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LETTERS

Detection of the Muoniated Methyl Radical

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The muoniated methyl radical has been detected in a sample of liquid ketene irradiated with positive muons. The muon and proton hyperfine coupling constants were measured at 184 K by transverse field muon spin rotation and avoided muon level-crossing resonance, respectively. After correction for the differing magnetic moments, the muon hyperfine constant is only 3% larger than that of the proton. This small isotope effect can be attributed to zero-point motion in the anharmonic C−H (C−Mu) stretch.

I. Introduction

The methyl radical is the simplest π radical and consequently has been subjected to intense theoretical study,[1] which has continued to recent times.[2,3] The focus of much of this work has been the calculation of hyperfine coupling constants. Remarkably, the proton hyperfine constant for methyl in the gas phase has only recently been determined experimentally, by IR laser spectroscopy.[4] Electron spin resonance studies of methyl in the condensed phases are far more numerous and include isotopic species[5] and temperature dependence.[6] Nevertheless, detailed information on the temperature dependence of methyl isotopomers is lacking.

One way to obtain more data is to study the muoniated methyl radical, i.e., the radical in which an H has been replaced by muonium (Mu): $^{\bullet}CH_2Mu$. Muonium is the single-electron atom with the positive muon as nucleus and is effectively a light isotope of hydrogen. The use of the muon to probe free radical structure and dynamics is well established,[7] and unlike ESR, muon spin rotation (μSR) and avoided level-crossing resonance (μALCR) can also be applied to radicals in the gas phase.[8] The light mass of the muon ($m_\mu \sim m_p/9$) should enhance isotope effects and thus extend the scope of studies of intramolecular dynamics.

However, almost all of the muoniated alkyl radicals studied to date have muonium in the β position, i.e., attached to a carbon adjacent to the radical center. This is a natural consequence of their mode of formation: unsaturated organic compounds are irradiated with positive muons, some of which pick up an electron on thermalization to form muonium, which adds to one end of an unsaturated bond or a conjugated π system. The single exception is the α-muoniated trimethylsilylmethyl radical, which was produced by the reaction of muonium with trimethylsilyldiazomethane.[9] The magnitudes of the muon and proton hyperfine coupling constants (hfcs) in this radical were found to increase with temperature, consistent with a nonplanar radical center.[10] In contrast, the unsubstituted methyl has a planar configuration and the proton hyperfine constant decreases with temperature.[6] (The hyperfine constant has a negative sign,[4] so a decrease in magnitude is actually an *increase* in the algebraic sense.)

Our initial attempts to produce the $^{\bullet}CH_2Mu$ radical by irradiating diazomethane failed, because of the extreme instability of this compound at the high concentrations required for μSR. An alternative strategy, described here, is to use ketene.

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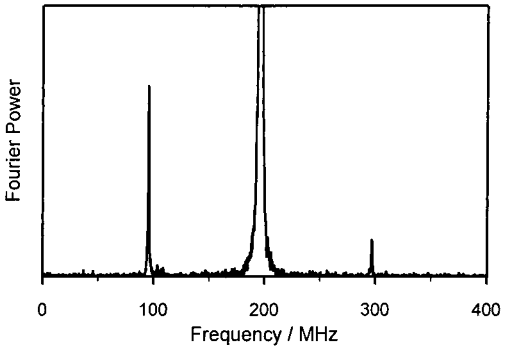
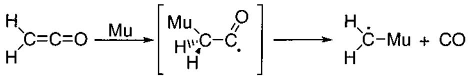


Figure 1. Fourier transform μSR spectrum at 14.5 kG from ketene at 184 K. The pair of precession frequencies at about 96 and 297 MHz are assigned to the $^{\bullet}CH_2Mu$ radical.

SCHEME 1: Reaction of Mu with Ketene



It is structurally similar to diazomethane but is more easily handled. A drawback is that it rapidly dimerizes at temperatures above 200 K, to give diketene (4-methylene-oxetan-2-one).[11] By analogy with the known reaction between the hydrogen atom and ketene, we expect that Mu reacts as shown in Scheme 1.

Density functional calculations by Sung and Tidwell[12] show that, of the various possible reactions, H atom addition to the methylene carbon of ketene has the lowest energy barrier. The acetyl radical thus formed is vibrationally excited and rapidly decomposes to give the methyl radical and carbon monoxide in the gas phase.[13,14] The acetyl radical is stabilized in low-temperature matrixes and has been detected by ESR; the yields of methyl, acetyl, and other radicals depend on temperature and matrix.[15]

II. Experimental Section

Ketene was produced by a standard method which involves the pyrolysis of acetone in a "Hurd lamp".[16] The ketene was trapped at 196 K and then purified by vacuum distillation, with the middle third fraction being retained. The liquid ketene was de-oxygenated by the freeze−pump−thaw technique and sealed in a nonmagnetic stainless steel cell with a 25 μm thick foil window to allow penetration of the muons. When not in use, the sample was stored at or below 196 K to minimize dimerization. NMR analysis of the sample after the muon experiments revealed the presence of acetone ($\leq$20% mole fraction), but this should not have a significant effect on the results.

Experiments were performed using a beam of polarized surface muons at the TRIUMF cyclotron facility in Vancouver, Canada. The sample cell was mounted on a coldfinger cooled with a closed-cycle helium refrigerator installed in the HELIOS spectrometer, which can be used for both μSR and μALCR experiments. Details of the experimental apparatus and techniques may be found elsewhere.[17,18]

III. Results and Discussion

A Fourier transform μSR spectrum from liquid ketene is shown in Figure 1. The pair of lines symmetrically placed about the muon Larmor frequency (at 196 MHz) are characteristic of a muoniated radical at high magnetic field. The absence of other muon precession frequencies shows that only one radical is present. The muon hyperfine constant (A_μ) is given by the difference of the two radical precession frequencies and is 201.53 ± 0.04 MHz. The μSR technique does not provide the sign of the hfc, just its magnitude.

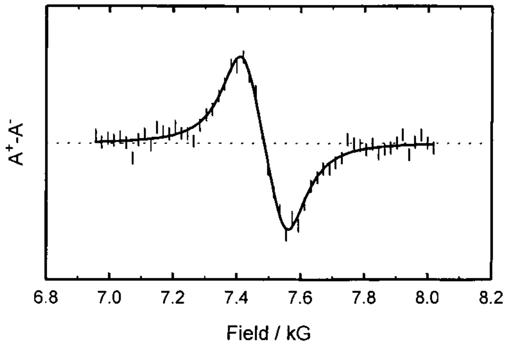


Figure 2. μALCR spectrum from ketene at 184 K. The resonance is assigned to the protons of the $^{\bullet}CH_2Mu$ radical.

TABLE 1: Hyperfine Coupling Constants of Isotopically Substituted Methyl Radicals in Various Media

	A_p/MHz	A_d'/MHz	A_μ'/MHz	isotope effect[a]
CH_2Mu[b]	−61.49		−63.31	1.030
CH_3[c]	−63.98			
CH_3[d]	−64.19			
CH_3[e]	−64.56			
CH_2D[f]	−64.74	−64.46		0.995

[a] Defined as A_X'/A_p. [b] In liquid ketene at 184 K. [c] In liquid acetone at 220 K.[23] [d] In liquid methanol at 210 K.[6] [e] In liquid methane at 96 K.[5] [f] In krypton matrix at 85 K.[5]

There is one resonance in the μALCR spectrum, which is shown in Figure 2. The proton hyperfine constant (A_p) was calculated from the resonance field position (B_{LCR}) by using eq 1:

$$B_{LCR} = \frac{1}{2}\left[\frac{(A_\mu - A_p)}{(\gamma_\mu - \gamma_p)} - \frac{(A_\mu + A_p)}{\gamma_e}\right] \qquad (1)$$

where γ_μ, γ_p, and γ_e represent the gyromagnetic ratios of the muon, proton, and electron, respectively. The magnitude of the proton hfc was calculated to be 61.49 ± 0.05 MHz assuming it has the same sign as the muon hfc.

To aid the comparison of hyperfine constants from different isotopes of hydrogen it is convenient to divide out the trivial isotope effect due to the differing magnetic moments. Thus, the reduced muon hfc is defined as $A_\mu' = A_\mu/3.183$. It is then evident that the reduced muon hfc determined from the μSR spectrum is very close to the proton hfc determined from the μALCR spectrum, and that both of these values are similar to the proton hfc in $^{\bullet}CH_3$,[5,6] as well as the reduced muon and proton hfcs in the muoniated trimethylsilyl derivative.[10] In contrast, the proton hfc of acetyl is much smaller, 11.2 MHz at 170 K.[19] The radical formed by Mu addition to the ketene dimer may also be excluded, because a separate investigation[20] showed that neither the muon nor the proton hfcs match the data from the current experiment.[21] There is therefore little doubt that the spectra obtained from muon irradiation of ketene are due to the $^{\bullet}CH_2Mu$ radical.

Table 1 compares the hfcs for $^{\bullet}CH_2Mu$ with selected literature values for $^{\bullet}CH_3$ and $^{\bullet}CH_2D$ (a scaled value of the deuteron hfc has been employed in equivalent manner to the reduced muon hfc). Defining the isotope effect as the ratio of reduced muon (or deuteron) hfc to proton hfc in the same radical, one finds a 3% increase for muonium substitution and 0.5% decrease for deuterium. This is in accord with expectations based on anharmonicity in the C−H bond stretch: the average C−Mu bond length is about 5% longer than C−H.[22]

A different isotope effect is apparent when one compares the proton hfcs of $^{\bullet}CH_2Mu$ and $^{\bullet}CH_3$. The former is approximately 4% smaller than the latter, an effect which exceeds the variation due to temperature and medium.[5,6] We tentatively attribute this to the higher zero-point energy in the out-of-plane vibrational mode of $^{\bullet}CH_2Mu$. In essence, the lighter isotopomer explores a wider range of out-of-plane deformation. We intend to explore this point with a detailed study of the temperature dependence of the hfcs in this radical.

The strength of the muoniated methyl signal in the μSR spectrum implies that there is efficient transfer of muon polarization from the precursor to the final radical product. This sets an upper limit of ∼10 ns on the lifetime of a muoniated acetyl precursor, which is consistent with the fact that it was not detected. On the other hand, $CH_3\dot{C}O$ has been detected by ESR in a low-temperature matrix. We plan to search for $MuCH_2\dot{C}O$ in a frozen sample of ketene.

IV. Conclusions

It has been demonstrated that the muoniated methyl radical can be formed by the reaction of muonium with ketene. This constitutes a new route for the production of α-muoniated radicals. The isotope effect on the hyperfine constants of the muon and proton in their chemically equivalent positions can be attributed to the differing zero-point energies of the C−Mu and C−H bonds and the anharmonicity of the vibrational potential. In addition, zero-point motion in the out-of-plane vibrational mode is probably the cause of the increased (less negative) proton hyperfine constants for $^{\bullet}CH_2Mu$ compared to $^{\bullet}CH_3$. The relative importance of different isotope effects can only be settled via a detailed theoretical treatment.

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