Muonated Cyclohexadienyl Radicals Observed by Level Crossing Resonance in Dilute Solutions of Benzene in Hexane Subjected to Muon-Irradiation

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Abstract

Benzene is used here as a scavenger of muonium to produce the muonated cyclohexadienyl radical in dilute solutions in n-hexane. The radical was identified by level crossing resonance spectroscopy (LCR) by observing the proton resonance of the -CHMu group occurring at 2.059T. Its yield is found to equal the sum of the muonium atom yield and the "missing" muon yield in hexane (total 35% of the incident muons). Consequently, the complete dispersement of muons in different chemical associations is now accounted for in a saturated hydrocarbon liquid, and is seen to be similar to that in water.

Introduction

When energetic muons are injected into a liquid hydrocarbon, about 65% of them immediately become incorporated into diamagnetic molecules (such as MuH), 10 to 20% form long-lived muonium atoms ($\mu^+ e^-$, symbol Mu), and the remainder are lost (the so-called 'missing' fraction). Whether they form, as in radiation chemistry[1], by 'direct' or 'indirect' processes is a question which lies at the heart of many muon chemistry studies, including this one.

Whereas the muon spin rotation (μSR) technique requires the muon state observed over the muon lifetime (2.2μs) to have been formed prior to any spin precession in a transverse magnetic field (typically $<<$ 1ns)[2], the new technique of level crossing resonance (LCR)[3] imposes no formation-rate restrictions on the muon species which are actually observed as the μ^+ decays. This is because the muon LCR allows muonium-containing free radicals to be observed even when they are being formed over a microsecond timescale, as in dilute solutions of reactive solutes as small as 10^{-4}M[4]. It also prevents spin-depolarization of the muon by internal hyperfine oscillations in the 'singlet' state of muonium (antiparallel μ^+ and e^- spin state) so that the whole initial muonium yield can be detected, because the muon spin vector is held fixed in a strong, decoupling, longitudinal magnetic field.

Benzene was selected as the solute for this study, because it is soluble in hydrocarbons and gives a Mu-radical which is already fully character-ized in spectroscopic properties[5]. Also the radical yield is known[6] for the pure liquid, for normalization purposes. n-Hexane was chosen as the solvent because it can be obtained fairly pure, and its muon yields have been determined by μSR: they are, diamagnetic fraction (P_D) = 0.65, muonium fraction (P_M) = 0.13, and 'missing' fraction (P_L) = 0.22[7]. The rate constant for Mu reacting with benzene in n-hexane has also been measured by μSR to be $k_M = (3.7 \pm 0.8) \times 10^9 \text{M}^{-1}\text{s}^{-1}$[8].

Experimental

These experiments were performed on the M20B beamline at the TRI-UMF cyclotron using energetic spin-polarized muons (4.1 MeV). Magnetic fields from 0.01 to 3.0T (1 Tesla(T) = 10^4 Gauss) along the beam direction (and parallel to the muon spins) were provided by a superconducting magnet. The hexane was purchased from Fluka Chemicals, the benzene from BDH, and they were used without further purification. All solutions were thoroughly deoxygenated by bubbling with pure N_2 before being pumped into the cell in a closed system.

In the LCR technique, the muon polarization is measured as a function of magnetic field. Resonant transfer of polarization from the muon to a particular nucleus (^{1}H(6) in this case, see Eq. (2) later) occurs at a specific magnetic field where the muon transition frequency is matched to that of the proton. This results in a decrease in the muon polarization averaged over the muon lifetime and is detected experimentally as a reduction in

muon decay asymmetry along the applied field direction. In order to reduce systematic errors, a small square wave field modulation (± 5mT) was used, which results in the differential appearance of the resonance. The resonance was recorded as $A^+ - A^-$ as the magnetic field is scanned (Fig. 1). ['A' is the integrated muon-decay asymmetry given by $(B - F)/(B + F)$, where F and B are the total number of positron events in the forward and backward telescopes, respectively, and superscripts + and – refer to the direction of the modulation field.]

A MINUIT reduced-χ^2 fitting program was used which allows the raw data to be analyzed using a difference of two Lorentzians for B_R (the LCR position), ΔB (width at half height of the LCR), and Amp (the amplitude of the LCR signal given as percentage).

Results

Figure 1 shows representative LCR spectra of benzene at three different concentrations in n-hexane. The LCR amplitudes decrease as the benzene concentration falls. For the dilute hexane solutions, the muons invariably stopped in the solvent and reacted as thermalized species with the solute (benzene) to form the muonated cyclohexadienyl radical. The solid lines of Fig. 1 are the computer fits. The resonance position B_R is given by Eq. (1)

$$B_R \approx 0.5[(A_\mu - A_p)/(\gamma_\mu - \gamma_p) - (A_\mu + A_p)/\gamma_e] \qquad (1)$$

where γ's are the magnetogyric ratios of the muon, proton and electron, and A_μ and A_p are hyperfine coupling constants. The resonance in neat

benzene centered at 2.072T has already[5] been assigned to the proton in the –CHMu group (H(6)) of the cyclohexadienyl radical arising from the addition of muonium to benzene, as in Eq. (2).

$$Mu + C_6H_6 \longrightarrow \quad \overset{Mu}{\underset{H}{\diagdown}} \quad [\dot{C}_6H_6(Mu)] \qquad (2)$$
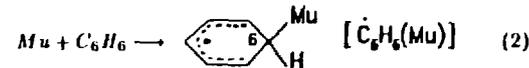
For the n-hexane solutions B_R was shifted by -12mT (or -0.6%) from the neat benzene value. We attribute this change to a solvent effect on the muon hyperfine coupling constant, as in $^{13}C_6H_6$ in cyclohexane[9]. There was no significant change in B_R from the 1M to the 3×10^{-4}M solutions. The linewidths (ΔB) changed negligibly from neat benzene to dilute solutions.

The yield (P_R) is defined as the fraction of incident muons which form the radical. Experimental values of P_R were evaluated in this case simply by equating them to the amplitude (Amp) of the H(6) resonance, with normalization being based on the neat benzene Amp value equated to P_R of 0.82 $\pm$ 0.04. These values are recorded in column 5 of Table 1. This is analogous to the procedure adopted for acetone solutions[10]. Whether or not the values of P_R determined here are correct in an absolute sense depends on the validity of the normalization. Our procedure seems appropriate because all linewidths were similar, and the value of $P_R = 0.82 \pm 0.04$ covers the yield from three independent sources: (i) the measured backward-to-forward muon-asymmetry (A_{bf}) in experiments with neat benzene on beamlines M15 and M20 gave P_R equal to 0.82 $\pm$ 0.04 using Eq. (3) as below[4]; (ii) Roduner determined $P_R = 0.80 \pm 0.02$ for pure benzene by transverse-field μSR[6];

and (iii) because it equals $1-P_D$.

An alternative method in calculating P_R from ΔB and Amp data was used in the case of acrylamide solutions in water[4], because pure acrylamide - a solid - could not be used for normalization purposes. For that situation Eq. (3) was established

$$P_R = \frac{Amp.(\Delta B)^2(\gamma_\mu - \gamma_p)^2}{A_{bf}.\nu_r^2} \qquad (3)$$

where ν_r is the frequency splitting of two nearly degenerate levels at B_R. In this equation ν_r is equal to $cA_\mu A_p/2B_R\gamma_e$, c being a constant equal to 1 when there is only one nucleus on resonance. Since ΔB changes negligibly for the present benzene solutions (column 3 Table 1), it is superfluous to use Eq. (3), except to check that the normalization was reasonable. With $\Delta B = 146G$, $Amp = 3.43\%$ for neat benzene and $P_R = 0.82$, Eq. (3) gives $A_{bf} = 0.24$. This value is about what was expected: it is higher than that used for acrylamide solutions and previously for pure benzene[4] because in the present experiments the cell position was optimized for maximum experimental asymmetry.

For the three lower benzene concentrations, the Mu-radical of Eq. (2) forms over the same timescale in which the muons decay, resulting in reduced LCR amplitudes. The extent of these reductions can be approximated by use of Eq. (4)[11],

$$P_R \quad \propto \quad \frac{k_M[S]}{k_M[S] + \lambda_0} \qquad (4)$$

where k_M is the rate constant for reaction (2) at a benzene concentration $[S]$ and the muon decay constant $\lambda_0 = 0.45 \times 10^6 s^{-1}$. Values of P_R corrected for this known effect on the LCR amplitude are given as positive values in column 6 of Table 1. Another correction given in column 6 (Table 1) is that expected for 'direct' effects on benzene during the thermalization process of the muon. It is presumed that direct effects are proportional to volume fraction (see below).

Figure 2 shows $P_{R(observed)}$ and $P_{R(corrected)}$ against benzene concentration, plotted (a) linearly, and (b) as $\log_{10}[C_6H_6]$ in order to display all data points. $P_{R(corr)}$ is taken as the scavengable yield of thermalized radical precursors.
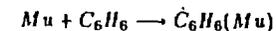
Discussion

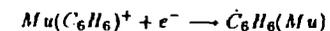Mu-radicals can form by any of the following mechanisms:

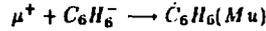(i) hot atom insertion at an epithermal stage:

$$Mu^* + C_6H_6 \longrightarrow \dot{C}_6H_6(Mu)$$
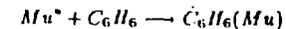
(ii) addition of thermalized Mu atoms:

$$Mu + C_6H_6 \longrightarrow \dot{C}_6H_6(Mu)$$

(iii) μ^+ capture followed by neutralization with e^- from the track:

$$\mu^+ + C_6H_6 \longrightarrow Mu(C_6H_6)^+$$

$$Mu(C_6H_6)^+ + e^- \longrightarrow \dot{C}_6H_6(Mu)$$

or

$$\mu^+ + C_6H_6^- \longrightarrow \dot{C}_6H_6(Mu)$$

In pure benzene all three may contribute. For benzene solutions in hexane the direct process of (i) should be reduced in accordance with volume fraction, since P_D falls linearly in benzene/cyclohexane mixtures[12,13]. At 1M this will be $\sim$ 9% of the contribution to pure benzene, which we assume to be $\sim (70 \pm 30)\%$ of total P_R; at 0.3M only 3%; and negligible for lower concentrations. Mechanism (iii) was shown to be unimportant for the micelle solutions, by the charge, in the aqueous acrylamide system[4], but ionic precursors cannot be ruled out entirely for these hexane solutions. Any μ^+ ions which happen to survive the thermalization process unassociated, could conceivably, be scavenged by dilute benzene with its large proton affinity[14] during their short lifetime prior to geminate neutralization, given sufficient mobility. However, for all the hexane solutions, mechanism (ii) is much more likely to be the dominant process. Mu has been observed in pure n-hexane by μSR with $P_M = 0.13$ and these Mu atoms have a lifetime of 10^{-6}s or so[7].

Figure 2(a) shows the Mu-radical yield (~ 0.35) to correspond very closely to $1-P_D$ for hexane, after making the correction for direct effects in the 1M and 0.3M cases. Thus, all the muons are now accounted for in hexane: 63%[10] to 65%[7] form diamagnetic species directly (P_D) and the rest can be scavenged by benzene at ≥ 0.1M to give Mu-radicals. Free

muonium atoms almost certainly account for a good fraction of these and probably them all. As in water, there is a significant missing fraction in pure hexane ($P_L = 0.22$), which may be muonium atoms lost during track expansion by depolarizing interactions or combination reactions.

If the fall-off in P_R at low benzene concentrations were due to the presence of an impurity (X) in hexane which competes for the radical precursor (presumed to be Mu here) by *homogeneous* kinetics:

$$Mu + C_6H_6 \xrightarrow{k_M} \dot{C}_6H_6(Mu) \qquad (5)$$

$$Mu + X \xrightarrow{k_X} MuX \qquad (6)$$

then

$$\frac{P_R}{P_{R(max)}} = \frac{k_M[C_6H_6]}{k_M[C_6H_6] + k_X[X]}$$

and

$$P_R^{-1} = P_{R(max)}^{-1}\left(1 + \frac{k_X[X]}{k_M[C_6H_6]}\right)$$

where $P_{R(max)}$ is the maximum radical yield obtainable at high benzene concentrations. If this were so, then a plot of P_R^{-1} against $[C_6H_6]^{-1}$ would be linear. The data of Table 1 are plotted in this form in Fig. 3; but it is seen to be strongly non-linear.

Evidently, Mu-radical formation and $\dot{C}_6H_6(Mu)$ radical survival, are in competition with *non-homogeneously* distributed reactive species such as those from the expanding radiation track of the high energy muon. Free radicals and unsaturates are produced by radiolysis in the muon track and

diffuse at rates comparable to those of Mu and Mu-radicals. Interactions with either will lead to a decreased P_R. The fact that this falls significantly with $[C_6H_6]$ only at $< 10^{-1}$M (see Fig. 2(a)) suggests that reaction (6) competing non-homogeneously with reaction (5) is much more important than interactions of $\dot{C}_6H_6(Mu)$ once formed. The sharp fall-off in P_D at low benzene concentrations may arise in part because Mu has a limited lifetime in hexane ($\sim 1\mu s$), regardless of whether this arises from reaction (7)

$$Mu + C_6H_{14} \longrightarrow MuH + \dot{C}_6H_{13} \qquad (7)$$
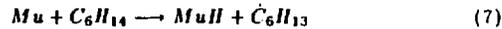
or from the presence of adventitous impurities.

In conclusion, hexane is seen to give muon yields which are similar to those of water[4]. This indicates that free electrons and μ^+ ions play, at most, a minor role in muonium formation and loss: because, from radiolysis studies, *geminate* ion-recombinations dominate in non-polar liquids like hexane, whereas it is the *free-ions* which dominate the radiation chemistry of water[13,15]. The muonium chemistry described here is consistent with muonium being formed epithermally, with some 30 to 40% reaching thermal energy unassociated in saturated solvents.

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Table 1

LCR positions, linewidths, amplitudes and calculated yields for the cyclohexadienyl radical from benzene in n-hexane solutions

$[C_6H_6]$ in hexane / mole dm^{-3}	B_R / T	ΔB / mT	$Amp\%$	$P_{R(obs)}$	Corrected $P_R^{a,b}$	$P_{R(corr)}$
11.24 (Neat)	2.0718(2)	14.6(3)	3.43(2)	0.82(4)[c]		0.82
1.0	2.0605(2)	14.5(3)	1.71(2)	0.41	-0.05(2)	0.36
0.3	2.0597(2)	14.3(3)	1.46(2)	0.35	-0.015(9)	0.34
0.1	2.0594(2)	14.8(3)	1.32(2)	0.32	0	0.32
0.01	2.0591(2)	14.4(3)	1.07(2)	0.26	0	0.26
0.003	2.0591(2)	14.3(3)	0.77(2)	0.18	+0.01	0.19
0.001	2.0587(2)	14.8(3)	0.60(2)	0.15	+0.02	0.17
0.0003	2.0587(2)	14.8(3)	0.33(2)	0.08	+0.03	0.11

Footnotes:

(a) Negative corrections: estimated direct effects (based on volume fraction of solutions assuming that two-thirds of radicals in benzene arise through direct or ionic processes.)

(b) Positive corrections: from Eq. (4), due to slow formation rate of the radical.

(c) Normalization to absolute scale (Amp of 3.43% equated to P_R of 0.82(4)). All other P_R values carry this 5% error.

Figure Legends

- Fig. 1. LCR spectra of muonated cyclohexadienyl radicals in hexane solutions at $[C_6H_6]$ of (a) 1.0M; (b) 0.003M; and (c) 0.0003M , given as differential asymmetry against longitudinal field.

- Fig. 2. Plot of radical yield (P_R) against concentration of benzene: (a) linear scale (□) $P_{R(obs)}$ and (○) denoting $P_{R(corr)}$; and (b) log scale of $[C_6H_6]$

- Fig. 3. Plot of $1/P_{R(corr)}$ against $1/[C_6H_6]$ (3×10^{-4}M not included because of significant decay of Mu)
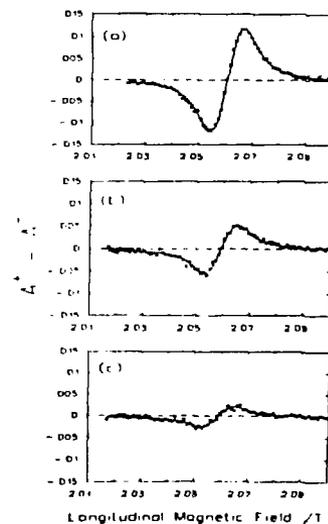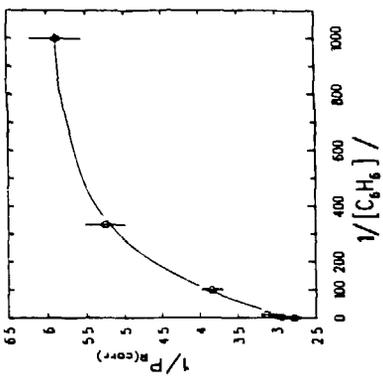

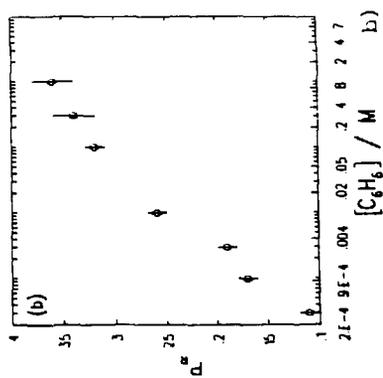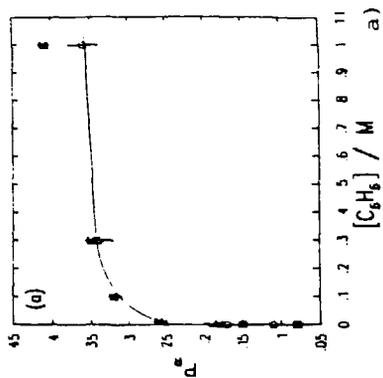Longitudinal Magnetic Field /T

Fig. 1

Fig. 3

Fig. 2