Investigating the solvent and temperature effects on the cyclohexadienyl radical in an ionic liquid

Becky Taylor, PJ Cormier, JM Lauzon and Khashayar Ghandi*

Department of Chemistry, Mount Allison University, Sackville, New Brunswick, Canada, E4L 1G3

Elsevier use only: Received date here; revised date here; accepted date here

Abstract

The cyclohexadienyl radical was studied in a novel green solvent; Tetradecyl(trihexyl)phosphonium chloride ionic liquid (IL 101). Both the solvent effects and how the hyperfine coupling changes with respect to temperature have been examined and compared to literature. This was done through experimental muon techniques at the TRIUMF National Laboratory in Canada as well as through \textit{ab initio} calculations. The ionic liquid solvent effects were found to be consistent with other solvents, when assuming ionic liquids to be a combination of ion pairs. In ionic liquid the hyperfine coupling constants of the proton and reduced muon decreased linearly with increasing temperature. The analysis showed that the majority of this relationship is due to a vibrational effect, although the solvent density plays a role too. The temperature effect on the entropy of the system was determined to be negligible. The temperature coefficient of the reduced muon hyperfine coupling was larger than that of the proton in IL 101 due to the effects of nearby ionic liquid molecules.

© 2001 Elsevier Science. All rights reserved

Keywords: cyclohexadienyl radical; hyperfine coupling; ionic liquid;

1. Introduction

The cyclohexadienyl radical can be formed from the addition of H to benzene. The reaction between Mu and benzene in the gas phase [1] and in solvents [2] produces the muoniated cyclohexadienyl radical (Figure 1), in which the C-Mu bond is elongated by \(\sim 5\%\) compared to the C-H bond [3].

The hyperfine coupling constants (hfcS) are sensitive means of examining the electronic structure of a radical and monitoring how this is altered through solvent interactions [2]. Two of the factors which affect the formation and hfcS of a free radical are the solvent used and the temperature at which the radical is formed.

Figure 1: Muoniated Cyclohexadienyl Radical. Top: the reaction between benzene and muonium. Bottom: a depiction of the methylene scissoring motion.

* Corresponding author. Tel.: +1-506-939-2076; e-mail: kghandi@mta.ca
Both of these effects have been previously studied for the cyclohexadienyl radical in a number of different solvents [2, 4]. The hyperfine coupling, $A_P$, of the $C_{\text{met}}$ proton (Figure 1) has been found to correlate linearly with $[\mu_s]$ which is the product of the magnitude and concentration of the dipole moments of the solvent [2]. This relationship is shown below

$$A_P = a + b[\mu_s]$$  \hspace{1cm} (1)

where $a$ and $b$ are empirical constants for individual radicals. The value of $[\mu_s]$ is calculated as follows:

$$[\mu_s] = \mu_s \frac{\rho_s}{M_s}.$$  \hspace{1cm} (2)

The $\mu_s$ value is the dipole moment, $\rho_s$ is the density and $M_s$ is the molecular weight of the solvent.

This study investigates the cyclohexadienyl radical in a novel solvent, a room temperature ionic liquid (RTIL). RTILs are salts which are liquids at temperatures $< 100^\circ$ C [5]. They are non volatile (having almost no vapour pressure) and many ionic liquids have no detrimental effects on the environment [6]. The RTIL used in this experiment was tetradecyl trihexyl phosphonium chloride, or IL 101. One purpose of this study was to examine the effects of the ionic liquid solvents on the cyclohexadienyl radical in comparison with molecular solvents. A second objective was to measure the temperature dependence of both the muon and proton hfcs of the cyclohexadienyl radical in ionic liquids. The results will be analyzed to determine how temperature affects the hfcs and to account for any difference between the proton coupling and that of the muon.

2. Experimental

Materials: Tetradecyl (triethyl) phosphonium chloride (ionic liquid 101 from Cytec) was purified by subsequent washes with sodium bicarbonate, water, and hexane, and dried by azeotropic distillation. The purity was checked by NMR. Benzene was added to 10mL of IL 101 to create a 1.4M solution and 7 mL of this was transferred to a cell to use for the $\mu$SR experiments. The benzene in IL 101 sample was freeze-pump-thawed a minimum of four times to remove oxygen.

$\mu$SR Experiments: TF and ALC-$\mu$SR experiments were conducted using the M20 beam line at the TRIUMF National Laboratory facility. The TF and ALC-$\mu$SR runs of the benzene in IL 101 were taken at temperatures from 283K to 343K. The ALC-$\mu$SR resonances were scanned through a range of 20,000-22,000 in steps of 10.

Computational: The ionic liquid molecule was optimized using the Gaussian 03 program [7]. The B3LYP Density Functional Theory (DFT) [8-10] was used at the basis set of 6311G. This was done to estimate the dipole moment of the solvent. The cyclohexadienyl radical was optimized in the presence of an ionic liquid model. The model consisted of a chloride and a phosphorous (cation) with three propyl groups and one ethyl group. The angle between the muon and $C_{\text{met}}$ proton was set between 35$^\circ$ and 155$^\circ$ in steps of 15$^\circ$ (Figure 1). This was done to mimic the scissoring motion of the methylene group. The basis set for this set of calculations using the B3LYP DFT method was 6311G. This was done to model the effect of a solvent molecule on the hfcs of the muon and proton.

3. Results and discussions

The muon hfcs were determined from TF- $\mu$SR data [11]. The reduced muon hfcs, $A'_\mu$, were calculated using equation 3 where $\gamma_p$ and $\gamma_\mu$ are the gyromagnetic ratios of the proton and the muon.

$$A'_\mu = \left(\frac{\gamma_p}{\gamma_\mu}\right)A_\mu.$$  \hspace{1cm} (3)

From ALC-$\mu$SR resonance the hfcs of the proton, $A_p$, was determined from the resonance field, $B$, and the muon hfcs as shown in the equation 4.

$$B_{LCR} = \frac{1}{2} \left[ \frac{A'_\mu - A_p}{\gamma_p} - \frac{A'_\mu + A_p}{\gamma_\mu} \right].$$  \hspace{1cm} (4)

The resonances fields and hfcs of the muon and proton are given in Tables 2 and 3 along with the temperature. Displayed in Figures 2 and 3, are the plots of the reduced muon and proton hfcs versus temperature in IL 101.

To compare the results of this experiment with those found in other solvents, values were determined from the linear fits of hfcs vs. temperature and taken at 308 K and 348 K. This corresponded to a proton hfcs of 126.39 +/- 0.57 MHz at 308K and at 348K it gave a proton hfcs of 125.88 +/- 0.60 MHz.
The value of [μs] for ionic liquid was found to be 26.7 D·mol/dm³ (where D is Debye, the atomic unit of a dipole) from equation 2 based on a dipole moment of 13.1 D from our ab initio calculations, a density of 0.890 g/cm³ and a molecular weight of 436.3g/mol. The results of previous literature [2] as well as the additional findings from this study are presented in Figure 4. IL 101 correlated to data from other studies fitting into the linear trend of increasing hfc with [μs] for molecular solvents.

In the IL 101 the hfcs decreased linearly with increasing temperature. The slope of the reduced $A_p$ versus temperature was found to be (-1.93 +/- 0.44) x10^{-2} MHz/K and of $A_p$ versus temperature was (-1.27 +/- 0.13) x10^{-2} MHz/K. The two slopes are not within each other’s error, indicating that there are some significant changes to the radical in ionic liquids as compared to gas phase and other solvents. Optimizations of the radical in the presence of an ionic liquid model showed that the geometry was only slightly non-planar giving a dihedral angle from C_p to the Cmet of ~1 degree (Figure 1), with the longer
bond (C-Mu) preferred towards the cation. Calculations mimicking the scissoring motion of the proton and muon while in this optimized geometry showed non-symmetric effects on the hfcs (see figure 5). Based on these results, the difference in the temperature coefficients of hfcs could be due to interaction of the radical with the nearby cation.

![Figure 5: Computational results of the hyperfine coupling with respect to the Mu-C-H angle. The longer C-Mu bond preferred being oriented next to the solvent molecule which increased its electronic interactions as compared to the C-H.](image)

The total temperature dependence of the proton hfc can be described as individual effects of vibration (VIB), solvent density (DENS) and disorder (HT) [2].

\[
\frac{\Delta A_p}{\Delta T} = \frac{\Delta A_{p,V}}{\Delta T} + \frac{\Delta A_{p,D}}{\Delta T} + \frac{\Delta A_{p,H}}{\Delta T}
\]  (5)

Temperature increase leads to an increase in the degree of vibrational motion. This vibrational effect is an average over all vibrations of the radical, but is mostly due to the scissoring motion [12] (see Figure 1). If we assume the solvent has minimal effect on \((\Delta A_{p,V}/\Delta T)_{VIB}\), its value can be approximated in solution by its value in the gas phase, which gives a value of \(-0.0125\) MHz/K for the cyclohexadienyl radical [1]. This accounts for 98% of the total temperature effect in IL 101. The density effect can be calculated from equation 6 where \(b\) is the empirical constant defined in equation 1, and \(\Delta \rho / \Delta T\) is the temperature coefficient of the solvent density.

\[
\left(\frac{\Delta A_p}{\Delta T}\right)_{DENS} = b \cdot \frac{\Delta \rho}{M_s} \cdot \frac{\Delta T}{\Delta T}
\]  (6)

The density of ionic liquid versus temperature has a linearly decreasing slope \(\Delta \rho / \Delta T\) of \(-0.55\) g/dm$^3$/K. From Figure 6 the value of \(b\) is approximated as 0.017 MHz·dm$^3$/mol·K. Using equation 6, the value of \((\Delta A_p/\Delta T)_{DENS}\) is determined to be \(-0.00028\) MHz/K. This accounts for 2% of the overall temperature effect. The rest of the temperature dependence is a result of the increasing disorder of a solution as the temperature increases. This should decrease the external field and therefore lower the hfc. The \((\Delta A_p/\Delta T)_{HT}\) value for ionic liquid 101 is 0% of the overall effect. Although the assumption of the negligible effect of solvent on \((\Delta A_p/\Delta T)_{VIB}\) is not realistic based on our computational studies explained earlier, we can still consider the ordering effect minimal compared to other two effects in ionic liquids. This is due to the bulky structure and significant bonding of the ionic liquid. The temperature range within this study was not sufficient to have any noticeable breaking of these bonds.

This work was financially supported by the Natural Sciences and Engineering Research Council of Canada. We thank the TRIUMF Centre for Molecular and Materials Science personnel for technical support. Torch cluster was used for computational work.

References