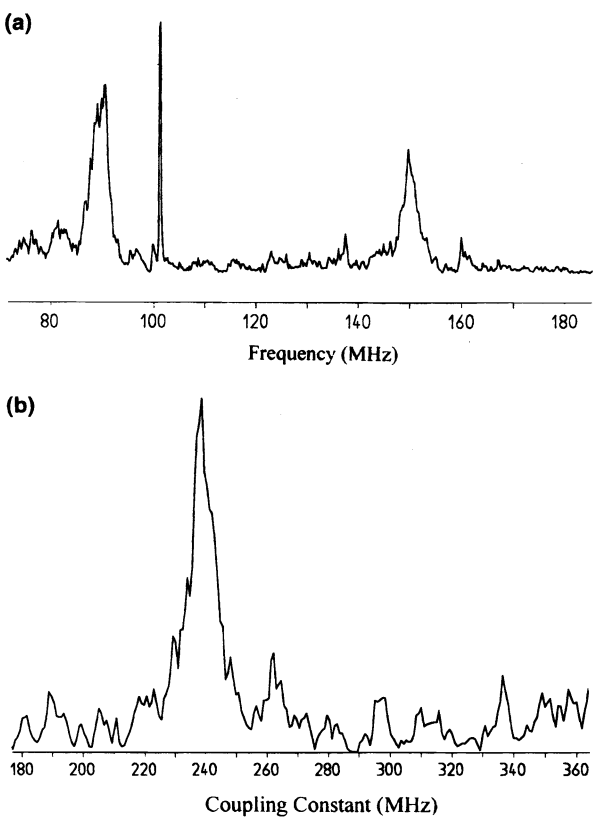
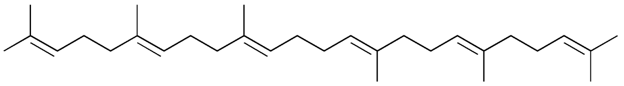


Fig. 9 (a) TF-MuSR spectrum recorded from a 50 wt% solution of squalene in diethyl ether, showing two broad signals from a mixture of radicals of type $RCH_2C^{\bullet}(Me)CH(Mu)CH_2R'$, with an almost common coupling constant, resulting from muonium addition to the 3, 7 and 11 (14, 18 and 22) positions of squalene (**28**). The sharp peak at *ca.* 100 MHz is the first harmonic of the cyclotron frequency, at *ca.* 50 MHz. (b) The correlation spectrum confirming the presence of only radicals with a similar functional identity (the scale is that of *coupling constant* directly).

14, 18 and 22) predominates over the others, three radicals are expected, but with an almost common coupling constant. Since the lines are very broad, it seems likely that any small differences in couplings that may be present are masked by their width. At *ca.* 241 MHz the coupling is typical for (smaller) tertiary radicals of similar structural type,[1,23,136] which may be considered as models for the squalene–Mu adduct radical.



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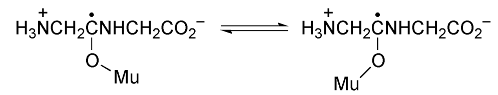
The lack of observation of radicals in neat squalene is apparently due to its very viscous nature and the large molecular size of the adduct radicals. Therefore, even though the *bulk* viscosity of squalene is reduced vastly by dilution with ether, at the molecular level, the reorientation rates are still greatly reduced from normal fluid media containing small molecules,[137] *i.e.* at this molecular level, it is the interactions between the large and relatively slowly moving molecules which are dominant, and are not so greatly reduced from those occurring in neat squalene.

Activation parameters were determined for the dynamics of radicals formed by muonium addition to solid samples of glycylglycine (GlyGly) and the doubly protected alanylalanine derivative, Boc-AlaAla-Bz.[19] GlyGly forms an adduct by muonium addition to the carbonyl group which isomerises by flipping the muon between opposite sides of the molecule (**29**), requiring an activation energy of 20.4 kJ mol^{-1}. This is very similar to that required for internal rotation about the C–O bond in the hydroxymethyl radical, $H_2C^{\bullet}$–OH.[138] In Boc-AlaAla-Bz, muonium addition to the benzene ring of the benzyl group occurs, exhibiting an activation energy of 9.4 kJ mol^{-1}, believed to be from torsion about the C–Ph bond. If the frequency factors which were also measured are taken to be the vibrational frequencies of these modes, they amount to 22 and 279 cm^{-1}, to be compared with a frequency of 2.7×10^{12} s^{-1}, deduced from transition-state theory for rotation about a single bond,[139] which is equivalent to 90 cm^{-1}.



$$H_3\overset{+}{N}CH_2\underset{\mathrm{OMu}}{\overset{\bullet}{C}}NHCH_2CO_2^- \rightleftharpoons H_3\overset{+}{N}CH_2\underset{\mathrm{OMu}}{\overset{\bullet}{C}}NHCH_2CO_2^-$$

29

Jayasooriya and his co-workers have used the LF-MuSRx method to probe "segmental" dynamics in chains of dioleoyl phosphatidylcholine, and have also measured methyl oleate as a "model" material.[140] Two peaks were measured for the phosphatidylcholine sample, with maxima at *ca.* 250 and 360 K, which afford activation energies of 7 and 31 kJ mol^{-1}, respectively, and are believed to represent two distinct dynamic processes, rather than phase-transitions, and unlike methyl oleate, there is no substantial increase in the muon relaxation rate at the chain melting temperature, implying that the melting process does not change markedly the microdynamics of the chain segment.

11 Organometallic species

In the subsequent examples of heterogeneous systems, the muon mainly takes-on the role of a spin-label to determine aspects of molecular sorption, particularly in zeolites, clays and porous carbons. However, such muon spin-labelling studies have also been made using LF-MuSRx of the intramolecular dynamics of radicals formed by muonium addition to Ph_4X (X = C, Si, Ge, Pb),[17] and to some metallocenes and benzene-metal π-complexes,[17,18] in which the muon acts as a spin-probe of torsional motion of the phenyl groups and of the overall motion of the cyclopentadienyl or benzene ring, about the metal atom. In ferrocene an activation energy of 5.4 ± 0.5 kJ mol^{-1} and an attempt frequency of 1×10^{12} s^{-1} were obtained[18] using LF-MuSRx, which agree very well with results from NMR[141] and neutron scattering[142] measurements. Therefore, it may be concluded that addition of Mu to form a free radical has little influence on the ring-dynamics of ferrocene. It is interesting that in benzene chromium tricarbonyl, the activation energy is around 15 kJ mol^{-1}.[17] For the torsional motion in tetraphenyl lead,[17] an activation energy of *ca.* 2 kJ mol^{-1} was determined occurring at a much lower attempt frequency of 4×10^{10} s^{-1}.

12 Radicals sorbed in solid materials

12.1 Catalytic media

There is now a considerable body of evidence which implicates hydrocarbon free radicals in processes such as the cracking and partial oxidation of hydrocarbons over zeolites and other metal oxide catalysts.[143,144] Because free radicals are so reactive they have normally only a fleeting existence, and are accordingly very difficult to study directly, being present only in low concentrations, and many will have fairly complex EPR spectra. Some success has been found using EPR, but such measurements are limited to low temperatures,[144] since under catalytically relevant conditions, the spectral signature of the radicals is rapidly lost through their diffusion and consequent termination reactions. The extreme sensitivity of MuSR has a profound advantage in such studies, and the first reported example of a TF-MuSR study of a free radical (1,1,2-trimethylallyl) sorbed on a catalytic surface (fumed silica) was reported about 12 years ago.[145] The same method was used a few years later to provide the first example of a radical (cyclohexadienyl) being observed in a zeolite (NaX) *at ambient temperature*,[146] and was later extended to other hydrocarbon radicals in NaX, and in another zeolite, Na-mordenite.[147]

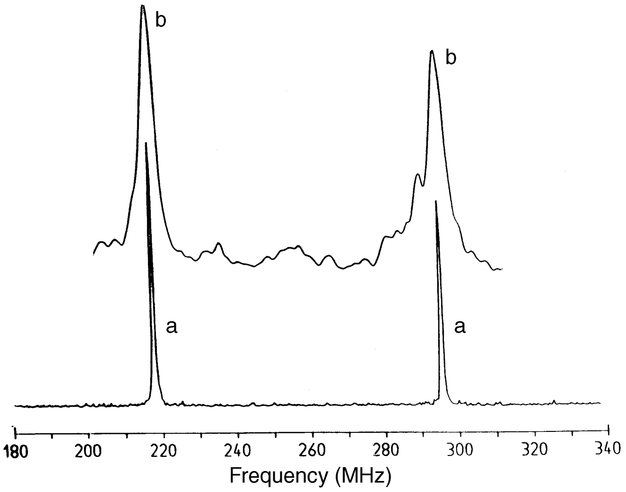


Fig. 10 TF-MuSR spectra of cyclohexadienyl radicals, recorded from (a) liquid benzene, and (b) from benzene sorbed in zeolite NaX.

Fig. 10 allows a comparison to be made between a MuSR spectrum of cyclohexadienyl radicals recorded (a) in liquid benzene and (b) sorbed in zeolite NaX, and it is obvious that sorption on the zeolite surface causes pronounced line-broadening. This may be thought of in similarity with the difference between, say, a ^1H or ^{13}C NMR spectrum recorded from molecules in liquid solution, and from those in a solid sample: the latter containing lines so broad that "magic-angle-spinning" is sometimes used to reduce the line-broadening effect which results from the detection of the full range of the chemical shift, and of the nuclear magnetic dipolar coupling (both effects being averaged out in solution).[5] In MuSR, there is a dipolar coupling between the muon and the unpaired electron, which in a restricted environment, causes line-broadening:[145–147] indeed, the linewidth is proportional to the time the molecule takes to reorient, the so called "rotational correlation time" τ. Since the reorientational rate increases with temperature, the τ values may be fitted to an Arrhenius type expression, eqn. (16):

$$\tau = \tau_o \exp(E_a/RT) \qquad (16)$$

from which the activation energy (E_a) and frequency factor (τ_o^{-1}) signify details of the molecular reorientation step. While this is conceptually straightforward, and may be considered as the starting point for studies of radicals in catalytic media, the technique is not the most effective possible using muons, and all further work has used ALC-MuSR and LF-MuSRx. ALC is the most incisive of the techniques available for determining the detailed dynamics of radicals sorbed on surfaces. Extracting such information, however, does depend on the availability of detailed theoretical models to analyse the effect of restricted molecular motion in modulating the muon, and other nucleus–electron dipolar couplings, which determine the lineshapes in ALC-MuSR spectra. This task has been undertaken, mainly by Roduner's group in Stuttgart, and in their collaboration with Fleming and Percival in Canada, with particular reference to the cyclohexadienyl radical, as formed by Mu addition to benzene molecules sorbed on the surfaces of "fumed" silica and in association with cations in zeolites. We note here that the feature of ALC in detecting other magnetic nuclei which are coupled to the unpaired electron,[6,7] has been exploited in measuring hyperfine couplings to nuclei from cations, such as Cu^+, Li^+, Na^+ and H^+, exchanged into ZSM5 zeolites.[148] The observation of these additional couplings confirms that the cyclohexadienyl radicals (and so the benzene molecules from which they are formed), really do "sit" on the cations, as has been supposed;[149] however, the radical does not so much "sit" on the H^+ ion but (at least below *ca.* 300 K) reacts with it, forming a cyclohexadiene radical cation[150]—in fact the first example of a radical ion containing a muon!

The reorientational dynamics of cyclohexadienyl radicals in two samples of high-silica H-ZSM5 (SiO_2/Al_2O_3 = 670, 900) was studied by ALC;[151] since the number of (Brønsted) acid sites is low in these materials, the cyclohexadienyl radicals will be present *per se*. Depending on the precise type of motion pertaining for the radical, a distinct lineshape is predicted.[151] Thus the preferred rotational axis can be deduced from the shape of the powder pattern.

In the case of H-ZSM5, a high reorientational mobility was found down to 50 K, indicating that the radicals are located at the more spacious channel intersections, and below 20 K the motion became frozen. At 298 K, the fit was consistent with a type of rotation essentially occurring about the axis perpendicular to the molecular plane, but with an extensive concomitant jump-reorientation motion of the rotation axis, as the radicals exchange between two different adsorption sites. Evidence was presented that, above 450 K, sites enforcing a reduced reorientational mobility became accessed, and these are probably located inside the channels of ZSM5. In a previous study of cyclohexadienyl radicals sorbed in silicalite[152] Na-ZSM5 (with SiO_2/Al_2O_3 = 670) and in Na-ZSM5 (with SiO_2/Al_2O_3 = 50), the effect of benzene loading on molecular mobility was investigated, and at close to the saturation capacity of 8 benzene molecules per unit cell, a restricted fraction was detected, even at 300 K, which must be from radicals formed within the channels. The preferred location of hydrocarbon radicals (specifically the tetramethylethylene radical cation) in the channel intersections of ZSM5 is supported by EPR measurements.[153] We note that a theoretical study of the effect of a Na^+ cation on the proton coupling constants in the cyclohexadienyl radical has been made,[154] which predicts that the CH_2 proton couplings are both enhanced by the presence of the cation, and that for the proton on the side of the ring opposite to the cation the most, while the ring adopts a distorted form.

Though it does not (certainly in its present simple form) approach the level of sophistication in describing molecular reorientation that is possible with ALC-MuSR, LF-MuSRx does provide an estimate of the activation energy associated with a particular kind of motion. This is suitably illustrated by a study[8,9] of benzene sorbed in cation-exchanged (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) zeolite X and (Na^+) zeolite A, as outlined below. The importance of zeolite X is that it has the faujasite structure, as does ultra-stable zeolite Y, which is used extensively in the petrochemical industry for catalytic cracking of hydrocarbons. This zeolite has a three-dimensional internal channel system with supercages: the supercages are some 13 Å in diameter, with access windows of 7.4 Å in cross-section, and there are 8 cages per unit cell;[155] therefore, molecules as small as benzene (kinematic diameter 5.5 Å) are readily admitted into its micropores. The activation parameters[9] were converted to free energies ($\Delta G^\ddagger$), enthalpies ($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$) of activation for cyclohexadienyl radicals sorbed in the range of group 1 and group 2 cation exchanged zeolite X samples. For the group 1 series, all at 18 wt% loading of benzene (LiX, NaX, KX), $\Delta G^\ddagger$ has an almost common value of *ca.* 10 kJ mol^{-1}, but the relative contribution made to this by $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ varies, with the entropy term becoming increasingly dominant as the cation radius increases ($r_{K^+} > r_{Na^+} > r_{Li^+}$). This reflects the decreasing importance of cyclohexadienyl–benzene-cation interactions, since the $\Delta H^\ddagger$ value falls from 7.9 kJ mol^{-1} in LiX to only 2.8 kJ mol^{-1} in KX, and is in order with previous measurements of the isosteric enthalpies of adsorption of benzene in Na^+, K^+, Cs^+ exchanged zeolite X.[156] In both NaX and KX, the motional process is dominated by the entropy change, and in

Table 6 Activation energies (E_a) and inverse frequency factors (τ_∞) as determined for the muonium adduct radicals formed from benzaldehyde, PhCHOMu$^\bullet$, sorbed in cation-exchanged zeolite X, according to eqn. (2), showing two distinct motional regimes

Zeolite	(E_a)/kJ mol^{-1}	τ_∞/s	E_a/kJ mol^{-1}	τ_∞/s
LiX	3.4 ± 0.4	$(1.7 \pm 0.5) \times 10^{-9}$	11.4 ± .1.7	$(5.5 \pm 3.4) \times 10^{-11}$
NaX	4.2 ± 0.5	$(1.6 \pm 0.4) \times 10^{-9}$	11.0 ± 0.7	$(7.2 \pm 2.1) \times 10^{-11}$
KX	2.1 ± 0.4	$(5.3 \pm 1.6) \times 10^{-9}$	8.0 ± 0.7	$(2.5 \pm 0.8) \times 10^{-10}$
MgX	Nd[a]	Nd[a]	12.2 ± 1.4	$(3.1 \pm 1.6) \times 10^{-11}$
CaX	3.1 ± 0.2	$(1.1 \pm 0.2) \times 10^{-9}$	8.3 ± 0.5	$(1.1 \pm 0.3) \times 10^{-10}$
SrX	3.1 ± 0.0	$(4.5 \pm 0.2) \times 10^{-10}$	6.2 ± 0.9	$(9.8 \pm 4.2) \times 10^{-10}$
BaX	3.1 ± 0.3	$(7.2 \pm 1.8) \times 10^{-10}$	13.6 ± 1.2	$(1.0 \pm 0.5) \times 10^{-11}$
$C_{(s)}$	2.9 ± 0.3	$(1.4 \pm 0.4) \times 10^{-9}$	11.5 ± 0.4	$(1.1 \pm 0.3) \times 10^{-11}$

[a] Nd, no fraction detected.

fact, the values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are quite similar to those determined for bulk benzene and for benzene sorbed in the large-pores of porous carbon.[11] It was concluded that the activation process is dominated by interactions/collisions between almost free benzene molecules, certainly in NaX and in KX. In all cases, $\Delta S^\ddagger$ is negative, and we have previously argued that this represents a "sticking" collision between the cyclohexadienyl radical and one or more benzene molecules in the activation step,[9] since reorientation of an effectively *isolated* molecule is expected to show a near zero $\Delta S^\ddagger$.[137]

We have also used LF-MuSRx to investigate the sorption and dynamics of cyclohexadienyl radicals and dimethylcyclohexadienyl radicals (derived from benzene and from *p*-xylene) in Na-ZSM5, in silicalite and in Na-mordenite.[157] Unlike the faujasites,[155] zeolites X and Y, which contain cages, ZSM5 and mordenite both contain channels only. For cyclohexadienyl radicals in ZSM5, silicalite and mordenite, a fraction was detected with a common reorientational activation energy of *ca.* 5 kJ mol^{-1}; however, in both ZSM5 and silicalite there appeared a secondary fraction with an activation energy of *ca.* 14 kJ mol^{-1}. This was absent in mordenite. Mordenite contains a single kind of linear channel, which has a cross-section of *ca.* 7 Å; therefore, there is only one broad location for sorbed molecules, namely within these channels, and the single distribution represents this. In ZSM5 and silicalite, the straight channels have a cross-section of *ca.* 5.5 Å; there is also a zig-zag channel system which provides a lateral interconnection of the straight channels. As we have already mentioned, at low loadings hydrocarbon molecules tend to locate at the intersections of these channels, but as the loading increases, molecules are forced to occupy more restrictive sites within the channels themselves: since loadings close to the saturation capacity of the zeolites were employed, we believe the two distinct motional distributions represent the channel intersection and channel locations, the latter having the higher activation energy. The results for dimethylcyclohexadienyl radicals are rather similar, but indicate slightly reduced activation energies. This is probably because more limited molecular excursions are permitted for these larger molecules within channels that are narrower than the long-axis of *p*-xylene; for benzene, free rotation is allowed. These results are in accord with those obtained from ^{2}H-quadrupole-NMR measurements.[158–160]

12.2 PhCH$^\bullet$–OMu radicals sorbed in zeolite X

The effect of electron withdrawing substituents in reducing the isotropic muon coupling in PhCH$^\bullet$–OMu was mentioned before. Considering that association between the aromatic ring and a cation exchanged into the zeolite might provide a similar electron withdrawing influence, we sorbed benzaldehyde into a series of cation-exchanged zeolite X samples. Changes in the isotropic muon couplings were indeed found, which accord with the formation of such π-complexes: in each series, Li^+, Na^+, K^+ and Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, the strength of this complexation was found to decrease with the increasing radius of the cation, the coupling being smallest for Li^+ and Mg^{2+} cations.[65] While representing an advance in the study of molecular sorption by zeolites, the effect noted is indirect, being one of perturbation on the π-electrons of the radical, and does not determine the influence of the cation on the reorientational motion of the sorbed species. Nonetheless, logic would suggest that such motion might be impeded, and increasingly so, by complexation of increasing strength. This was investigated, and the reorientational activation parameters for PhCHOMu$^\bullet$ radicals sorbed in cation-exchanged zeolite X were measured using LF-MuSRx.[10] Representative plots are shown in Figs. 3 and 4.

In all cases, other than MgX, two clear maxima were identified. The nearly common activation energy of *ca* 3 kJ mol^{-1} (Table 6) measured for the *low-temperature range* among all the samples is striking, and since it is the same as that attributed previously[12] to benzaldehyde sorbed in the larger pores of porous carbon—*i.e.* in an effectively *bulk* phase—we believe that some proportion of the benzaldehyde is also sorbed as bulk in zeolite X. This fraction could not be detected positively in MgX. In contrast, the activation energies measured in the *higher temperature range* vary appreciably according to which exchange-cation is present. In both series, $Li^+ \longrightarrow K^+$ and $Mg^{2+} \longrightarrow Sr^{2+}$, the activation energy (E_a) falls as the cation radius increases, in accord with the reduced polarising-power and hence weaker π-complexation to the cation, as we inferred from the change in the isotropic muon couplings measured in these samples. The relatively large E_a value measured in BaX is anomalous, and is ascribed to a fraction excluded from the supercages by large Ba^{2+} cations which obstruct their access windows.

12.3 Environmental surfaces

Free radicals feature strongly throughout Nature and hence are central to environmental processes. In consequence of the intense solar UV radiation in the upper atmosphere, halogenated organic materials, such as organic solvents and CFC's, undergo photolysis forming free radicals, mainly in the stratosphere. Until fairly recently atmospheric processes have been viewed as being those of pure gas reactions,[161] but it is now thought that atmospheric aerosols, clouds and dust particles can provide surfaces on which reactions can occur with great efficiency.[162] Indeed, the presence of a background atmospheric dust load, evenly spread through the atmosphere, has been established.[163] The quantity of atmospheric dust (mainly clays) blown skywards by the desert winds is thought to amount to perhaps *5–10 billion tonnes* annually.[164,165] To edge towards a model system combining some of these ideas—specifically to study the interaction of halocarbon radicals with clay materials—a study was made of 1,1-dichloroethyl radicals ($MuCH_2CCl_2^\bullet$) sorbed on porous silica and on kaolin.[13] An activation energy of 10.6 ± 1.4 kJ mol^{-1} was determined for the reorientational diffusion of 1,1-dichloroethyl radicals sorbed on silica gel by TF-MuSR spectroscopy, which is confirmed by LF-MuSRx measurements, which give a value of 10.9 ± 0.7 kJ mol^{-1}. Also according to TF-MuSR measurements, the activation energy for this radical sorbed in kaolin powder is 11.0 ± 1.3 kJ mol^{-1}, which is within the experimental error obtained from an LF-MuSRx study (12.3 ± 0.8 kJ mol^{-1}). The LF-MuSRx method also reveals the presence of an additional, more mobile, fraction of 1,1-dichloroethyl radicals in both silica and kaolin with respective activation energies of 2.6 ± 0.4 and 2.4 ± 0.2 kJ mol^{-1}. This, secondary, fraction is "invisible" to TF-MuSR.

In the lower atmosphere the higher concentration of oxygen makes an important contribution, and so the chemistry of the troposphere is dominated by oxidation reactions, mediated largely by $^{\bullet}$OH radicals.[161] The plant kingdom emits enormous quantities of hydrocarbons into the atmosphere, especially terpenes from forests. Indeed the "Blue-Ridge-Mountains-of-Virginia", of Laurel and Hardy fame, appear blue behind the haze caused by the tropospheric oxidation of pinenes and other terpenes.[165]

When benzene is loaded into activated carbon, yielding muonated cyclohexadienyl radicals, two relaxation maxima are found (Fig. 11).[11] The data obtained in the high temperature range yield activation parameters, E_a = 26 kJ mol^{-1} and τ_∞ = 2 × 10^{-16} s, while the lower temperature data set yields 6 kJ mol^{-1} and 6 × 10^{-12} s, actually very similar to the values obtained in bulk benzene. It is proposed that these differing mobilities are a consequence of benzene molecules being confined in pores of differing size: the fraction with lowest activation energy being from the larger pores (>20 Å), hence the similarity in behaviour to bulk benzene, while the more restricted motional behaviour corresponds to benzene confined to micropores (4–20 Å). According to transition-state theory, the pre-exponential factor in the latter corresponds to a large positive entropy of activation of +52 J mol^{-1} K^{-1}, which is believed to represent the substantial increase in reorientational freedom conferred to the benzene molecules as they escape ("pop-out") from these small pores into more spacious regions.

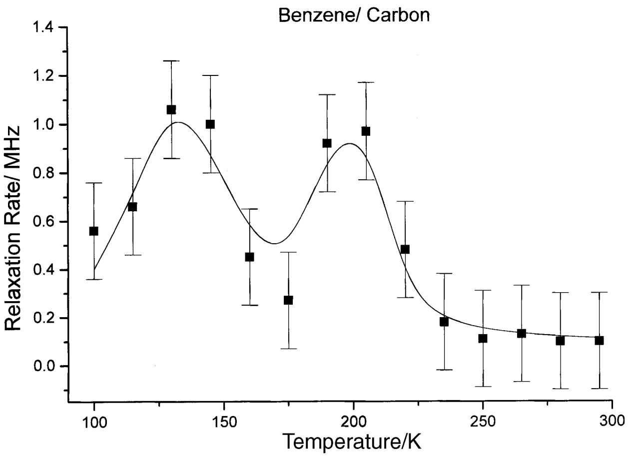


Fig. 11 LF-MuSRx plots for muonium adducts of benzene in activated carbon, at a 20 wt% loading of benzene, showing 2 maxima (see text).

No such *positive* $\Delta S^\ddagger$ value is found for toluene or benzaldehyde sorbed in the same porous carbon,[12] which strongly implies that these molecules are unable to penetrate the very small carbon pores (*i.e.* those toward the low-end of the 4–20 Å range, which designates the "micropore" region). This accords with our view[11] that the access holes to the micropores are very narrow, and only just admit the molecules of unsubstituted benzene; we suggest that increasing the molecular dimension by even a CH_3 or CHO substituent is sufficient to discourage admission of the substrate. The second fraction, measured for sorbed benzene, presents activation parameters which are all very similar (Tables 1 and 2) to those measured in bulk-benzene: this is reasonable if it is resident in the meso- and macro-pores of the carbon structure (*i.e.* those of dimension > 20 Å).

In our previous studies of sorbed radicals using LF-MuSRx,[12–14] we ascribed *negative* $\Delta S^\ddagger$ values to reorientational events that were not those of *single* molecules, but rather involved "sticking-collisions" between molecules,[9,13] so increasing the molecular "ordering" as the activated state for the process is achieved. We believe the situation is similar in these present examples.

13 Concluding remarks

Having read this very general overview, I hope the reader is convinced of the merits of MuSR, and ideally thinks that its suite of methods may be able to do something for them! I have used muons extensively in my research over several years now, in parallel with a main EPR programme, to address problems that would have remained intractable without them.

I have emphasised work which is relevant to "biological" media, and to radicals formed in heterogeneous systems, such as zeolite catalysts, and especially in environmentally important solids: porous carbons, silica, clays, since they are components of atmospheric aerosols. I would predict greater mention of these in the future.

14 Acknowledgements

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15 References

1 D. C. Walker, *Muon and Muonium Chemistry*, Cambridge University Press, Cambridge, 1983.
2 E. Roduner, *The Positive Muon as a Probe in Free Radical Chemistry. Lecture Notes in Chemistry*, Springer, Heidelberg, 1988.
3 *Hyperfine Interactions, Proceedings of the 7th* International Conference on Muon Spin Rotation/Relaxation/Resonance (*μSR'96)*, K. Nagamine, R. M. Macrae, R. Kadono and K. Nishiyama, Eds., Baltzer, The Netherlands, 1997.
4 A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance*, Chapman and Hall, London, 1979.
5 R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, Pitman, Melbourne, 1983.
6 E. Roduner, *Chem. Soc. Rev.*, 1993, **22**, 337.
7 E. Roduner, M. Schwager and M. Shelley, *Radicals on Surfaces*, A. Lund and C. J. Rhodes, Eds., Kluwer, Dordrecht, 1995, p. 259.
8 C. J. Rhodes, T. C. Dintinger and C. A. Scott, *Magn. Reson. Chem*, 2000, **38**, 62.
9 C. J. Rhodes, T. C. Dintinger and C. A. Scott, *Magn. Reson. Chem*, 2000, **38**, 729.
10 C. J. Rhodes, in *EPR of Free Radicals in Solids: Trends in Methods and Applications*, A. Lund and M. Shiotani, Eds., Kluwer, Dordrecht, 2002.
11 C. J. Rhodes, T. C. Dintinger, I. D. Reid and C. A. Scott, *Magn. Reson. Chem.*, 2000, **38**, S58.
12 C. J. Rhodes and I. D. Reid, *Spectrochim. Acta, Part A*, 2002, **58**, 1209.
13 C. J. Rhodes, T. C. Dintinger, I. D. Reid and C. A. Scott, *Magn. Reson. Chem.*, 2000, **38**, 281.
14 C. J. Rhodes, I. D. Reid and U. Zimmermann, unpublished results.
15 S. F. J. Cox, *Solid State Nucl. Magn. Reson.*, 1998, **11**, 103.
16 S. F. J. Cox and D. S. Sivia, *Appl. Magn. Reson.*, 1997, **12**, 213.
17 U. A. Jayasooriya, J. A. Stride, G. M. Aston, G. A. Hopkins, S. F. J. Cox, S. P. Cottrell and C. A. Scott, *Hyperfine Interact.*, 1997, **27**, 106.
18 U. A. Jayasooriya, G. M. Aston and J. A. Stride, *Appl. Magn. Reson.*, 1997, **13**, 165.
19 C. J. Rhodes, T. C. Dintinger and C. A. Scott, *Magn. Reson. Chem.*, 2002, **40**, 421.
20 C. Christides, S. F. J. Cox, W. I. F. David, R. M. Macrae and K. Prasides, *J. Chim. Phys. Phys. Chim. Biol.*, 1993, **90**, 663.

21 M. J. Ramos, D. McKenna, B. C. Webster and E. Roduner, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 255.

22 M. J. Ramos, D. McKenna, B. C. Webster and E. Roduner, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 267.

23 C. J. Rhodes and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 1187.

24 (*a*) E. Roduner and I. D. Reid, *Isr. J. Chem.*, 1989, **29**, 3; (*b*) T. A. Claxton and A. M. Graham, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**, 2307.

25 D. A. Geeson, C. J. Rhodes, M. C. R. Symons, S. F. J. Cox, C. A. Scott and E. Roduner, *Hyperfine Interact.*, 1986, **32**, 769.

26 C. J. Rhodes, M. C. R. Symons, C. A. Scott, E. Roduner and M. Heming, *J. Chem. Soc., Chem. Commun.*, 1987, 448.

27 A. J. Bowles, A. Hudson and R. A. Jackson, *Chem. Phys. Lett.*, 1970, **5**, 552.

28 F. Ji, P. W. Percival, J.-C. Brodovitch, B. Addison-Jones and S. Wlodek, *Hyperfine Interact.*, 1994, **87**, 853.

29 R. V. Lloyd and D. E. Wood, *J. Am. Chem. Soc.*, 1977, **99**, 8269.

30 S. Ogawa and R. W. Fessenden, *J. Chem. Phys.*, 1964, **41**, 994.

31 C. J. Rhodes and E. Roduner, *J. Chem. Res. (S)*, 1991, 196.

32 I. D. Reid, C. J. Rhodes and E. Roduner, *Tetrahedron Lett.*, 1992, **33**, 5617.

33 R. V. Lloyd and R. V. Williams, *J. Phys. Chem.*, 1985, **89**, 5379.

34 B. P. Roberts, *Tetrahedron Lett.*, 1991, 5385.

35 M. Heming and E. Roduner, *Hyperfine Interact.*, 1986, **32**, 747.

36 D. A. Geeson, M. C. R. Symons, E. Roduner, H. Fischer and S. F. J. Cox, *Chem. Phys. Lett.*, 1985, **116**, 186.

37 J. K. Kochi, *Adv. Free-Radical Chem.*, 1975, **5**, 189.

38 E. L. Cochran, F. J. Adrian and V. A. Bowers, *J. Chem. Phys.*, 1964, **40**, 213.

39 C. J. Rhodes, *J. Chem. Soc., Perkin Trans. 2*, 1992, 235.

40 C. J. Rhodes, M. C. R. Symons, C. A. Scott, E. Roduner and M. Heming, *J. Chem. Soc., Chem. Commun.*, 1987, 447.

41 J. E. Bennett and J. A. Howard, *Chem. Phys. Lett.*, 1971, **9**, 460.

42 C. J. Rhodes and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 4495.

43 D. Griller, J. W. Cooper and K. U. Ingold, *J. Am. Chem. Soc.*, 1975, **97**, 4269.

44 C. J. Rhodes, I. D. Reid and E. Roduner, *J. Chem. Soc., Chem. Commun.*, 1992, 1210.

45 C. J. Rhodes, H. Morris and I. D. Reid, *Hyperfine Interact.*, 1997, **106**, 203.

46 C. J. Rhodes, M. C. R. Symons, E. Roduner and C. A. Scott, *Chem. Phys. Lett.*, 1987, **139**, 496.

47 B. Addison-Jones, P. W. Percival, J.-C. Brodovitch, F. Ji, D. Sharma and S. Vlodek, *Hyperfine Interact.*, 1994, **87**, 847.

48 E. Roduner and B. C. Webster, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 1939.

49 C. J. Rhodes, E. Roduner, I. Reid and T. Azuma, *J. Chem. Soc., Chem. Commun.*, 1991, 208.

50 D. H. Whiffen, *Mol. Phys.*, 1963, **6**, 223.

51 E. Roduner, G. A. Brinkman and P. W. F. Louwrier, *Chem. Phys.*, 1984, **88**, 143.

52 R. F. Kiefl, P. W. Percival, J.-C. Brodovitch, S.-K. Leung, D. Yu, K. Venkateswaran and S. F. J. Cox, *Chem. Phys. Lett.*, 1988, **143**, 613.

53 C. J. Rhodes and E. Roduner, *Chem. Phys. Lett.*, 1990, **171**, 457.

54 M. Ricco, R. De Renzi, G. Guidi, C. Bucci, P. Podini, R. Tedeschi and C. A. Scott, *Hyperfine Interact.*, 1986, **32**, 757.

55 R. M. Macrae, C. J. Rhodes, K. Nishiyama and K. Nagamine, *Chem. Phys. Lett.*, 1996, **259**, 103.

56 C. J. Rhodes and M. C. R. Symons, *Magn. Reson. Chem.*, 1996, **34**, 631.

57 D. Buttar, R. M. Macrae, B. C. Webster and E. Roduner, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 220.

58 R. M. Macrae, B. C. Webster and E. Roduner, *Muon Studies in Solid State Physics, IOP Short Meetings*, no. 22, 1988, p. 95.

59 A. Hill, S. F. J. Cox, R. de Renzi, C. Bucci, A. Vecli and M. C. R. Symons, *Hyperfine Interact.*, 1984, **17–19**, 815.

60 S. F. J. Cox, D. A. Geeson, C. J. Rhodes, E. Roduner, C. A. Scott and M. C. R. Symons, *Hyperfine Interact.*, 1986, **32**, 763.

61 K. Venkateswaran, R. F. Kiefl, M. V. Barnabas, J. M. Stadlbauer, B. W. Ng, Z. Wu and D. C. Walker, *Chem. Phys. Lett.*, 1988, **145**, 289.

62 M. Heming, E. Roduner, B. D. Patterson, W. Odermatt, J. Schneider, H. Baumeler, H. Keller and I. M. Savic, *Chem. Phys. Lett.*, 1986, **128**, 100.

63 D. Buttar, R. M. Macrae, B. C. Webster and E. Roduner, *Hyperfine Interact.*, 1990, **65**, 927.

64 G. M. Aston, J. A. Stride, U. A. Jayasooria and I. D. Reid, *Hyperfine Interact.*, 1997, **106**, 157.

65 C. J. Rhodes, C. S. Hinds and I. D. Reid, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4265.

66 C. J. Rhodes, I. D. Reid and R. A. Jackson, *Hyperfine Interact.*, 1997, **106**, 193.

67 C. J. Rhodes, R. M. Macrae and I. D. Reid, *J. Chem. Soc., Chem. Commun.*, 1999, 2157.

68 B. R. Knauer and J. J. Napier, *J. Am. Chem. Soc.*, 1976, **98**, 4395.

69 G. M. Aston, J. A. Stride, U. A. Jayasooriya and I. D. Reid, *Hyperfine Interact.*, 1997, **106**, 157.

70 C. J. Rhodes, M. C. R. Symons and E. Roduner, *J. Chem. Soc., Chem. Commun.*, 1988, 3.

71 C. J. Rhodes, T. C. Dintinger, C. S. Hinds, H. Morris and I. D. Reid, *Magn. Reson. Chem.*, 2000, **38**, S49.

72 R. M. Macrae and I. Carmichael, *J. Phys. Chem. A*, 2001, **105**, 3641.

73 C. J. Rhodes, H. Morris and I. D. Reid, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2107.

74 P. W. F. Louwrier, G. A. Brinkman, C. N. M. Bakker and E. Roduner, *Hyperfine Interact.*, 1986, **32**, 753.

75 C. J. Rhodes, H. Morris, C. A. Scott, I. D. Reid and E. Roduner, *Magn. Reson. Chem.*, 1997, **35**, 687.

76 D. C. Walker, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 1.

77 Z. Wu, M. V. Barnabas, J. M. Stadlbauer, K. Venkateswaran, G. B. Porter and D. C. Walker, *J. Am. Chem. Soc.*, 1991, **113**, 9096.

78 Z. Wu, J. M. Stadlbauer and D. C. Walker, *J. Am. Chem. Soc.*, 1992, **114**, 3988.

79 H. Zeldes and R. Livingston, *J. Phys. Chem.*, 1972, **76**, 3348.

80 P. Neta and R. H. Schuler, *J. Am. Chem. Soc.*, 1972, **94**, 1056.

81 R. Gelabert, M. Moreno and J. M. Lluch, *J. Phys. Chem.*, 1994, **98**, 7858.

82 A. Berndt, in *Landolt-Börnstein, Magnetic Properties of Free Radicals*, Springer-Verlag, Berlin, 1989, New Series II/17c, p. 127.

83 J. C. Ronfard Haret, A. Lablanche Combier and C. Chachaty, *J. Phys. Chem.*, 1974, **78**, 899.

84 H. J. Bower, J. A. McRae and M. C. R. Symons, *J. Chem. Soc. (A)*, 1968, 1918.

85 C. J. Rhodes, H. Morris and I. D. Reid, *Magn. Reson. Chem.*, 2001, **39**, 438.

86 C. J. Rhodes, H. Morris and I. D. Reid, *Hyperfine Interact.*, 1996, **106**, 233.

87 J. M. Dust and D. R. Arnold, *J. Am. Chem. Soc.*, 1983, **105**, 1221; J. M. Dust and D. R. Arnold, *J. Am. Chem. Soc.*, 1983, **105**, 6531.

88 D. R. Arnold, *Substituent Effects in Radical Chemistry*, H. G. Viehe, J. Janousek and R. Merenyi, Eds., D. Reidel, Dordrecht, 1986.

89 A. M. de P. Nicholas and D. M. Arnold, *Can. J. Chem.*, 1986, **64**, 270.

90 E. Roduner, *Radiat. Phys. Chem.*, 1986, **28**, 75.

91 A. J. Swallow, *Prog. React. Kinet.*, 1978, **9**, 195.

92 M. R. Grimmett, *Adv. Heterocycl. Chem.*, 1970, **12**, 103.

93 B. Lamotte, PhD Thesis, University of Grenoble, 1968.

94 B. Lamotte and P. Gloux, *J. Chem. Phys.*, 1973, **59**, 3365.

95 C. J. Rhodes and E. Roduner, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1497.

96 E. Roduner, *Hyperfine Interact.*, 1984, **17–19**, 785.

97 J. M. Stadlbauer, K. Venkateswaran, G. B. Porter and D. C. Walker, *Hyperfine Interact.*, 1994, **87**, 877.

98 L. Sylvander, L. Stella, H.-G. Korth and R. Sustmann, *Tetrahedron Lett.*, 1985, **26**, 749.

99 H.-G. Korth, P. Lommes, R. Sustmann, L. Sylvander and L. Stella, *Substituent Effects in Radical Chemistry*, H. G. Viehe, J. Janousek and R. Merenyi, Eds., Reidel, Dordrecht, 1986.

100 H. G. Viehe, Z. Janousek, R. Merenyi and L. Stella, *Acc. Chem. Res.*, 1985, **18**, 148.

101 C. J. Rhodes and E. Roduner, *Tetrahedron Lett.*, 1988, **29**, 1437.

102 I. MacInnes and J. C. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1077.

103 G. Leroy, *Adv. Quantum Chem.*, 1985, **17**, 1.

104 G. Leroy, D. Peeters, M. Sana and C. Wilante, *Substituent Effects in Radical Chemistry*, H. G. Viehe, J. Janousek and R. Merenyi, Eds., Reidel, Dordrecht, 1986.

105 A. Katritsky, M. C. Zerner and M. M. Karelson, *J. Am. Chem. Soc.*, 1986, **108**, 7213.

106 C. J. Rhodes and E. Roduner, *Hyperfine Interact.*, 1990, **65**, 975.

107 H.-D. Beckhaus and C. Ruchardt, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 770.

108 W. Strub, E. Roduner and H. Fischer, *J. Phys. Chem.*, 1987, **91**, 4379.

109 D. C. Nonhebel and J. C. Walton, *J. Chem. Soc., Chem. Commun.*, 1984, 731.

110 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 493.

111 R. A. Jackson and C. J. Rhodes, *J. Chem. Soc., Perkin Trans. 2*, 1985, 121.
112 R. A. Jackson, *J. Chem. Soc., Perkin Trans. 2*, 1983, 523.
113 C. J. Rhodes and E. Roduner, *J. Chem. Soc., Chem. Commun.*, 1988, 1228.
114 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317.
115 E. Roduner, *Prog. React. Kinet.*, 1986, **14**, 1.
116 C. Bucci, G. Guidi, M. Manfredi, R. Tedeschi, P. R. Crippa, G. M. Munari, A. Vecli and P. Podini, *Hyperfine Interact.*, 1979, **6**, 425.
117 M. V. Barnabas, K. Venkateswaran, J. M. Stadlbauer, Z. Wu and D. C. Walker, *J. Phys. Chem.*, 1991, **95**, 10204.
118 C. J. Rhodes, C. S. Hinds and H. Morris, unpublished results.
119 C. von Sonntag, *The Chemical Basis of Radiation Biology*, Taylor and Francis, London, 1987.
120 Z. M. Baq and P. Alexander, *Fundamentals of Radiobiology*, Pergamon, Oxford, 1966.
121 M. Tubiana, J. Dutreix and A. Wambersie, *Introduction to Radiobiology*, Taylor and Francis, London, 1990.
122 S. A. Everett, M. F. Dennis, K. B. Patel, S. Maddix, S. C. Kundu and R. L. Willson, *J. Biol. Chem.*, 1996, **271**, 3988.
123 B. Halliwell and J. M. C. Gutteridge, *Free Radicals in Biology and Medicine*, Clarendon Press, Oxford, 1989.
124 B. Kalyanaraman, *Biochem. Soc. Symp.*, 1995, **61**, 55.
125 C. J. Rhodes, in *Toxicology of the Human Environment – the critical role of free radicals*, C. J. Rhodes, Ed., Taylor and Francis, London, 2000, p. 285.
126 C. Schoneich, K.-D. Asmus, U. Dillinger and F. v. F. Bruchhausen, *Biochem. Biophys. Res. Commun.*, 1989, **161**, 113.
127 L. McGinley, *The Wall Street Journal*, January 19th, 1996.
128 P. M. Rowe, *Lancet*, 1996, **347**, 249.
129 S. N. Muller, R. Batra, M. Senn, B. Giese, M. Kisel and O. Shadyro, *J. Am. Chem. Soc.*, 1997, **119**, 2795.
130 B. Halliwell and J. M. C. Gutteridge, *Free Radicals in Biology and Medicine*, Clarendon Press, Oxford, 1989.
131 C. J. Rhodes, T. C. Dintinger, H. A. Moynihan and I. D. Reid, *Magn. Reson. Chem.*, 2000, **38**, 646.
132 K. Mukai, H. Morimoto, S. Kikuchi and S. Nagaoka, *Biochim. Biophys. Acta*, 1993, **1157**, 313.
133 K. Mukai, S. Itoh and H. Morimoto, *J. Biol. Chem.*, 1992, **267**, 22277.
134 J. Mann, *Secondary Metabolism*, Clarendon Press, Oxford, 1978.
135 G. S. Kelly, *Altern. Med. Rev.*, 1999, **4**, 29.
136 C. J. Rhodes, T. C. Dintinger, H. A. Moynihan and I. D. Reid, *Free Radical Res.*, 2000, **33**, 75.
137 S. R. Harrison, R. S. Pilkington and L. H. Sutcliffe, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 669.
138 P. J. Krusic, P. Meakin and J. P. Jesson, *J. Phys. Chem.*, 1971, **75**, 3438.
139 G. Golde, K. Möbius and W. Kaminski, *Z. Naturforsch., Teil A*, 1969, **24**, 1214.
140 N. J. Clayden, U. A. Jayasooriya and S. P. Cottrell, *Phys. Chem. Chem. Phys.*, 1999, **1**, 4379.
141 A. Kubo, R. Ikeda and D. Nakamura, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 1543.
142 A. B. Gardner, J. Howard, T. C. Waddington, R. M. Richardson and J. Tomkinson, *J. Chem. Phys.*, 1981, **57**, 453.
143 J. K. A. Clarke, R. Darcy, B. F. Hegarty, E. O'Donoghue, V. Amir-Ebrahimi and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1986, 425.
144 *Radicals on Surfaces*, A. Lund and C. J. Rhodes, Eds., Kluwer, Dordrecht, 1995.
145 M. Heming and E. Roduner, *Surf. Sci.*, 1987, **189**, 535.
146 C. J. Rhodes, E. Roduner and I. D. Reid, *J. Chem. Soc., Chem. Commun.*, 1993, 512.
147 C. J. Rhodes, E. C. Butcher, H. Morris and I. D. Reid, *Magn. Reson. Chem.*, 1995, **33**, S134.
148 M. Stolmar and E. Roduner, *J. Am. Chem. Soc.*, 1998, **120**, 583.
149 B. Zibrowius, J. Caro and H. Pfeifer, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 2347.
150 E. Roduner and H. Dilger, *J. Am. Chem. Soc.*, 2001, **123**, 7717.
151 E. Roduner, M. Stolmar, H. Dilger and I. D. Reid, *J. Phys. Chem. A*, 1998, **102**, 7591.
152 M. Stolmar, E. Roduner, H. Dilger, U. Himmer, M. Shelley and I. D. Reid, *Hyperfine Interact.*, 1997, **106**, 51.
153 E. Roduner, R. Crockett and L.-M. Wu, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 2101.
154 B. C. Webster and R. M. Macrae, *Physica B*, 2000, **289–290**, 598.
155 J. Karger and D. M. Ruthven, *Diffusion in Zeolites – and other microporous solids*, Wiley, New York, 1992.
156 M. A. Hepp, V. Ramamurthy, D. R. Corbin and C. Dybowski, *J. Phys. Chem.*, 1992, **96**, 2629.
157 T. C. Dintinger, PhD Thesis, Liverpool John Moores University, 2000.
158 J. B. Nagy, E. G. Derouane, H. A. Resing and G. Ray Miller, *J. Phys. Chem.*, 1983, **87**, 833.
159 R. R. Eckman and A. J. Vega, *J. Phys. Chem.*, 1986, **90**, 4679.
160 I. Kustanovich, D. Fraenkel, Z. Luz and S. Vega, *J. Phys. Chem.*, 1988, **92**, 4134.
161 R. P. Wayne, *Chemistry of Atmospheres*, Clarendon Press, Oxford, 1985.
162 R. van Dingenen, N. R. Jensen, J. Hjorth and F. Raes, *J. Atmos. Chem.*, 1994, **18**, 211.
163 D. J. Wuebbles, *J. Geophys. Res.*, 1983, **88**, 1433.
164 I. Tegen and I. Fung, *J. Geophys. Res.*, 1994, **99**, 22897.
165 R. P. Turco, *Earth Under Siege*, Oxford University Press, Oxford, 1997.