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Detection of a secondary muoniated radical

Brett M. McCollum^a, Jean-Claude Brodovitch^a, Jason A. C. Clyburne^b, Paul W. Percival^{a,*}
and Robert West^c

^a*TRIUMF and Department of Chemistry, Simon Fraser University, Burnaby BC, Canada V5A 1S6*

^b*Department of Chemistry, Saint Mary's University, Halifax NS, Canada B3H 3C3*

^c*Organosilicon Research Center, University of Wisconsin, Madison WI 53706 USA*

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Abstract

Muoniated free radicals are formed by addition of muonium to unsaturated molecules. Successful detection by transverse-field μ SR usually requires pure or highly concentrated samples and a muonium reaction rate in excess of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ to ensure that the muon spin polarization is coherently transferred to the radical. For this reason muoniated radicals reported to date are all the primary radical products of Mu reaction. Thus it was expected that Mu addition to a silylene would result in detection of a silyl radical. However, the muon hyperfine constant determined by experiment is much smaller than the value predicted by density functional calculations. Instead, it is consistent with a disilanyl radical, the secondary radical formed by reaction of the initially formed silyl radical with a second silylene molecule. From an analysis of the signal amplitude it was deduced that the second-order rate constant for reaction of the muoniated silyl radical with the parent silylene is $5.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This work represents the first example of direct detection of a secondary radical product by transverse-field μ SR.

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Keywords: Muonium; Radical; Silylene; Disilanyl

1. Introduction

Three decades have passed since the first detection of muoniated radicals [1] by transverse-field muon spin rotation (TF- μ SR). A common feature of the large number and variety of radicals so detected is that they are formed by muonium (Mu) addition to unsaturated compounds. (The possibility of ionic mechanisms has been discussed but such channels

seem to be minor [2].) With the exception of a few radicals which have no magnetic nucleus except the muon (e.g. $^{12}\text{C}_{60}\text{Mu}$), TF- μ SR studies of radicals are carried out at high magnetic fields. This ensures that the electron Larmor frequency is greater than the muon hyperfine constant (hfc), so that the spectrum of muon precession frequencies collapses into two values, whose difference gives the muon hfc. Since the muon precession frequencies are different in muonium and the radical, the muonium reaction rate must be very fast (typically 10^{10} s^{-1} or more) to avoid

* Corresponding author. Tel.: +1-778-782-4477; fax: +1-778-782-3765; e-mail: percival@sfu.ca

loss of signal due to incoherent precession. This is why TF- μ SR studies of radicals are limited to pure or concentrated samples of the precursor molecules, and those molecules must react with muonium with second-order rate constants in excess of $10^9 \text{ M}^{-1}\text{s}^{-1}$. As a consequence, muoniated radicals reported to date are all the primary radical products of Mu reaction. This is often quoted as an advantage of μ SR over electron spin resonance, since ESR studies of transient radicals are frequently complicated by simultaneous detection of secondary and later products.

In the course of a study of muoniated radicals formed by muonium addition to carbenes [3], silylenes and germynes [4,5], we detected a radical whose muon hfc is inconsistent with the primary product of Mu addition to the substrate (a silylene). Instead, we believe that we have detected the secondary radical formed by reaction of the primary radical with a second silylene molecule.

2. Experimental

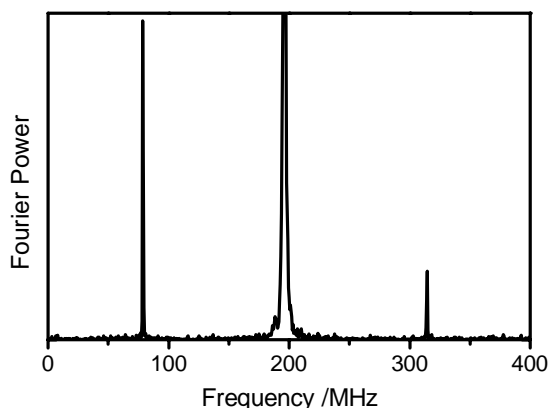


Fig. 1. Fourier power TF- μ SR spectrum obtained from a solution of silylene **1**. The pair of signals at about 80 MHz and 315 MHz is characteristic of a muoniated radical. The truncated peak at 196 MHz is due to muons incorporated in diamagnetic molecules.

The N-heterocyclic silylene **1** was synthesized by standard procedures [6] at the Organosilicon Research Center of the University of Wisconsin. A sample was dissolved in oxygen-free tetrahydrofuran and sealed in a stainless-steel cell for μ SR

experiments, which were carried out at the M20 beam line of TRIUMF, using the HELIOS spectrometer. Details of the μ SR experimental techniques and apparatus are available in greater detail elsewhere [7].

Hyperfine constants were predicted by quantum calculations using the Gaussian03 suite of programs [8] as described in detail elsewhere [5].

3. Results and discussions

Fig. 1 displays the TF- μ SR spectrum recorded from a 1.55 M solution of **1** in tetrahydrofuran at 299 K in a transverse magnetic field of 14.5 kG. The separation of the two radical precession frequencies gives the muon hyperfine constant: 235.39(2) MHz. Initially it was assumed that the spectrum was due to the muoniated silyl radical **1-Mu**, formed by direct addition of Mu to the silylene, as shown in Fig. 2. However, density functional calculations predict a much higher muon hfc: 618 MHz [4,5].

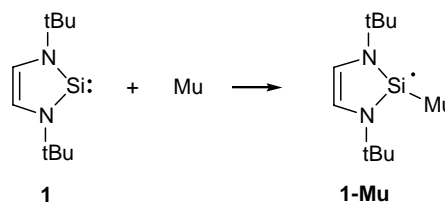


Fig. 2. Formation of a muoniated silyl radical by Mu addition to **1**.

On the other hand, the muon hfc of 196 MHz predicted for the muoniated disilanyl radical **2-Mu** (see Fig. 3) is a much better match to the measured value, given that the computations do not take into account the isotope effect on vibrational averaging, which can easily account for the 17% underestimate in the hfc. In addition, an ESR study of the silacyclopentyl radical found a value of 65.5 MHz for the α Si-H [9], which corresponds to 209 MHz for the muoniated analogue.

One reason to suspect the formation of a disilanyl is the known tendency of silylenes to dimerize. Indeed, *N,N'*-di-tert-butyl-1,3-diaza-2-sila-2-ylidene (silylene **1** without the double bond) is known to exist in equilibrium with the corresponding disilene in concentrated solution [10]. If silylene **1** behaves in similar fashion we should expect that Mu would add to the disilene **2** to form the disilanyl radical **2-Mu**,

as shown in mechanism (a) of Fig. 3. We reject this hypothesis for two reasons: (1) Despite the behaviour of its saturated counterpart, **1** has been found to be stable in solution [10] (2) If silylene **1** existed in equilibrium with its dimer, we would expect two radical products, the silyl and the disilanyl. The relative yields would depend on the monomer–dimer equilibrium but would also favour the more reactive silylene.

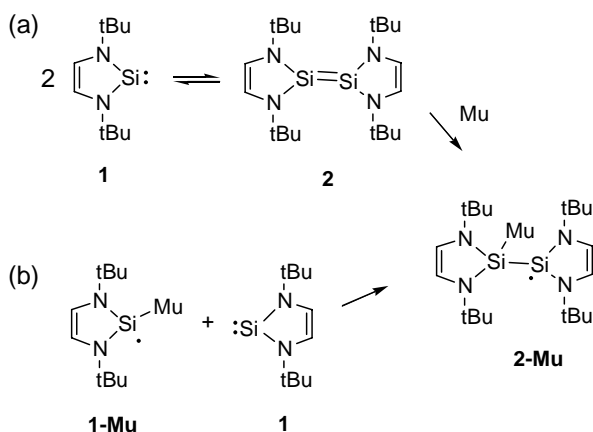


Fig. 3. Possible mechanisms for formation of the muoniated disilanyl radical **2-Mu**: (a) by addition of muonium to the dimer **2**; (b) by reaction of **1-Mu** with an additional molecule of **1**.

There is no doubt that silylene **1** can react with free radicals, since the adducts have been studied by ESR [11]. Furthermore, a coupling reaction similar to mechanism (b) has been proposed to explain disilane products in the reaction of silylenes with halocarbons [12]. Of particular interest here, is whether muon spin polarization is conserved in the two-step mechanism. The first step, muonium to radical, has been treated in the past [13,2], and extension to the case of radical transformation is straightforward. We find that the muon polarization at the two precession frequencies is given by

$$P(\omega_{12}) = \frac{1}{2} \left\{ \left[\frac{C}{1 + \Delta_{1212}^2} + \frac{S}{1 + \Delta_{1412}^2} \right]^2 + \left[\frac{C \Delta_{1212}}{1 + \Delta_{1212}^2} + \frac{S \Delta_{1412}}{1 + \Delta_{1412}^2} \right]^2 \right\}^{1/2} \quad (1)$$

and

$$P(\omega_{43}) = \frac{1}{2} \left\{ \left[\frac{C}{1 + \Delta_{4343}^2} + \frac{S}{1 + \Delta_{2343}^2} \right]^2 + \left[\frac{C \Delta_{4343}}{1 + \Delta_{4343}^2} + \frac{S \Delta_{2343}}{1 + \Delta_{2343}^2} \right]^2 \right\}^{1/2} \quad (2)$$

where C and S are functions of mixing coefficients

$$C = c_{R1}^2 c_{R2}^2 + c_{R1} s_{R1} c_{R2} s_{R2} \quad (3)$$

$$S = s_{R1}^2 c_{R2}^2 - c_{R1} s_{R1} c_{R2} s_{R2}$$

and

$$\Delta_{klmn} = (\omega_{kl} - \omega_{mn}) / \lambda$$

expresses the competition between the first-order rate of transformation from primary (R1) to secondary (R2) radicals (λ) and the change in their precession frequencies ω_{kl} and ω_{mn} , respectively. The mixing coefficients are of the form

$$c = \left\{ 1 + \frac{(\omega_e + \omega_\mu)}{[\omega_0^2 + (\omega_e + \omega_\mu)^2]^{1/2}} \right\}^{1/2}, \quad s^2 = c^2 - 1 \quad (4)$$

where ω_0 represents the muon hyperfine constant of the appropriate radical, and ω_e and ω_μ are the electron and muon Larmor frequencies, which depend on magnetic field strength.

Under the high-field conditions of our experiments, $s_{R1}, s_{R2} \ll c_{R1} c_{R2} \approx 1$ and $\Delta_{1412} > \Delta_{1212}$ so that the polarization at the lower radical frequency is simply

$$P(\omega_{12}) = \frac{1}{2} \left[\frac{\lambda^2}{\lambda^2 + (\omega_{12R1} - \omega_{12R2})^2} \right]^{1/2} \quad (5)$$

The precession frequency for the secondary radical was observed directly: the lower radical peak displayed in Fig. 1 ($\omega_{12R2} / 2\pi = 78.7$ MHz). The corresponding frequency for the primary silyl radical can be calculated from the muon hfc predicted by the density functional calculation. Allowing for a typical isotope effect of 17%, we find 722.5 MHz for the hfc and $\omega_{12R1} / 2\pi = -162.0$ MHz at the experimental field of 14.467 kG. Substituting these values into Eq. (5) allows us to predict the extent of polarization transfer as a function of reaction rate λ . This is displayed in Fig. 4.

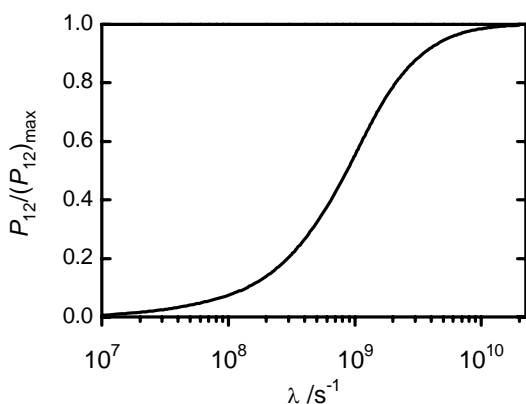


Fig. 4. Predicted transfer of muon spin polarization at 14.5 kG for the lower precession frequency of a muoniated radical with $h\nu$ 722.5 MHz reacting at rate λ to form a new radical with $h\nu$ 235.4 MHz.

If it is assumed that little or no polarization is lost in the first stage, formation of the primary radical, then Fig. 4 can be used to transform a measurement of the secondary radical signal amplitude into an estimate of the reaction rate. By comparing our results for **2-Mu** with the corresponding signal amplitude for the Mu adduct of a carbene (the largest radical signal measured under similar conditions), we estimate polarization transfer of 51%, which corresponds to $\lambda = 8.9 \times 10^8 \text{ s}^{-1}$. Given the silylene concentration of 1.55 M, this translates to a second-order rate constant of $5.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for reaction of the silyl radical with the parent silylene, i.e. the reaction shown in Fig. 3(b).

Kinetic data on the reactions of silyl radicals is sparse and there is no direct equivalent to our determination. However, we note that silyl radicals are generally very reactive and their self termination rate constants are typically in the $10^9 \text{ M}^{-1}\text{s}^{-1}$ range [14]. It has been suggested that the rate constants for silyl radicals in solution are diffusion-limited, resulting in an inverse correlation with size as diffusion constants fall and reaction radii are essentially constant [15]. Since the silylene **1** and the silyl **1-Mu** should have similar reaction radii it is reasonable to expect our silyl coupling reaction to mimic the behaviour of silyl self-termination reactions. Our results are consistent with this analysis.

In summary, we find that our observation of a muoniated radical in a concentrated solution of a

silylene can be well explained by a two-step reaction mechanism: Mu adds to a silylene to form a silyl radical which subsequently reacts to form a disilanyl radical; this is the species detected by TF- μ SR. We believe that this work represents the first example of direct detection of a secondary radical product by TF- μ SR.

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