

Free Radicals Formed by H Atom Addition to Allenes as Determined by Muon Spin Spectroscopy

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ABSTRACT: Allyl and vinyl radicals are important intermediates in diverse areas of chemistry, ranging from combustion to synthesis. However, questions remain about the competitive formation of these radicals from allenes. Here we present a study of prototypical allyl and vinyl radicals formed by H atom addition to allenes. They were studied by forming the analogous muonium adducts, since muonium (Mu) behaves as a light isotope of hydrogen, and muoniated species can be characterized by muon spin spectroscopy. Two techniques were employed: Transverse-Field Muon Spin Resonance (TF- μ SR), and Muon Level Crossing Resonance (μ LCR), which allow for the measurement of muon hyperfine constants (hfc) and other nuclear hfc, respectively, and thus aid identification of the formed radicals. TF- μ SR has already been used to determine that two radicals are formed by Mu addition to 1,1-dimethylallene, but μ LCR techniques were undeveloped at the time of that study, so assignments were based on ESR data of similar allyl and vinyl radicals. We report here the muon spin spectroscopy of multiple radicals detected from positive muon irradiation of 1,1-dimethylallene and 1-methoxyallene in solution. The radicals were identified by comparison of muon and proton hfc with ESR data and the results of DFT calculations. The conclusion is that muonium (and by extension, the H atom) can add to all three carbons of the allene system, albeit with preference for the central carbon.

INTRODUCTION

As part of an on-going examination of the reactivity of low-valent main-group compounds towards free radical addition,¹⁻⁴ we planned to carry out comparative reactivity studies of some cumulated dienes, C=C=M (M = C, Si, Ge). As a first step we examined two substituted allenes: 1,1-dimethylallene (**1**) and 1-methoxyallene (**2**). The ideal probe of reactivity is the H atom, because its small size and simple structure avoid additional electronic effects, i.e. it can be viewed as an unbiased probe. This is important for allenes in particular, because the selectivity of free radical attack is known to depend on the nature of the reactant – electrophilic radicals tend to add to the terminal carbons and nucleophilic radicals to the central carbon, although other factors can modify this principle.^{5,6} However, H is not commonly used as a reagent for solution studies because its generation (typically by photolysis or radiolysis) invariably produces other reactive radicals, and the ensuing reactions lead to multiple products.

An alternative to the hydrogen atom is muonium, a single-electron atom with a positive muon as the nucleus ($\text{Mu} = \mu^+e^-$). Despite the light nucleus ($m_\mu = 0.1134$ u) the reduced mass of the atom is close to that of H, so Mu can be viewed as a light isotope of hydrogen.⁷⁻¹¹ The muon is radioactive (lifetime $\tau = 2.2$ μ s) and has spin ($I = 1/2$), which makes it a very selective probe of complex reaction systems. When Mu adds to an unsaturated molecule the resulting muoniated radical can be detected by muon spin spectroscopy (μ SR).¹²⁻¹⁵ Allyl radicals derived from dienes were among the earliest to be detected by μ SR,^{12,16} and subsequent work included Mu addition to 1,1-dimethylallene.¹⁷ However, these studies employed only the transverse-field muon spin rotation technique (TF- μ SR),

which allows the determination of the muon hyperfine constant (hfc) but does not provide information on the hfc of other spin-active nuclei (e.g. protons in alkyl and allyl radicals). The necessary technique, avoided level-crossing resonance (μ LCR), was only subsequently developed and applied to organic radicals.^{18,19} The present paper reports the characterization of radicals derived from allenes using both TF- μ SR and μ LCR.

EXPERIMENTAL PROCEDURES

Muon spin spectroscopy experiments were carried out at the TRIUMF cyclotron facility in Vancouver, using the HELIOS spectrometer installed at the M15 muon beam line. HELIOS incorporates a superconducting solenoid magnet whose axis is aligned parallel to the beam. For TF- μ SR experiments the spin polarization of the beam is rotated 90° from its momentum, so that it is transverse to the magnetic field; μ LCR experiments utilize the natural longitudinal spin orientation. The beam was tuned for positive muons of about 4.1 MeV, which is sufficiently low that the muons stop in the sample, which was mounted in a helium-flow cryostat inserted into the solenoid bore. HELIOS employs plastic scintillator positron detectors which are arranged in a transverse geometry for TF- μ SR, and forward-backward for μ LCR, as described elsewhere.²⁰

Concentrated solutions of the two allenes (1,1-dimethylallene and 1-methoxyallene) were made by mixing the allenes with equal volumes of tetrahydrofuran (THF). They were degassed by the freeze-pump-thaw method before being sealed in stainless-steel target cells.

Although the spin precession signals obtained from TF- μ SR experiments are conveniently displayed as Fourier transform spectra (e.g. Figure 1) quantitative analysis was accomplished

by fitting the original signals in time space, using Wimda,²¹ a multi-parameter curve-fitting program for μ SR histograms. μ LCR spectra comprise plots of muon asymmetry as a function of magnetic field. Since square-wave field modulation was used (either ± 48 G or ± 96 G) the resonance signals were fitted (using Microsoft Excel) with the difference of two Lorentzian curves.

EXPERIMENTAL RESULTS

Radicals derived from 1,1-dimethylallene

TF- μ SR experiments were performed at temperatures of 170, 200, 230 and 260 K. The 260 K spectrum is shown in Figure 1. It shows the characteristic precession signals of two distinct radicals. One has muon spin precession frequencies of 138.7 MHz and 175.5 MHz, corresponding to a muon hyperfine constant (A_μ) of 36.8 MHz, and the other has precession frequencies of 38.4 MHz and 276.6 MHz, corresponding to $A_\mu = 238.2$ MHz. At lower temperatures the smaller hfc decreases and the larger hfc increases, as shown in Table 1. These data are consistent with the values (at 210 K and 288 K) found by Rhodes et al.¹⁷ and assigned to the 1,1-dimethylallyl radical **1a** and the substituted vinyl radical **1b** (see Scheme 1). It is **1a** that has the smaller hfc.

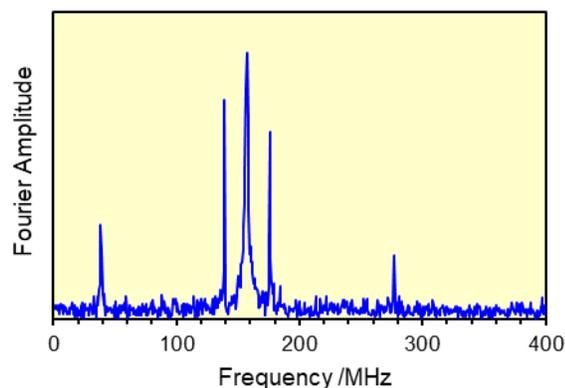


Figure 1. Fourier transform TF- μ SR spectrum obtained from a sample of 1,1-dimethylallene in THF at 260 K. The peak at 157 MHz is due to muons in diamagnetic environments, whose spins precess at the muon Larmor frequency for the applied magnetic field (here 11.59 kG). The signals symmetrically arranged about the diamagnetic peak arise from muoniated free radicals. The inner, more intense pair corresponds to a muon hyperfine constant of 36.8 MHz. The outer, weaker pair corresponds to a muon hyperfine constant of 238.2 MHz.

Table 1. Muon Hyperfine Constants (MHz) for the Two Radicals Derived from 1,1-Dimethylallene

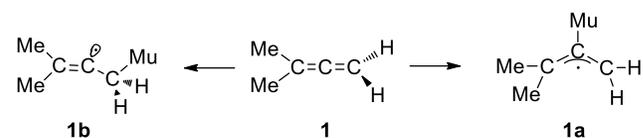
Temperature /K	1a	1b
260	36.79(1) ^a	238.22(3)
230	36.01(1)	246.16(3)
200	35.27(1)	257.42(4)
170	34.59(1)	272.69(7)

^aThe numbers in parentheses refer to statistical uncertainty from the fits.

Although the Fourier transform signals of **1b** appear to be weaker than those of **1a**, this is mostly because the **1b** lines are broader. Fits of the precession signals in time space confirm

that radical **1b** decays faster than **1a**. From the ratio of the initial amplitudes of the precession signals we deduce that the relative yield of the radicals (**1a/1b**) is 1.2 ± 0.1 .

Scheme 1. Muonium addition to 1,1-dimethylallene (1)



The same sample was also studied by μ LCR at 170 K and 260 K. Figure 2 displays field regions where resonances were detected at 260 K. Such resonance signals occur at fields where muon and proton spin-levels mix. However, at very low field there are additional mechanisms which lead to loss of muon spin polarization, resulting in a curved background (the so-called repolarization curve).¹⁵ For purposes of display the spectrum shown in Figure 2a has had this background removed. In all, there are five resonances shown, some of them (two each in Figures 2a and 2b) close together so that the spectral shapes overlap. The magnetic field at which each resonance occurs depends on both the muon hfc A_μ and the proton hfc A_p .^{18,19}

$$B_{\text{LCR}} = \frac{1}{2} \left| \frac{(A_\mu - A_p)}{(\gamma_\mu - \gamma_p)} - \frac{(A_\mu + A_p)}{\gamma_e} \right| \quad (1)$$

where γ_μ , γ_p and γ_e are the muon, proton, and electron gyro-magnetic ratios, respectively. In principle the existence of two radicals, and thus two values of A_μ , leads to ambiguity in determination of A_p . In practice, however, the choices are limited by expectations based on ESR literature. For example, the resonance close to 10 kG (Figure 2c) must be associated with radical **1b** ($A_\mu = 238.2$ MHz) since the alternative ($A_\mu = 36.8$ MHz) would imply unreasonable proton hfcs (-150 MHz or +222 MHz) for an allyl radical. Similar considerations lead to assignment of the four low-field resonances to radical **1a**.

A different type of ambiguity arises from the unsigned (absolute value) nature of B_{LCR} (Equation 1). In particular, the two resonances close to zero field (Figure 2a) provide different values of A_p according to whether $A_p > A_\mu$ or vice-versa. The results listed in Table 2 were chosen on the basis of published ESR data for the 1,1-dimethylallyl radical,²² with the alternatives included as footnotes.

Table 2. Proton Hyperfine Constants (A_p) Derived from the Muon Avoided Level-crossing Resonances Detected at 260 K and 170 K

Radical	260 K		170 K	
	B_{LCR} /kG	A_p /MHz	B_{LCR} /kG	A_p /MHz
1a	0.248(5)	31.95(9) ^a	0.272(5)	29.33(10) ^b
1a	0.407(4)	44.07(7) ^c	0.493(2)	43.49(4) ^d
1a	3.969(2)	-37.00(4)	3.866(3)	-37.26(5)
1a	4.082(3)	-39.08(5)	3.982(3)	-39.42(6)
1b	10.058(6)	50.27(11)	–	–

^aAlternative value 41.14 MHz. ^bAlternative value 39.40 MHz. ^cAlternative value 29.02 MHz. ^dAlternative value 25.24 MHz.

In most cases the relative magnitudes of A_μ and A_p are obvious and it is possible to determine their relative signs (a particular

advantage of μ LCR, in contrast to standard ESR spectra which provide only line splittings). Thus, the resonances close to 4 kG (Figure 2b) imply negative proton hfc's, which are assigned to the α -CH₂ group of **1a**. The pair of ambiguous positive hfc's is assigned to the β -methyl groups on C1. The inequivalence of this pair of hfc's is consistent with the planar allyl structure of **1a** (Scheme1). Furthermore, the hfc's are roughly half of the typical value (75 MHz)²³ for a β -CH₃ group in a localized radical, consistent with a π -orbital in which the unpaired spin density is shared between C1 and C3.

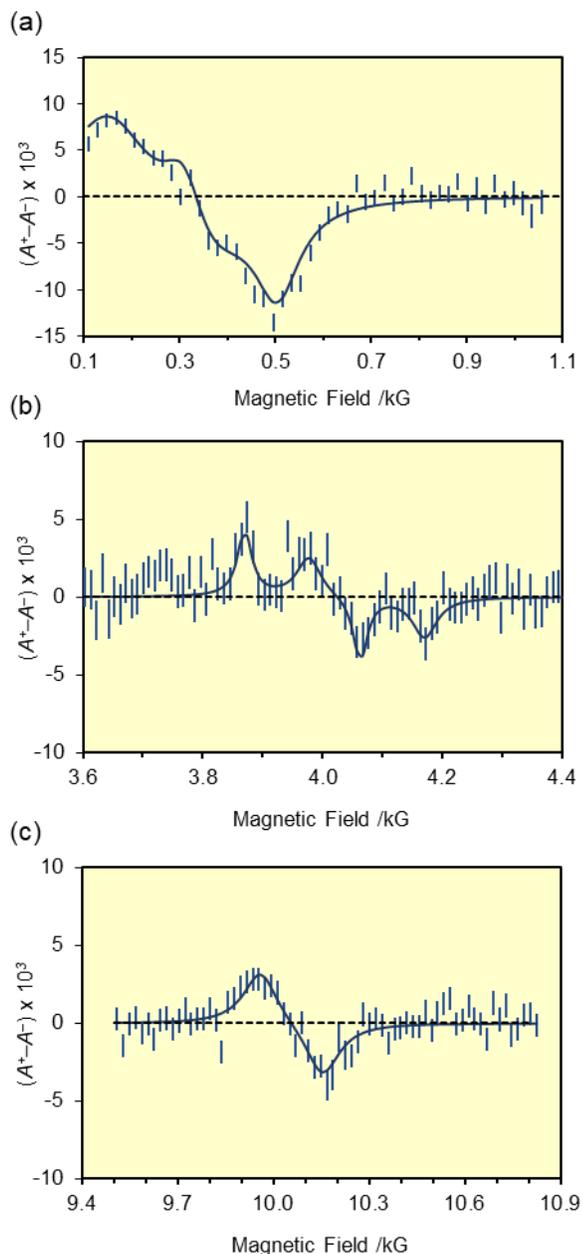


Figure 2. Segments of the μ LCR spectrum obtained from a sample of 1,1-dimethylallene in THF at 260 K. There are two overlapping resonances in each of (a) and (b) and a single one in (c).

The highest-field resonance (recorded only at 260 K) is assigned to the protons of the muoniated methyl group ($-\text{CH}_2\text{Mu}$) attached to the α carbon of **1b**. Their hfc (50.3 MHz) is consistent with the methyl proton hfc reported for the methylvinyl radical $\text{H}_2\text{C}=\text{C}^{\cdot}\text{CH}_3$ in liquid ethane at 101 K

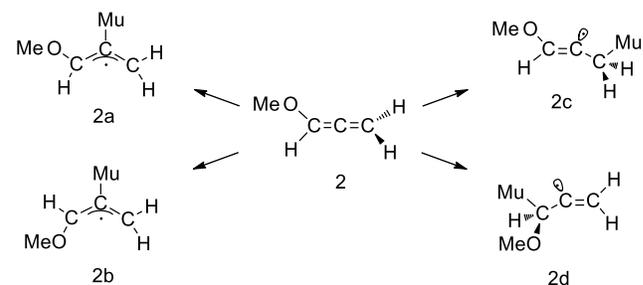
(54.6 MHz).²⁴ It is instructive to compare our proton hfc with the muon hfc ($A_\mu = 238.2$ MHz) for the same radical (**1b**). Defining a reduced muon hfc, $A_\mu' = 0.31413A_\mu$, to account for the different magnetic moments of the muon and proton, we find a hyperfine isotope effect of $A_\mu'/A_p = 1.49$, a typical value for the muoniated methyl group.¹⁰ Alternatively, comparing A_μ' to the methyl proton hfc of $\text{H}_2\text{C}=\text{C}^{\cdot}\text{CH}_3$ the isotope effect is 1.37. Such isotope effects are usually ascribed to a conformational effect, a preference for the C-Mu bond to eclipse the orbital containing the unpaired electron on the neighbouring carbon. Incomplete averaging of methyl rotation results in temperature dependence of the hfc's: A_μ falls with temperature and A_p rises (as shown for the muoniated tert-butyl radical).²⁵ The muon hfc's listed in Table 1 are consistent with this. A roughly temperature-independent average for the CH_2Mu group can be defined as $\langle A \rangle = (A_\mu' + 2A_p)/3$. For **1b** this works out to be 58.5 MHz, reasonably close to the methyl proton hfc in $\text{H}_2\text{C}=\text{C}^{\cdot}\text{CH}_3$.

A smaller, positive temperature-dependence is evident (Table 1) for the muon hfc in **1a**, where Mu is attached to C2. This is in accord with the previous μ SR study¹⁷ as well as earlier ESR results on similar 1-substituted allyl radicals.²² It is consistent with torsional oscillations about C2, resulting in σ - π overlap between the C-Mu(H) bond and the singly-occupied molecular orbital.

Radicals derived from methoxyallene

Allyl and vinyl radicals are also to be expected from addition of muonium to methoxyallene (**2**), but the lower symmetry of the mono-substituted allene results in *E/Z* isomerization. Furthermore, to aid subsequent discussion we should not exclude the possibility of Mu addition to C1 as well as C3. Scheme 2 shows the possible muoniated radical products.

Scheme 2. Muonium addition to methoxyallene (**2**)



TF- μ SR spectra were obtained from the sample of methoxyallene in THF at temperatures of 210, 245, 280 and 300 K, as well as neat liquid methoxyallene at 260, 280 and 300 K. The strongest signals were observed at the lowest temperature, and these are displayed in Figure 3a.

There are several notable differences from the dimethylallene case (Figure 1). First, although there is a weak precession signal at 53.4 MHz, the matching frequency on the high side of the diamagnetic signal is not discernable. This is also the case for another precession signal, at 118 MHz. The lack of a high frequency precession signal can arise when the formation rate of the muoniated radical competes with the change of precession frequency from its precursor (typically muonium), resulting in spin dephasing of the product.¹³⁻¹⁵ It is still possible to determine the muon hfc from the single radical precession frequency (ν_{R1}) and the muon Larmor frequency:

$$A_{\mu} = 2 \frac{(v_{\mu} - v_{R1})(v_e + v_{R1})}{v_e - v_{\mu} + 2v_{R1}} \quad (2)$$

where v_{μ} and v_e are the muon and electron Larmor frequencies. The first signal corresponds to a muon hfc of 286.5 MHz, consistent with a muoniated methyl group in a vinyl radical, similar to **1b**. The second signal, with muon hfc 156.7 MHz, has no equivalent in the dimethylallene system. It may also be a substituted vinyl radical, but with Mu attached to C1 instead of C3. Although very weak, the existence of this signal was confirmed with a sample of neat liquid methoxyallene, for which the radical formation rate was sufficient to give the upper radical precession frequency, as evident in Figure 3c.

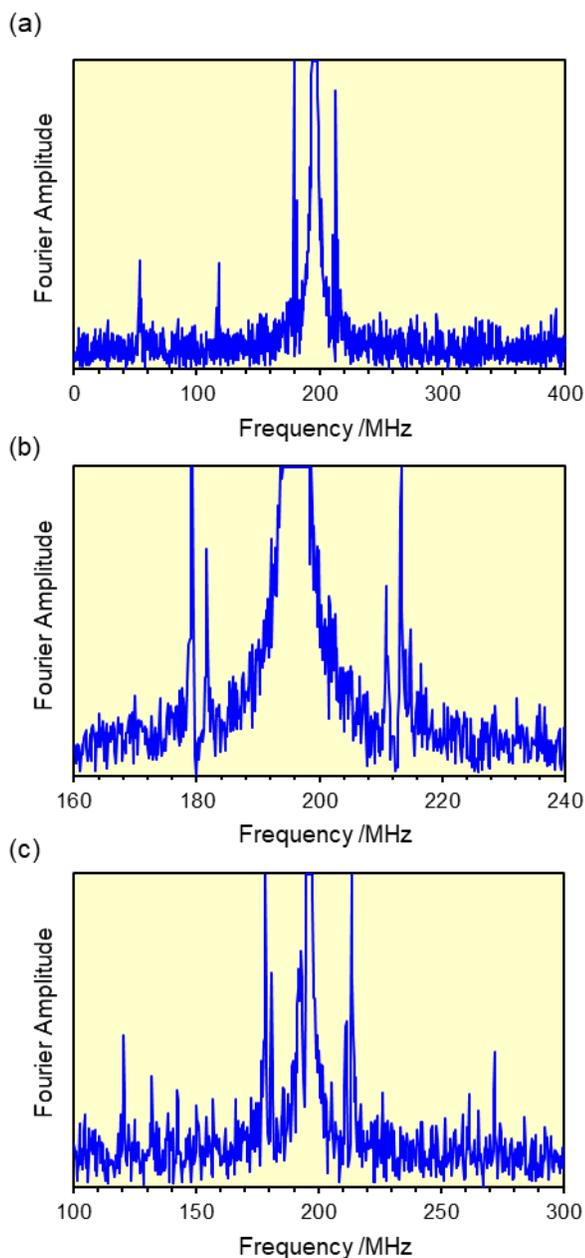


Figure 3. Fourier transform TF- μ SR spectra obtained from (a) a sample of methoxyallene in THF at 210 K; (b) the same spectrum expanded; (c) pure liquid methoxyallene at 260 K.

Yet another notable difference from dimethylallene is the doubling of the allyl radical signals, as shown in the expanded plot of Figure 3b. This is consistent with the loss of symmetry caused by the methoxy substituent. The muon hfc's are listed in Table 3.

Table 3. Muon Hyperfine Constants (MHz) for the Radicals Derived from Methoxyallene^a

Temp./K	Sample	2a	2b	2c	2d
210	solution	34.03(1)	29.17(3)	286.5(1)	156.7(1)
245	solution	34.86(2)	30.00(3)	272.9(1)	–
260	liquid	35.21(3)	30.40(6)	–	154.0(1)
280	solution	35.67(1)	30.76(2)	263.7(4)	–
280	liquid	35.65(2)	30.82(4)	–	150.1(1)
300	solution	36.12(2)	31.20(3)	258.4(5)	–
300	liquid	36.19(3)	31.44(4)	–	148.7(1)

^aAssignment to specific radical structures relies on the results of DFT calculations.

Hyperfine constants for the two 1-methoxyallyl radicals (H-substituted equivalents to **2a** and **2b**) have been reported by Sustmann et al.^{26,27} The allylic (C2) protons have hfc's in the ratio 1.15, very close to our value of 1.17. Similarly, two distinct 1-methylallyl radicals have been detected by ESR after H-abstraction from the cis and trans forms of 2-butene.²⁸ Despite other differences in the spectra, the hfc of the proton in the allylic (C2) position is reported to be almost the same for the two isomeric methylallyl radicals, in contrast to our results for the muon hfc in the methoxyallyl radicals (**2a** and **2b**). The positive temperature-dependence of the muon hfc in **2a** and **2b** is the same as noted earlier for **1a**.

The higher muon hfc's assigned to radicals **2c** and **2d** are consistent with expectations for a muoniated methyl group (**2c**, similar to **1b**) and a radical in which Mu and the methoxy group are attached to the same carbon (**2d**). In the latter case the preferred conformation has an increased dihedral angle between the C-Mu bond and the σ -orbital containing the unpaired electron.

In principle the above explanation for the different muon hfc's of the vinyl radicals could be tested by determining the proton hfc's for the substituted methyl groups from μ LCR spectra. However, no convincing resonances were detected in the expected field ranges, presumably because the weak signals were lost in noise. The best μ LCR signals for methoxyallene in THF are shown in Figure 4. The two resonances (at 3.844 kG and 3.967 kG) can be attributed to the three protons attached to C1 and C3 in **2a** (the most abundant radical as indicated by TF- μ SR spectra). The lower-field signal is 1.4 times more intense than the other, consistent with a degeneracy factor of 2.¹⁸ The corresponding proton hfc's are -35.9 ± 0.1 MHz (two equivalent protons) and -38.2 ± 0.1 MHz, very close to values found for **1a**.

COMPUTATIONAL RESULTS

Proton hyperfine constants for various allyl and vinyl radicals were calculated to confirm the assignments discussed above. Gaussian-16²⁹ was used to optimize radical geometries, using DFT at the UB3LYP/6-311G(d,p) level, after which single-point calculations with the EPR-III basis set were used to determine hyperfine constants. Although this basis set has been

optimized for the computation of hfcs by DFT methods, it does not account for vibrational effects.³⁰ These are often ignored for proton hfcs but can be substantial for Mu. The agreement between computed and ESR experimental values (Table 4) validates the method, and the comparison with our μ SR results shows that the Mu/H isotope effect is small for radical **1a**. This is not the case for **1b**, where there is a conformational isotope effect in the CH₂Mu group. Taking the average hfc for the group, we calculated 60.6 MHz, which can be compared with 58.5 MHz for our experimental result. ESR results for related methyl-substituted vinyl radicals are 54.6 MHz²³ and 61.5 MHz.³¹

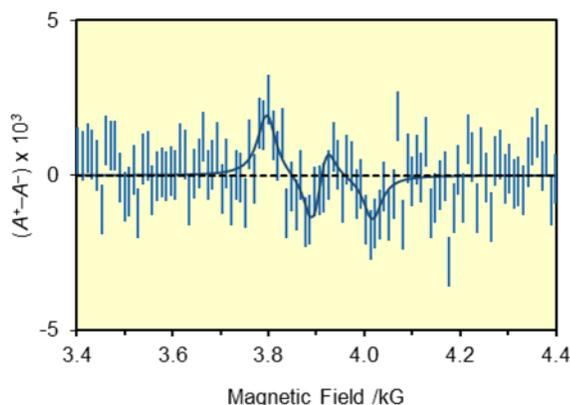


Figure 4. Weak resonances in the μ LCR spectrum obtained from a sample of methoxyallene in THF at 275 K.

Table 4. Comparison of Calculated Hyperfine Constants (MHz) for 1,1-Dimethylallyl with Experimental Data for Radical 1a

	calc. ^a	ESR ^b	μ SR ^c
H/Mu	11.2	10.6	11.6 ^d
CH ₃ (trans)	44.7	43.0	44.1
CH ₃ (cis)	36.2	34.6	32.0
H (trans)	-40.6	(-39.1) ^e	-39.1
H (cis)	-38.3	(-37.1) ^e	-37.0

^aUB3LYP/6-311G(d,p)//UB3LYP/EPR-III. ^bAverage of values for 153 K and 363 K (Krusic et al.²²). ^cThis work, values at 260 K. ^dReduced muon hyperfine constant. ^e Assumed negative.

Table 5 compares our experimental data for the muoniated radicals formed from 1-methoxyallene with our calculations for radicals **2a–2d**. The apparent disagreement for **2c** and **2d** can be ascribed to the muonium conformation effect. Thus, the calculated value listed for CH₂Mu in **2c** is an average of three proton hfcs, corresponding to free rotation of the methyl group in the high-temperature limit. In contrast, the reduced muon hfc is 30% higher, indicating a preferred conformation with enhanced overlap of C-Mu with the orbital containing the unpaired electron. There is an inverse effect for **2d**, since in this case the methoxy substituent takes the preferred orientation.

A more extensive report of computational results can be found in the file of Supporting Information.

Table 5. Comparison of Calculated and Experimental Values of Hyperfine Constants (MHz) for Radicals Derived from 1-Methoxyallene

	nucleus	calc. ^a	ESR ^b	expt. ^c
2a	H/Mu	10.1	10.2	11.2
2a	H (cis \times 2)	-40.2, -36.3	36.7	-35.9 ^d
2a	H (trans)	-43.3	39.2	-38.2 ^d
2b	H/Mu	9.7	8.8	9.7
2c	CH ₂ Mu	63.3 ^e		82.8
2d	CHMuOMe	66.8 ^f		47.2

^aUB3LYP/6-311G(d,p)//UB3LYP/EPR-III. ^bSustman et al.^{26,27} values at 213 K. ^cThis work; reduced muon hfc at 280 K unless otherwise specified. ^dThis work; proton hfc at 275 K. ^eAverage conformation. ^fAverage of two conformations.

FURTHER DISCUSSION

Given the general importance of allenes in organic synthesis and, specifically, the recent interest in their functionalization via radical addition,^{6,32} it would be desirable to understand the factors that determine the regioselectivity of radical addition to allenes. It has long been known that the nature of the attacking radical affects the selectivity of reaction at the centre versus the terminal carbons.⁵ By using the H-atom analogue, muonium, we eliminate this factor. The general expectation is that H atoms add to alkenes and dienes to form the most stable radical products, and this is well supported by studies utilizing muonium.^{16,33} A recent review⁶ asserts that this principle also applies to allenes: “thermodynamics largely controls the selectivity in radical additions to allenes”. However, our results do not support this view. Radical **1a** is lower in energy than **1b** by 93 kJ mol⁻¹, yet the relative yields are almost equal (55%, 45%). We therefore conclude that the competition is governed by kinetics. i.e. it is the activation energies rather than the reaction energies that determine the products. In similar vein, the lack of Mu addition to C1 of dimethylallene is explained by a higher activation energy (no doubt due to steric hindrance) rather than the conventional explanation of the greater stability of the tertiary radical over the primary. In contrast, C1 and C3 of methoxyallene are both open to attack, as evident by the detection of both **2c** and **2d**, in addition to the more abundant allyl radicals **2a** and **2b**.

As a caveat we point out that the above discussion assumes that the detected radicals are all formed by direct addition of muonium to the allenes. In principle, two-step ionic pathways exist in the end-of-track muon radiolysis spur: either μ^+ attachment followed by charge neutralization, or initial electron attachment followed by muon addition.^{34,35} One possible indication of such an ionic pathway is delayed formation of the radical product. This is rare, but in recent years we have reported several instances of related behaviour, where the amplitudes of precession frequencies vary sinusoidally with the delay between the muon stop and the time window used to Fourier transform the data.^{14,36-38} Careful examination of the allene data set revealed some effect for radicals **2b** and **2d** but not the others. The phenomenon of oscillating signal amplitudes is under examination in other systems where the effect is more marked. For the current work we can only remark that we cannot rule out the possibility of a small contribution to radical formation via an ionic reaction mechanism.

CONCLUSIONS

By using muonium as an H-atom analogue we have shown that unbiased free radical attack can occur at all three carbons of the allene system. Furthermore, the competition is kinetically controlled. This is relevant to the use of allenes in organic synthesis, in particular their functionalization via radical addition.

ASSOCIATED CONTENT

Supporting Information. Optimized geometries and hyperfine constants for radicals **1a**, **1b**, **2a**, **2b**, **2c**, and **2d** as calculated at the UB3LYP/6-311G(d,p)/UB3LYP/EPR-III level. Full listing of reference 29. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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TOC Graphic

