STUDIES OF THE MUONIUM ATOM IN LIQUID MEDIA

by

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ABSTRACT

The μSR (muon spin rotation) and MSR (muonium spin rotation) techniques have been applied to study the reaction of muonium atoms in liquid media. Specifically, the temperature dependence of five types of reactions of muonium atoms in aqueous solution were measured between 1 and 92°C. Results indicated that for an electron-transfer reduction with MnO₄⁻, for an addition to π-bonds in maleic acid and for a spin-conversion reaction with Ni²⁺, the rate constants were all diffusion-limited. An activation energy for diffusion of 4.2 kcal.mole⁻¹ was found, while the A-factors varied somewhat in the range of 10⁻¹³ M⁻¹s⁻¹. For these diffusion-controlled reactions there is no kinetic isotope effect when compared with H-atoms. On the other hand, a large kinetic isotope effect was found for the abstraction reaction of muonium with formate ion (HCO₂⁻) and this rate constant was activation-controlled. Also, the reaction with NO₃⁻ was studied and tends to exhibit a curved Arrhenius plot even over such a short temperature range. Such curvature is consistent with either a contribution from quantum mechanical tunnelling or alternative reaction paths.

Other temperature-dependence studies of both the muon and muonium atoms in CS₂, H₂O, and CCl₄ are also reported. The muon relaxation rate constant in CS₂ was found to change somewhat from 1 to 40°C. In the case of H₂O, both the muon asymmetry and muonium relaxation rate constant were found to increase slightly from 1 to 92°C. However for CCl₄, there was no change found for the muon asymmetry in the temperature range of 2 to 58°C.
In addition, the interactions of muonium with O\textsubscript{2} and with porphyrins in water were both studied using the MSR technique. In the case of O\textsubscript{2}, the rate constant, which could be due to spin-conversion, was found to be $(2.4\pm0.5)\times10^{10}$ M\textsuperscript{-1}s\textsuperscript{-1} and is compared with the diffusion-controlled limit and the corresponding gas phase reaction. For the reaction of muonium with porphyrins, the rate constants with hemin and the protoporphyrin were found to be $2.7\times10^{9}$ and $6\times10^{8}$ M\textsuperscript{-1}s\textsuperscript{-1}, respectively. The reaction mechanism is probably mainly through the addition to the conjugated double bond for the protoporphyrin and by reduction or partial spin-conversion for the hemin solutions.

The theory behind the \textmu{}SR and MSR techniques has been very briefly discussed but the experimental system for liquid phase studies at TRIUMF is described in some detail with respect to the transverse field technique.
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CHAPTER 1

INTRODUCTION
Muonium is the atom formed when a positive muon ($\mu^+$) is combined with an electron [1]. Muons are short-lived elementary particles classified as leptons. They are generated as the decay products of pions which are the mesons responsible for nuclear binding. Some of the physical parameters of the muon are given in Table 1.1.

**TABLE 1.1**

Physical parameters of the muon.

<table>
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<th>Parameter</th>
<th>Value</th>
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<tr>
<td>Spin</td>
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<tr>
<td>Mass</td>
<td>$m_\mu = 206.77m_e = 0.11261m_p$</td>
</tr>
<tr>
<td>Magnetic moment</td>
<td>$\mu_\mu = 3.1833\mu_p = 4.835 \times 10^{-3}\mu_e$</td>
</tr>
<tr>
<td>Lifetime</td>
<td>$\tau_\mu = 2.1971\mu\text{sec}$</td>
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Most importantly, the muonium atom has its Bohr radius ($a_o = 0.532\text{Å}$) and ionization potential ($I_p = 13.539\text{eV}$) values almost identical to that of the hydrogen atom. From the chemical point of view, the muonium atom resembles the hydrogen atom, with a difference only in mass ($m_{\text{Mu}} = 1/9m_H$). Therefore, it can be regarded as an ultralight, radioactive, isotope of hydrogen [1,2]. With this in mind, one can then examine with improved sensitivity (relative to deuterium and tritium) such aspects as kinetic isotope effects and quantum mechanical tunnelling, by comparing reactions of Mu with those of H.

1.1A. History and Background.

The earliest experimental observations of positive muons were by Garwin et al [3] and Friedman et al [4] in 1957. Although these two groups employed slightly different apparatus, their methods were forerunners of the present $\mu$SR (muon spin rotation) technique used today. The period from 1957
to 1970 was a slow developmental stage for those in the muon community. However, important experimental foundations for the study of muon chemistry was paved by scientists studying the physical aspects of the muon and the muonium atom [5,6,7,8,9]. In addition, a series of theoretical papers by Soviet groups led the way to fundamental understanding of the reaction and formation of Mu atoms[10,11,12]. During the 1970's, continuing experiments including measurements of the muon magnetic moment [13], the muon anomalous magnetic moment [14], and the hyperfine splitting of the muonium atom [15], helped to stabilize and expand the field of muon and muonium chemistry immensely.

Muonium chemistry in liquid media was first studied by a group at Dubna [5,6,7] and then more extensively by a group at Lawrence Berkeley Laboratory (LBL) [1,16,17]. However, it was not until 1976 that the first direct detection of muonium in water was observed by Percival et al at Swiss Institute for Nuclear Research (SIN) near Zurich [18]. Since then, an impressive program of Mu chemistry in liquids has been carried out by this group at SIN [19], including studies in muonium-substituted transient radicals [20]. At TRIUMF, before 1978, the main investigation of Mu chemistry was centred around gas-phase studies [21,22]. However, since then, Jean et al [23,24,25,26] have started and maintained a very competitive program of Mu chemistry in the liquid phase. In addition, the direct observation of Mu in various hydrocarbon media was successfully carried out recently at TRIUMF [27]. Also, the application of Mu as a nuclear probe in large macromolecular and biological systems is beginning to take hold as a major project here at U.B.C. [28]. The field of Mu chemistry in the liquid phase is fast becoming of broad prospective and reaching into several conventional areas of chemical study.


Muons are unstable particles and they are produced from the decay of pions. At TRIUMF, the pions are generated by bombarding a $^9$Be target (T2) with 450-500 MeV protons from the cyclotron to give the following nuclear reaction.

$$^{9}\text{Be} + ^1\text{p} \rightarrow ^{10}\text{Be} + ^\pi^+$$ (1.1)

The pion decays ($\tau=26\text{nsec}$) to give a muon and a muon neutrino.

$$^\pi^+ \rightarrow ^\mu^+ + ^\nu_\mu$$ (1.2)

Subsequently, the $^\mu^+$ itself decays ($\tau=2.2\mu\text{sec}$) giving an easily detectable positron, an electron neutrino and a muon anti-neutrino.

$$^\mu^+ \rightarrow ^e^+ + ^\nu_e + ^\bar{\nu}_\mu$$ (1.3)


For the pion decay process (equation 1.2), the pion has zero spin and since all $^\nu_\mu$ in nature have negative helicity (spin in opposite direction to its momentum), this forces the $^\mu^+$ to have negative helicity according to conservation of angular momentum. In a fortunate sense, this "weak interaction" provides a 100% polarized $^\mu^+$ beam. Again, in the $^\mu^+$ decay (equation 1.3), due to the non-conservation of parity implicit in the definite helicity of neutrinos, the $^e^+$ emitted also tends to come off along the direction of the $^\mu^+$ spin. As a result, the angular distribution of the positrons are anisotropic. In general, the number of positrons emitted at an angle $\theta$ relative
to the muon spin is given by 1+acosθ [29]. Here, a is the so-called asymmetry parameter. It is a function of the energy of the emitted e⁺ with an average value of 1/3 and a maximum value of 1 (for positrons of maximum energy, 52 MeV [1]). It is this variation of the positron distribution which allows one to observe the evolution of the muon polarization and which consequently gives one a sensitive way of measuring Mu reaction probabilities.

### 1.B.3. The μSR technique.

When a μ⁺ is stopped in a target perpendicular to a magnetic field (B), its spin precesses at its Larmour frequency,

$$\omega_\mu = \gamma_\mu B$$

(1.4)

where $\gamma_\mu = 13.6$ kHz/gauss. To observe this μ⁺ precession phenomena, one can simply place a small positron counter in the plane of the μ⁺ precession at angle $\phi_o$ with respect to the initial muon spin direction; so at time t the angle between the μ⁺ spin and the e⁺ detector when the μ⁺ decays will be $\phi_o + \omega_\mu t$. As a result, the e⁺ detection probability $[dN_e(t)/d\Omega]$ will be proportional to $1+A_\mu \cos(\phi_o + \omega_\mu t)$, where $A_\mu$ is the experimental muon asymmetry (proportional to the muon polarization) and its magnitude depends on detector dimensions, target geometry and beam polarization. This method, the "μSR" (muon spin rotation) technique, allows one to monitor the magnitude and time dependence of the muon polarization for all muons in diamagnetic states, such as free μ⁺ or MuH or MuC₂, etc. The field dependence of the μ⁺ precession in CCl₄ is illustrated in Fig. 1.1.
Figure 1.1: Time histograms showing the field dependence of the $\mu^+$ precession signal at (a) 100 G and (b) 1500 G for target solution of $\text{CCl}_4$. The line is the computer fit to the muon components in equation (1.5). The plots have the constant background and exponential muon decay removed leaving the signal $A(t) = A_\mu \cos(\omega_\mu t + \phi_\mu)$. 
1.B.4. The MSR technique.

In 1976 [18] it was found, provided the liquid is relatively pure and oxygen-free, that Mu can be observed directly by the MSR (muonium spin rotation) technique. This method is a result of the hyperfine interaction between the magnetic moment of the μ⁺ and that of the electron (hyperfine field = B₀ = 1585 gauss) giving rise to two net spin states of F=0 (singlet) or F=1 (triplet). The observable spin state is that of the triplet which precesses in weak fields (B)<<B₀ at 1.39 MHz/G, about 103 times faster than the free muon in the same magnetic field. Experimentally, the positron detection probability in this MSR method now acquires another term of the form θ = φ₀+ωₘushman with a new empirical asymmetry Aₘu. Therefore, one has the Mu precession superposed upon the μ⁺ precession, while both are superposed upon the exponential decay of the muon. In addition, there might be exponential damping on the μ⁺ and Mu oscillatory terms due to possible phenomenological depolarization and/or chemical reaction. In general, the positron time distribution takes the form of,

$$\frac{dN_e(t)}{d\Omega} = N_0 \left[ B_G + e^{-t/\tau} \left[ 1 + A_\mu e^{-\lambda_\mu t} \cos(\omega_\mu t + \phi_0) + A_{Mu} e^{-\lambda_{Mu} t} \cos(\omega_{Mu} t + \phi_{Mu}) \right] \right]$$

(1.5)

where $N_0$ is a normalization factor, $B_G$ is the time-independent background, $\tau_\mu$ is the muon lifetime (2.2μsec), $A_\mu$ and $A_{Mu}$ are the experimental asymmetries, $\lambda_\mu$ and $\lambda_{Mu}$ are the rates of decay of the signals, $\omega_\mu$ and $\omega_{Mu}$ are the precession frequencies, and $\phi_0$ are the initial phases of the respective μ⁺ and Mu precessions.
1.C. Present theories of muonium formation in liquids.

In liquid phase studies, the highest muon asymmetry obtained is that of CCl₄. Its value is also equal to that found in metals such as Al and Cu [22]. For this reason, its value has been used as a normalizing standard for all other solvents. In this thesis, the value of \( P_D \) is taken as the observed muon asymmetry in the liquid of interest divided by the asymmetry found under identical conditions in CCl₄.

\[
P_D = \frac{A_u}{A_{CCl_4}}
\]

i.e. \( P_D \) represents the fraction of incident muons which are observed in diamagnetic states. For the case of muonium, \( P_M \) (the muonium fraction) is twice the value of the muonium asymmetry (due to the fact that only the half of the muonium ensemble which are triplets is observable in the MSR technique) divided by the muon asymmetry in CCl₄.

\[
P_M = \frac{2A_{Mu}}{A_{CCl_4}}
\]

In most solvents, the sum of \( P_M \) and \( P_D \) is usually found to be not equal to 1. The difference \((1-P_D-P_M)\) is referred to as the "missing fraction", \( P_L \), which at present is attributed to either muonic free-radical formation or rapid spin depolarization perhaps by intra-spur spin-exchange reactions [19]. These yields of muon (\( P_D \)), muonium (\( P_M \)), and muonic radicals (all or part of \( P_L \)) are observed on a time scale of \( \approx 10^{-7} \) sec but had to be formed within \( \approx 0.3 \) nsec, the Mu hyperfine time. Originally, the value of \( P_D \) was referred to as the hot diamagnetic fraction [1] because it was thought to arise from
abstraction or exchange reactions with the solvent by hot (epithermal) \( \mu^+ \) or Mu during the final stages of thermalization. This is basically what is known as the "hot model" in muonium chemistry. Essentially, the model views epithermal \( \mu^+ \) abstracting an electron from the medium so that Mu is formed beyond the trail of ionizations (spurs) of the \( \mu^+ \) track. During its thermalization a certain fraction of Mu react with the medium, some of which give diamagnetic muonic species and the rest reach thermal energy as free Mu atoms. According to radiation chemistry, a trail of "spurs" is a result of energy deposition to the medium from the passage and thermalization of a high energy charged particle, such as a positive muon. Typically, these spurs are regarded to result from the deposition, on average, of ~100 eV of energy in a sphere of about 2 nm diameter in water. Therefore, these spurs are minute regions in the particle's track containing high concentrations of very reactive free radicals, electrons, positive ions, and excited molecules [30]. In positronium studies, Mögensen has postulated a "spur model" in which he argues that the positron (e\(^+\)) reaches thermal energy while still in the neighbourhood of reactive free radicals, electrons and ions generated in spurs in its thermalization track [31]. Recently, this has prompted an analogous "spur model" of Mu formation by Percival et al [32]. Here, the spur model pictures a \( \mu^+ \) being thermalized within the last spur of its own track in which it can then either encounter a radiation-produced electron to become Mu or it can escape into the medium; also, Mu can either perform intraspur reactions or escape from the spur. Therefore, this model attempts to explain the initial distribution of muons between diamagnetic and paramagnetic species simply based on the relative probabilities of reaction or escape of thermalized muons.
from the reactive species of the terminal spur. These two contrasting models, HOT and SPUR, have been in direct conflict for the proper mechanism of muonium formation in liquids. At this moment, both models are still under constant criticisms and investigations from the muon community \[32,33\]. The schematics of these two models are illustrated in Fig. 1.2. In the figure, the time scales are meant to be differentiating guidelines between the two mechanisms and that the times of formation are only estimated.

1.D. Reaction kinetics in the liquid phase.

Contrary to gas phase studies, our knowledge of molecular motion and of molecular energy levels in liquids is not very well developed. Nevertheless, our approach toward encounters of molecules in solutions must be quite different to that in gases. For example, \(N_2\) gas molecules at STP occupy about 0.2% of the total volume while as the liquid this same figure rises to ~70% or more. This difference means that, while the motion in gases is largely unhindered, molecules in solutions have to jostle their way past one another in order to make any substantial displacement. Clearly, the encounter frequency is much smaller in solutions than that in gases. However, there is an important factor involved in this difference. In solutions, since molecules diffuse slowly into the region of a possible reaction partner, they also migrate slowly away from it. Therefore, once partners of a reaction get into each other's vicinity - into the same "solvent cage" - they collide with one another many times before escaping this solvent cage. In other words, once an encounter has occurred, the chances of undergoing a reaction is greatly enhanced compared to the gas phase. As a matter of
Figure 1.2: Diagrams showing the contrasting HOT and SPUR models for muonium formation in liquids.
fact, the time spent by a molecule in one of these solvent cages can be as long as 100 psec; and during this period, the molecule can make between 100-1000 collisions with its neighbour molecules [34].


In order for molecule A to react with molecule B they must first come into contact with each other, and this requires the molecules to be in the same solvent cage where they are then referred to as the "encounter pair" [35]. The activation energy of a reaction ($E_a$) is now a complicated quantity (relative to gases) because the encounter pair is surrounded by solvent molecules and its reaction path is determined by all the neighbouring interactions. However, this situation can be depicted by the following reaction scheme:

$$A + B \xrightarrow{k_d} \{AB\} \xrightarrow{k_p} P ;$$

where $\{AB\}$ is the encounter pair, $k_d$ and $k_d$ are the diffusive-approach and separation rate constants, respectively, and $k_p$ is the reaction rate constant giving product P. The steady state concentration of $\{AB\}$ can be found from the following rate equation:

$$\frac{d[\{AB\}]}{dt} = k_d[A][B] - k_d[\{AB\}] - k_p[\{AB\}] = 0 ,$$

which gives:

$$[\{AB\}] = \left( \frac{k_d}{(k_d+k_p)} \right) [A][B] .$$
Substituting equation (1.10) into the rate expression for the formation of \(P\) gives the overall equation as:

\[
\frac{d[P]}{dt} = k_p [(AB)] = \left( \frac{k_p k_d}{(k_d + k_p)} \right) [A][B].
\] (1.11)

Notice in equation (1.11) that the overall rate law is second-order, and the bimolecular rate constant, \(k_2\), is given as:

\[
k_2 = \frac{k_p k_d}{(k_d + k_p)}.
\] (1.12)

From equation (1.12), two limits can be recognized. If the rate of break-up of the encounter pair is much slower than the rate at which it forms products; that is \(k_d \ll k_p\), then \(k_2\) becomes equal to \(k_d\),

\[
k_2 \approx \frac{k_p k_d}{k_p} = k_d.
\] (1.13)

In this limit, the rate of the reaction is determined by the rate at which the species diffuse together through the medium. This is called the "diffusion controlled limit", and the reaction is diffusion controlled. Typically, these reactions have \(k_2 \geq 10^9 \text{ M}^{-1}\text{s}^{-1}\) or \(E_a \approx 4 \text{ kcal.mole}^{-1}\). For example, radical and atom recombination reactions are often diffusion controlled because the combination of species with unpaired electrons involves very little activation energy. The other limit arises when a substantial activation energy is involved in the reaction step, and then \(k_p \ll k_d\). This gives rise to the "activation controlled limit" and the overall rate constant
becomes:

\[ k_2 = k_p \begin{bmatrix} k_d \\ k_{-d} \end{bmatrix} = \frac{k_p K}{k_{-d}} \tag{1.14} \]

where \( K \) is the equilibrium constant for the \( A, B \) and \( \{AB\} \) species. In this case, the rate depends on the accumulation of energy in the encounter pair, as a result of its interaction with the solvent molecules, and on their rate of passage over the reaction energy barrier.


The idea that an "intermediate complex" was formed during transition from the initial reagents to the final products has been known for some time and it was first demonstrated by Bjerrum [36] and Brönsted [37]. However, their derivations using one dimensional coordinates cannot describe the great variety of kinetic features of reaction between complicated molecules. Various other groups [38,39,40] developed this idea further to suggest that the chemical reaction be considered as the movement of the reacting system along a potential energy surface or "phase space". In 1935, the "transition state theory" or the "activated complex theory" were independently formulated by Eyring [41] and by Evans and Polanyi [42]. Their treatments of chemical reaction rates consider the movement of the configurational point over a potential energy surface such that the energy barrier between the initial and final states is minimum. The highest point along this path is referred to as the transition state or activated complex. The potential energy surface of most reactions is three-dimensional, and consists of two "valleys"
connected by a saddle or a "pass" on the energy barrier (Fig. 1.3a). The transition state is considered to situate on the saddle point of this free energy surface \[43\]. The curve in Fig. 1.3b shows the mapping of the potential energy surface $E$ for the reaction:

$$A + B \rightarrow X^\ddagger \rightarrow \text{Products} \quad (1.15)$$

along the reaction coordinate through the saddle point, which corresponds to the activated state. The section of the curve at the apex with an arbitrarily selected length $\Delta \ell$ corresponds to the activated complex ($X^\ddagger$). This approach led to considerable simplification of the equations for reaction rates and made it possible to examine the influence of the reactant structure and the nature of the solvent on the reaction rate.

Application of statistical mechanics to the activated complex theory \[34\] gives the following expression for the chemical reaction rate of equation (1.15) as:

$$k_2 = \kappa \left[ \frac{kT}{\hbar} \right] \left[ \frac{Q_{X^\ddagger}}{Q_A Q_B} \right] \exp \left( \frac{\Delta \varepsilon_0}{kT} \right) \quad (1.16)$$

where $\kappa$ is a transmission coefficient allowing for the possibility that not all activated complexes lead to products since some may be reflected back to the reactants; $\frac{Q_{X^\ddagger}}{Q_A Q_B}$ is the partition function quotient permitting evaluation of molecular complexity; and $\Delta \varepsilon_0$ is the difference between the lowest energy levels of $A$ and $B$, and $X^\ddagger$, which corresponds to the activation energy for the reaction.
Figure 1.3:  (a) Diagram of the reaction path through the energy barrier.  
(b) Curve of the potential energy plotted against the reaction coordinate.  
(after Entelis and Tiger [43]).
1.D.3. Isotope effects and Quantum mechanical tunnelling.

The application of the activated complex theory to the study of kinetic isotope effects has been quite satisfactory especially with the substitution of deuterium for hydrogen in reactant molecules. For example, if a reaction involves cleavage of an H-X bond, it is frequently found that deuterium substitution reduces the rate by a factor of about ten at room temperature [34]. However, a large isotope effect of this kind is confined to reactions involving hydrogen atom and is rarely seen for other atoms. Fortunately, we have now a superlight isotope of hydrogen, Mu, which we can use to test severely the theory of absolute reaction rates. With Mu, we might expect an even bigger isotope effect and therefore it can be used to investigate reaction mechanisms.

At low temperature, quantum mechanical tunnelling can often make an important contribution to the overall reaction process. This is demonstrated by the curvature of Arrhenius plots at low temperatures. For particle m encountering a barrier of height V with wavefunction ψ, its motion can be solved via the Schrödinger equation. The solution for m having energy E penetrating a barrier of height V is a wavefunction ψ of the oscillating form [34] (see Fig. 1.4). But once inside the barrier (x>x₀), ψ is non zero and decays according to:

\[ \psi(x) = \alpha \exp\left\{-\frac{2m(V-E)}{\hbar^2}x_0\right\} \]  \hspace{1cm} (1.17)

Since \( \psi(x)\neq0 \), this means there is a probability of finding m inside the barrier even when E<V. This phenomenon in which a particle seemingly penetrates into the forbidden classical region is termed quantum mechanical
Figure 1.4: The dependence of a wave function ($\psi$) on the potential. For $x<x_0$, $\psi$ is oscillatory. For $x>x_0$, $\psi$ decreases exponentially (after Pilling [34]).
tunnelling. It has been observed that hydrogen atoms tunnel to an observable extent, and they do so more effectively than deuterium atoms because of their lighter mass [44]. This effect might be much more pronounced with the now much lighter Mu atom. Indeed, there is preliminary evidence from the muonium lifetime in neat methanol at low temperatures that this is so [45]. It is for this reason, and for reaction kinetics in general, that the temperature dependence of Mu atom reaction rates with different substrates is an important, fundamental, and interesting study in the field of muonium chemistry.

1.E. Description of thesis content.

In the previous sections, it has been mentioned that Mu can be used to study kinetic isotope effects and consequently can be employed as a convenient handle on hydrogen atom reactions which are not accessible to study by conventional methods. Because of the novelty of the MSR technique in liquid phase studies, this thesis is mainly concerned with Mu reactions with solutes in aqueous solutions. In chapter 3, the MSR method is applied to study the temperature dependence of various solutes ($\text{MnO}_4^-$, $\text{Ni}^{2+}$, maleic acid, $\text{HCO}_2^-$ and $\text{NO}_3^-$) in aqueous solutions reacting with the muonium atom. In addition, changes in the muon asymmetry and relaxation rate of $\text{CCl}_4$, water and $\text{CS}_2$ were investigated as a function of temperature. In chapter 4, two collaborative studies are presented. The first involves the interaction between Mu and $\text{O}_2$ in water. The second describes chemical reactions between Mu and porphyrins, demonstrating the initial attempts of applying the MSR technique as a nuclear probe in biological systems. It should be noted that most of the results in chapter 3 will be published in J. Phys. Chem., and those of
chapter 4 have already been published in two Chem. Phys. Letters. Also, the experimental results in chapter 4 were obtained in conjunction with a post-doctoral Research Associate, Dr. Y.C. Jean, who is now at the University of Missouri (Department of Physics), Kansas City. It is hoped that the brief description of the MSR technique in chapters 1 and 2 will give the reader a better enjoyment of the presentation of results in the latter chapters. However, it is recommended that references 1, 2, 22 & 46 be read by those wishing to further understand the physics of the MSR technique in liquid chemistry studies.
CHAPTER 2

EXPERIMENTAL METHOD
Due to the nature and uniqueness of the MSR technique, all the experiments were carried out at the TRIUMF cyclotron (Tri-University Meson Facility). The cyclotron, located on the U.B.C. campus, was completed in 1974 and its capability of producing two simultaneous beams of protons enabled the facility to include such fields of research as medium-energy nuclear physics and muon chemistry, as well as applied research, including isotope production, neutron activation analysis and nuclear fuel research. Also, at present, the use of π⁻ mesons is being investigated in cancer research and treatment by the biomedical group. Fig. 2.1 depicts the TRIUMF site and shows the many available beam line channels, experimental parts and facilities. All the experiments for this thesis were conducted on the M-20 muon channel. In "conventional" mode, a high momentum muon beam was selected (<100 MeV/c) from the decay of pions during their flight down the M20-muon channel. Fig. 2.2 shows the channel tuning for high momentum giving a high flux of muons at the experimental target. However, this type of high energy muon beam is not well suited for studies in liquids since it is desirable to stop muons in a small amount of sample. In 1971, a new type of μ⁺ beam (Arizona mode) using muons from the decay of pions that stop near the surface of the production target (i.e. come to rest in T2 in Fig. 2.2) was investigated by a group from the University of Arizona operating at the Lawrence Berkeley Laboratory 184'' cyclotron [47]. This was achieved by tuning for a momentum of <30 MeV/c, and the resulting beam gave a significant increase in muon stopping density over that of a conventional beam. At TRIUMF, our interchange of targets with the gas chemistry group and use of small target sample
Figure 2.1: Schematic diagram showing the TRIUMF site at U.B.C.
Figure 2.2: Schematic diagram showing the set-up of quadruple and bending magnets for the M20-muon channel at TRIUMF. It also differentiates between the types of muons available by tuning for high or low momentum.
cells necessitated the tune for this, so called, "surface" muon beam on the M20-beam channel. However, it should be noted that the use of conventional "backward" \( \mu^+ \) for the studies of liquids is occasionally used at TRIUMF and is the mode being used by groups at S.I.N. The use of either type is really that of preference based on apparatus limitation, sample geometry and type of experiment.

2.A. Electronic logic and Experimental set-up.

The basic MSR technique involves starting an ultrafast digitizing clock when a muon enters the target and stopping the clock when (and if) the muon's decay positron is detected in the positron counters. This measured time interval is stored in a time histogram in a PDP-11 mini-computer. The process is repeated until a time spectrum, such as that in Fig. 1.1, is obtained.

This spectrum can then be compared with the form of equation (1.5) by a linear-least squares fitting program (MINUIT [48]) on an IBM 370/168 computer. The detailed electronic and computer logistics can be found in reference [46].

The counters and target set-up are shown in Fig. 2.3. Incident muons which are collimated to \( \frac{11}{2}'' \) beam by lead bricks, trigger the thin (TM) counter (-15 mil) sending a "\( \mu \)-stop" signal to the "start" input of a time digitizing converter (TDC) clock; then decay positrons detected either by the left (L1.L2.L3) or the right (R1.R2.R3) coincidence telescopes trigger a signal to the "stop" input of the TDC clock. The resultant time interval is then routed to the appropriate left or right histograms. Each histogram is divided into 2048 bins of 2 ns/bin. The apparatus set-up was a modification of that used in gas-phase studies [46]. The additional "snout" was simply
Figure 2.3: Diagram of apparatus geometry. The incident $\mu^+$ triggers the TM counter (15 mil); later, decay $e^+$ triggers either the left ($L1 \cdot L2 \cdot L3$) or right ($R1 \cdot R2 \cdot R3$) positron telescopes. The 2" carbon absorber is used to degrade low energy $e^+$. The targets are either placed 45° with respect to beam (regular mode) or perpendicular to the $\mu^+$ beam for temperature dependence studies. The magnetic field is physically out of the paper which is called the transverse field method.
an extension beam pipe used to bring the surface muons as close to the targets as possible. The 2''-carbon absorbers between the e\(^+\) counters served to reduce 'accidentals' and to discriminate against low-energy decay positrons, thereby raising the experimental asymmetry \([1,21,46]\). The magnetic field is provided by a pair of Helmholtz coils 24'' in diameter which gives a vertical field direction which is thus transverse to the muon direction. As drawn in Fig. 2.3, there were two possible positions for the targets. The common setup was for the target to be placed at a 45\(^\circ\) angle to the \(\mu^+\) beam. This was used for the \(\text{O}_2\) and porphyrin experiments. For reasons which will be explained in the next section, the temperature cell was placed perpendicular to the incident \(\mu^+\) beam. Not shown in the diagram are the many Pb-bricks which must be "painfully" stacked around the counters to prevent 'contaminations' from beam positrons which seriously interfere with the time histograms of decay positrons.

2.B. Sample preparation and Target holders.

As mentioned in the previous sections, all the experimental results were obtained via the MSR(\(\mu\)SR) technique with the 4.1 MeV "surface" muon beam. All solutions were made from carefully purified, triply-distilled water and deoxygenated with high purity He gas before and during each experimental run. All chemicals were at least of reagent-grade. In the case of porphyrins, the hemin and protoporphyrin powders were obtained from the Strem Chemical Company and were used without further purification. The solutions were freshly prepared before each experiment by dissolving the porphyrins in 0.1 N NaOH solutions, these were then titrated with 0.1 N HCl to a pH of 8.8. The
reference solvent was prepared by titration of the same NaOH and HCl aqueous solutions to pH=8.8.

For most experiments (except the temperature dependence measurements), the liquid samples were contained in a specially designed plastic cell (see Fig. 2.4a). The body of the cell was made of teflon and was cylindrical, 100 mm in diameter and 6 mm deep. Its 'muon windows' consisted of very thin sheets of mylar (0.076 mm). The windows were held onto the teflon cell by rubber pressure rings and sealed against possible air diffusion with silicone grease. Then the whole cell was held together with screws and plexiglas plates. It should be noted that the fraction of muons stopped in the mylar window was less than 5% and therefore did not affect the MSR results to any significant extent. Also, the incident surface muons were completely stopped within the first 0.5 mm of aqueous solution. These "regular" cells were used for the O₂ and porphyrin measurements and were placed at an angle of 45° to the incident muon beam.

For the temperature dependence measurements, a special temperature-regulated cell was designed (see Fig. 2.4b). Similar to the regular cell, the reaction vessel was made of Teflon with thin mylar windows (two pieces of mylar, total of 0.076 mm separated by an airgap of 10 mm) at the front to let the weakly penetrating muons into the medium but prevent too much heat exchange. However, for temperature regulation, a copper jacket was pressed against the rear mylar window of the cell through which water was flowed from a thermostated bath at selected temperatures from 0 to 96°C (see Fig. 2.5). Copper-constantan thermocouples sticking into the solution continuously monitored the temperature of the solution which was actually being
Figure 2.4: Side view of (a) regular teflon cell, and (b) temperature teflon cell.
Figure 2.5: Schematic diagram of the temperature-dependence experimental set-up.
bombarded by the muons. There was a small temperature gradient (~1°C between front and back) even though the cells were only 6 mm deep and the solution was continuously being stirred by the deoxygenating He gas. Moreover, there was never more than a 5°C difference between the bath and cell temperature, so possible errors in the temperature scale of the Arrhenius plots were small. Also, in order to avoid unknown variations in the impurity levels, the same solution was studied at several temperatures whenever this could be done without having to change the solute concentration. In several cases, the bubbling solution was left untouched and only the bath temperature changed. Furthermore, the highest temperature experiment was invariably done first to ensure that any extra impurities which may be leached from the cell at the elevated temperature would be common to all solutions and hence to the background $\lambda_0$ ("background" muonium relaxation constant). Notice in Fig. 2.3 that the temperature targets were placed perpendicular to the beam. The reasons for this are that in the 45°-mode operation, the $e^+$ decaying toward the right detectors were being heavily degraded by the Cu-jacket and at the same time produced a strong Cu-signal (23 MHz). These two phenomena together effectively smeared out the MSR signal in the right histogram. Therefore, the perpendicular geometry was the best site for the cells in the temperature experiments.

In the O$_2$ experiment, the water contained in the regular cell was continuously bubbled with a mixture of N$_2$ and O$_2$ gases. Selected O$_2$ concentrations were made by adjusting the flow rates of N$_2$ and "compressed" air on two supply lines, each measured by a pre-calibrated flow meter. These gases
were thoroughly mixed and saturated with water vapour at 23°C by bubbling through a water-trap prior to reaching the reaction vessel. Gas mixtures between 1 and 20% O₂ were used and the O₂ concentration was then evaluated (to an accuracy of ≈ 7 × 10⁻⁵ M) from the measured total pressure using the published solubility of O₂ at 23°C of 1.29 × 10⁻⁵ M⁻¹kPa⁻¹ [49].

2.C. Data analysis.

The time dependence of the muonium signal was normally obtained at the characteristic muonium spin-precession frequency (1.39 MHz/G) in a weak transverse magnetic field of 6-9 G, whereas the time dependence of the muon signal was obtained with a field of ~80 G. The MSR experiments usually required about 10⁷ events/histogram while that of μSR needed about 10⁶ events/histogram.

Representative MSR signals (asymmetry histograms) are shown in Fig. 2.6 for a solution at two temperatures (a,b) and two solutions at one temperature (c,d). The lines are the computer fits of the data points to equation (2.1) using the χ²-fitting program MINUIT,

\[ A(t) = A_μ \cos(\omega_μ t + φ_μ) + A_M \exp(-λt)\cos(ω_M t + φ_M) \]  \hspace{1cm} (2.1)

The parameter λ (muonium relaxation constant) varies with the addition of a reactive solute S at concentration [S] in accordance with equation (2.2),

\[ λ = λ_0 + k_M [S] \]  \hspace{1cm} (2.2)

where λ₀ is the "background" muonium relaxation constant found in pure water (or other media such as the reference solvent in the porphyrin experiments). The linear relationship of λ and [S] in equation (2.2) is illustrated in Fig. 2.7.
Figure 2.6: Typical MSR asymmetry histograms showing the decay of muonium signal at 9 gauss for 5×10^{-5} M KMnO_4 at (a) 3°C, (b) 58°C, and for (c) 3.5×10^{-4} M NaNO_3, (d) 1.4×10^{-3} M NaNO_3, both at 1°C. The lines drawn are the computer's best $\chi^2$-fit of the data points to equation (2.1).
Figure 2.7: Plot of observed decay constants against NO$_3^-$ concentration in water at 1°C.
It is worth emphasizing that never more than one muon at a time is in
the solution, so \((\lambda - \lambda_0)\) represents a pseudo first-order rate constant as in
equation (2.2) and a plot of \(\lambda\) versus \([S]\) gives the slope as \(k_{\text{Mu}}\), which then
represents the bimolecular rate constant for reaction of \(\text{Mu}\) with substrate \(S\).
Furthermore, the time scale over which the relaxation was observed (0.2-20 \(\mu\)s)
is much later than the slowing down process of the muon, so \(k_{\text{Mu}}\) is indeed a
thermal rate constant. It must be noted that solute concentrations for the
experiments were selected so that the value of \(\lambda\) fell within the working
range of \(-5 \times 10^6\) to \(-2 \times 10^5\) \(s^{-1}\) where the \(\chi^2\)-minimization of data points are
statistically reliable.

For temperature dependence measurements, the extracted muonium rate
constants \((k_{\text{Mu}})\) change with temperature. This can be expressed by the
familiar Arrhenius equation,

\[
k_{\text{Mu}} = A \exp(-E_a/RT)
\]

(2.3)

A plot of \(\ln k_{\text{Mu}}\) against \(1/T\) yields the slope as the activation energy \((E_a)\)
and the intercept as the pre-exponential factor \((A)\). Again, these results
of the plots are obtained via a MINUIT fitting of the data points assuming
a linear relationship between \(\ln k_{\text{Mu}}\) and \(1/T\).

In general, the statistical errors from the computer fits were less
than the variations found from one experiment to another due to unknown
random errors arising from small changes in cell positions, field inhomogeneities, impurity levels, solute concentrations, etc. Sometimes they
were less, even, than the difference in values between left and right
detectors. Realistic "probable errors" in \(k_{\text{Mu}}\) values may be about 20%.
However, the values of $k_{\mu}$ in this thesis were always within -20% of previously published values where these were available from the work of other groups at TRIUMF [23] or S.I.N. [19].
CHAPTER 3

TEMPERATURE DEPENDENCE STUDIES
3.A. Results: Effects of temperature on--

3.A.1. Reaction rate constants of various solutes with muonium.

In this study of the Arrhenius parameters for muonium atom reactivity in aqueous solutions, five different types of reactions were investigated in the temperature range of 0 to 92°C. The solutes chosen were the formate ion \( \text{HCO}_2^- \), maleic acid \( \text{cis-H(HO}_2\text{C):C(CO}_2\text{H)}\text{H} \), permanganate ion \( \text{MnO}_4^- \), nickel (II) ion \( \text{Ni}^{2+} \), and nitrate ion \( \text{NO}_3^- \). Of these, three are fast reactions (\( \text{MnO}_4^- \), maleic acid, & \( \text{Ni}^{2+} \)), one moderately fast reaction (\( \text{NO}_3^- \)), and the other is a slow reaction (\( \text{HCO}_2^- \)). By comparing to the analogous hydrogen atom reactions [50] (see Table 3.1), the fast reactions were expected to consist of Mu addition to a carbon-carbon double bond (maleic acid), oxidation of Mu by \( \text{MnO}_4^- \), and spin conversion of the paramagnetic triplet Mu(\( \uparrow\uparrow\downarrow \)) with \( \text{Ni}^{2+} \) (though no H-atom analogue is observable), while the slow reaction of \( \text{HCO}_2^- \) is that of a hydrogen abstraction by Mu and the \( \text{NO}_3^- \) is an unknown reaction type (Table 3.1).

The results are given in Table 3.2. When plotted as \( \log k \) versus \( 1/T \), the three solutes, \( \text{MnO}_4^- \), maleic acid and \( \text{Ni}^{2+} \), each gave an \( E_a \) of about 4.2 kcal.mole\(^{-1}\) and an extrapolated A-factor of about \( 10^{13} \text{M}^{-1}\text{s}^{-1} \) (Table 3.3). For the case of \( \text{HCO}_2^- \), a large \( E_a \) of 8 kcal.mole\(^{-1}\) and a moderate A-value of \( 4\times10^{12} \text{M}^{-1}\text{s}^{-1} \) were obtained. The most puzzling result is that of \( \text{NO}_3^- \). If one merely does a linear least square fit (neglecting any noticeable curvature), then one gets a very small \( E_a \) of 1.5 kcal.mole\(^{-1}\) and an apparently low A-factor of \( 2\times10^{10} \text{M}^{-1}\text{s}^{-1} \). On the other hand, the slope of the three high temperature points gives an \( E_a \) of 4.8 kcal.mole\(^{-1}\) and an A-factor of
TABLE 3.1
Proposed mechanisms of reactions studied. (nature of reaction is based on comparison with that of the hydrogen atom)

\[
\begin{align*}
\text{Mu} + \text{HCO}_2^- & \rightarrow \text{MuH} + \text{CO}_2^- \\
\text{Mu} + \text{HO}_2\text{C} \equiv \text{C} \equiv \text{CO}_2\text{H} & \rightarrow \text{HO}_2\text{C} \equiv \text{C} \equiv \text{CO}_2\text{H} \\
\text{Mu} + \text{MnO}_4^- & \rightarrow \mu^+ + [\text{MnO}_4^{2-}] \\
\text{Mu}^{++} + \text{Ni}^{2+} & \rightarrow \text{Mu}^{++} + \text{Ni}^{2+} \\
\text{Mu} + \text{NO}_3^- & \rightarrow [\text{MuNO}_3^-]
\end{align*}
\]
## TABLE 3.2

Variation of $k_{\text{Mu}}$ with temperature.

<table>
<thead>
<tr>
<th>Solute</th>
<th>Conc/$10^{-3}$M</th>
<th>Temp/°C</th>
<th>$^{+}k_{\text{Mu}}$/M$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO$_2^-$</td>
<td>125</td>
<td>1</td>
<td>1.9x10$^6$</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>21</td>
<td>3.4x10$^6$</td>
</tr>
<tr>
<td></td>
<td>62.5</td>
<td>59</td>
<td>2.0x10$^7$</td>
</tr>
<tr>
<td></td>
<td>31.3</td>
<td>92</td>
<td>7.6x10$^7$</td>
</tr>
<tr>
<td></td>
<td>15.6</td>
<td>92</td>
<td>7.3x10$^7$</td>
</tr>
<tr>
<td>MnO$_4^-$</td>
<td>0.05</td>
<td>3</td>
<td>1.2x10$^{10}$</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>22</td>
<td>5.6x10$^{10}$</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>58</td>
<td>2.5x10$^{10}$</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>88</td>
<td>3.0x10$^{10}$</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.7;1.40</td>
<td>1</td>
<td>1.3x10$^9$</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>20</td>
<td>1.9x10$^9$</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>56</td>
<td>1.8x10$^9$</td>
</tr>
<tr>
<td></td>
<td>0.175</td>
<td>81</td>
<td>3.1x10$^9$</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>92</td>
<td>3.6x10$^9$</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>0.1</td>
<td>3</td>
<td>8.9x10$^9$</td>
</tr>
<tr>
<td></td>
<td>--</td>
<td>22</td>
<td>8.9x10$^{10}$</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>61</td>
<td>2.5x10$^{10}$</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>91</td>
<td>5.6x10$^{10}$</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.05</td>
<td>1</td>
<td>7.3x10$^9$</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>21</td>
<td>1.1x10$^{10}$</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>59</td>
<td>3.3x10$^{10}$</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>92</td>
<td>3.3x10$^{10}$</td>
</tr>
</tbody>
</table>

$^{+}$The statistical errors are not given but are typically ±10%. However, the values of $k_{\text{Mu}}$ are really only reproducible to about ±20%.

$^\S$Data obtained by Percival et al [67] for Mu reactions at room temperature.
TABLE 3.3

Results of Arrhenius plots for reactions of various solutes with Mu in aqueous solutions.

<table>
<thead>
<tr>
<th>SOLUTE</th>
<th>$E_a$ (kcal.mole$^{-1}$)</th>
<th>$A$ (M$^{-1}$s$^{-1}$)</th>
<th>*$k_{Mu}$ (M$^{-1}$s$^{-1}$)</th>
<th>*$k_H$ (M$^{-1}$s$^{-1}$)</th>
<th>$k_{Mu}/k_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO$_2^-$</td>
<td>8.0±0.4</td>
<td>(4.1±0.2)×10$^{12}$</td>
<td>3.4×10$^6$</td>
<td>1.2×10$^8$</td>
<td>0.03</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>4.5±0.4</td>
<td>(2.3±0.2)×10$^{13}$</td>
<td>1.1×10$^{10}$</td>
<td>8×10$^9$</td>
<td>1.4</td>
</tr>
<tr>
<td>MnO$_4^-$</td>
<td>4.4±0.4</td>
<td>(3.5±0.3)×10$^{13}$</td>
<td>2.5×10$^{10}$</td>
<td>2.4×10$^{10}$</td>
<td>1</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>3.8±0.6</td>
<td>(8.7±1.3)×10$^{12}$</td>
<td>1.1×10$^{10}$</td>
<td>&lt;2.6×10$^5$</td>
<td>&gt;4×10$^4$</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>1.5±0.2</td>
<td>(2.1±0.2)×10$^{10}$</td>
<td>1.4×10$^9$</td>
<td>9×10$^6$</td>
<td>156</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>4.8±1.2</td>
<td>(2.9±0.2)×10$^{12}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^6$NO$_3^-$</td>
<td>0.8±0.3</td>
<td>(0.6±0.2)×10$^9$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

†Quoted errors are standard deviations of the statistical errors given by $\chi^2$ computer fits. The actual realistic errors, taking into consideration the many possible experimental errors involved, may be at least 20-25%.

* $k_{Mu}$ and $k_H$ [50] are room temperature values.

#Values obtained from drawing a straight line through the three highest temperature points only in Fig. 3.1.

$^6$Same, but from three lowest temperature points only.
The actual Arrhenius plots of these solutes are depicted in Fig. 3.1 with the straight lines being the linear least square fits produced by the computer.


In typical solvents such as water, CCl$_4$, alcohols, etc. (except solutions of paramagnetic materials [51]), the muon asymmetry does not relax at any appreciable rate within 5 μsec. However, it was noticed during the analysis of the data in the preparation of this thesis that pure liquid CS$_2$ displays considerable muon relaxation within our experimental time histogram of 4 to 5 μsec. This decrease in the muon asymmetry after subtraction of the intrinsic exponential decay of $\mu^+$ is shown in Fig. 3.2. So the temperature dependence of this relaxation rate was studied. The results at 80 gauss (Table 3.4) showed a very small increase of both the muon asymmetry ($A_\mu$) and the relaxation rate constant ($\lambda_\mu$) from 1.5 to 40°C. An apparent $E_a$ of 0.4±0.1 kcal.mole$^{-1}$ was obtained by plotting log $\lambda_\mu$ versus 1/T assuming $\lambda_\mu$ obeys the Arrhenius expression.
Figure 3.1: Arrhenius plots of various solutes reacting with the muonium atom from 0° to 92°C.
Figure 3.2: Plot showing the muon asymmetry (and its relaxation rate) for liquid CS$_2$ at 80 gauss at 1.5°C (top) and 40°C (bottom).
TABLE 3.4

Muon asymmetry ($A_\mu$) and relaxation rate ($\lambda_\mu$) in CS$_2$.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>$A_\mu$</th>
<th>$10^{-6}\lambda_\mu$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.093±0.002</td>
<td>0.201±0.005</td>
</tr>
<tr>
<td>40.0</td>
<td>0.104±0.002</td>
<td>0.221±0.005</td>
</tr>
</tbody>
</table>
3.A.3. Muonium relaxation rate constant in H\textsubscript{2}O.

The intrinsic muonium relaxation rate constant in pure water (\(\lambda_0\)) was investigated at 9 gauss as a function of temperature. Its value varies slightly from \((3.0 \pm 0.3) \times 10^6\, \text{s}^{-1}\) at 2°C to \((4.0 \pm 0.4) \times 10^6\, \text{s}^{-1}\) at 92°C. As a result, a plot of \(\log \lambda_0\) versus \(1/T\) yielded an activation energy (\(E_a\)) of about \(0.6 \pm 0.1\) kcal.mole\(^{-1}\) (Fig. 3.3). This extremely small \(E_a\) can be compared to some previous work done by Myasishcheva et al [52] in which they reported an \(E_a\) of \((0.135 \pm 0.320)\) kcal.mole\(^{-1}\) for this same process, though it should be noted that these authors were using an analysis method where the values of \(k_{Mu}\) were incorrectly derived. At this moment, because of the possible errors involved in measuring \(\lambda_0\) (in fact, its origin is not known) due to factors such as target geometry and magnetic field inhomogeneities, one can conclude only that the \(E_a\) obtained in this study is either very small or non-existent. Certainly it is not as large as the 4 kcal.mole\(^{-1}\) obtained for solutes. In fact, when the \(E_a\) is very small, the temperature dependence of the pre-exponential term in the Arrhenius expression (where the particle's mean velocity is proportional to \(T^{\frac{1}{2}}\)) can dominate, so that a plot of \(\ln k\) versus \(\ln T\) has a slope of 1/2, as seems to be the case for gas phase studies [53]. However, a plot of \(\ln \lambda_0\) versus \(\ln T\) for pure water gave a value of slope = \(n = 1.5 \pm 0.3\) (Fig. 3.4).
Figure 3.3: Plot of the temperature dependence of the relaxation rate constant ($\lambda_0$) in pure water.
Figure 3.4: Plot of $\ln \lambda_0$ vs. $\ln T$ for pure water.
3.A.4. Muon asymmetry in CCl₄ and H₂O.

A study of the muon asymmetry in CCl₄ was carried out from a temperature of 0 to 58°C. Fig. 3.5 gives the results, from which it can be seen that there is no apparent change within this temperature range. It has been established that CCl₄ has the highest possible muon asymmetry (0.303±0.003) in these experiments; as a result it is used as the reference to obtain A₀ for evaluating P_D for other solvents. In fact, one criterion at the beginning of each beam-period is to adjust the experimental and electronic set-ups such that P_D for pure water equals 0.62.

From 0 to 90°C, the muon asymmetry of water at 80 gauss was found to increase in a roughly linear fashion. The total change in the asymmetry was about 0.02. As a result, the P_D value for water increases by about 6% in this temperature range as depicted by Fig. 3.6. Previous temperature studies by Percival et al [32] below the freezing point found that the muon asymmetry increases about 10% from 90°K to 160°K. In addition, studies by Myasishcheva et al [52] also found P_D to increase by about 4% from 0 to 90°C; although in their case the absolute magnitudes of the muon asymmetry were quite different from this study and their method of extrapolating rate constants was incorrect [18].
Figure 3.5: Plot of muon asymmetry in CCl₄ as a function of temperature.
Figure 3.6: Plot showing the change in $P_D$ of water as a function of temperature. (The solid line is the least squares fit to a straight line.)
3.B. Discussion of results on...

3.B.1. \( k_{\text{Mu}} \) of various solutes in aqueous solutions.

From Table 3.3, there seems to be a clear distinction between the \( E_a \)'s and the different types of reactions. The fast reactions (\( k \sim 10^{10} \text{ M}^{-1}\text{s}^{-1} \)) of \( \text{MnO}_4^- \), maleic acid and \( \text{Ni}^{2+} \) gave \( E_a \) values of \(-4.2 \text{ kcal.mole}^{-1} \) which are indicative of diffusion controlled reactions in water [34]. On the other hand, the much larger value of \( E_a \approx 8 \text{ kcal.mole}^{-1} \) obtained for the slow reaction of \( \text{HCO}_2^- \) indicates it is an activation controlled reaction [34,54]. For \( \text{NO}_3^- \), the Arrhenius plot does not indicate either simple diffusion or activation controlled behaviour as reflected by the extremely small \( E_a \) of \(-1.5 \text{ kcal.mole}^{-1} \) (solid line in Fig. 3.1). In fact, the data points show slight but continuous curvature in the temperature range studied.

Although the \( E_a \)'s obtained for the diffusion-controlled reactions are about the same, the A-factors are quite different and vary by almost a factor of 4 between \( \text{MnO}_4^- \) and \( \text{Ni}^{2+} \). However, before one can interpret these A-factors, one must remember that these A-factors differ mainly because the \( \chi^2 \)-fitting gave different values of \( E_a \)'s. Since the \( E_a \)'s are all statistically within each other's error bars, one can assume the reactions of \( \text{Mu} \) with these solutes in diffusion-controlled processes should all give rise to the same \( E_a \). One way to determine a common \( E_a \) for these three reactions is to take the average of the experimental \( E_a \) values. This gives \( \overline{E_a} = 4.2 \text{ kcal.mole}^{-1} \).

But probably a better method is to normalize the other two sets of data points against the best fitted data line (in this case, maleic acid), fit all the resulting data points together on the same line to get a common
E_a (E'_a), then recalculate the A-factor (A') of the three solutes using the points given by the previously fitted lines and the now common E'_a. The Arrhenius plots of the original fitted lines and the normalized line giving E'_a are shown in Fig. 3.7, while the A' results of this normalization scheme are given in Table 3.5. One can see clearly that the A-factor for MnO_4^- has the largest value,

\[ A'_{\text{MnO}_4^-} > A'_{\text{Ni}^{2+}} \geq A'_{\text{M.A.}} \]  \hspace{1cm} (3.1)

whereas the value for Ni^{2+} is only slightly bigger than that of maleic acid. Since these three are diffusion-controlled reactions, one can qualitatively consider the A-factors as represented by [34]:

\[ A \propto (D_{\text{Mu}} + D_s)(R_{\text{Mu}} + R_s) \]  \hspace{1cm} (3.2)

where D's are diffusion coefficients and R's are effective reaction radii of each species. Because Mu is a particularly small species with an expected high diffusion constant, D_{\text{Mu}} >> D_s and R_s >> R_{\text{Mu}} , and therefore the A-factors of each solute correlate with R_s. This seems to suggest that

\[ R_{\text{MnO}_4^-} > R_{\text{Ni}^{2+}} \geq R_{\text{M.A.}} \]  \hspace{1cm} (3.3)

R_s is the 'reaction radius', which is the effective distance that Mu must approach the solute before reaction occurs. The order in equation (3.3) however seems to differ from the molecular radii of the solutes. It is not clear what is the "molecular size" of Ni^{2+}(aq), for instance, because its solvation shell affects its diffusion but probably is not involved in the electron spin conversion process. From the point of view of isolated molecules
Figure 3.7: Arrhenius plots showing (top) the original \( \chi^2 \)-fits of the individual sets of data points for \( \text{MnO}_4^- \), maleic acid and \( \text{Ni}^{2+} \), and (bottom) the fit of the normalized data points (using the best fitted line maleic acid) to give a common \( E_a \) (\( E_a' = 4.1 \text{ kcal.mole}^{-1} \)) for these diffusion controlled reactions.
TABLE 3.5

Data and normalized results of the diffusion controlled reactions.

<table>
<thead>
<tr>
<th>SOLUTE</th>
<th>$^*E_a$ (kcal.mole$^{-1}$)</th>
<th>$^*A$ (M$^{-1}$s$^{-1}$)</th>
<th>$^{\dagger}E'_a$ (kcal.mole$^{-1}$)</th>
<th>$^{\ddagger}A'$ (M$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maleic acid</td>
<td>4.5</td>
<td>2.3×10$^{13}$</td>
<td>4.1</td>
<td>1.3×10$^{13}$</td>
</tr>
<tr>
<td>MnO$_4^-$</td>
<td>4.4</td>
<td>3.5×10$^{13}$</td>
<td>4.1</td>
<td>2.2×10$^{13}$</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>3.8</td>
<td>8.7×10$^{12}$</td>
<td>4.1</td>
<td>1.5×10$^{13}$</td>
</tr>
</tbody>
</table>

$^*E_a$ and $A$ are original values of $\chi^2$-fitted lines in Fig. 3.7(a).

$^{\dagger}E'_a$ is the fitted value in the normalized Arrhenius plot shown in Fig. 3.7(b).

$^{\ddagger}A'$ is the recalculated value using $E'_a$ in the Arrhenius expression with the original $\chi^2$-fitted lines in Fig. 3.7(a).
the decreasing size should be maleic acid > MnO₄⁻ > Ni²⁺. The order in (3.3) is thus of interest since it reflects on the type of reaction and the closeness to the reaction centre that Mu must approach for reaction. Perhaps the order in equation (3.3) can be qualitatively interpreted as follows. The maleic acid has the smallest $R_s$ because Mu must break into the π-bond cloud before reaction; therefore it must get within close distance of the carbon atom to be incorporated into the molecule. On the other hand, for MnO₄⁻, the larger $R_s$ suggests that the transfer of the electron from Mu can occur over much further distance from Mn (relative to maleic acid, a factor of ≈1.5 judging from difference in $A'$), possibly via some sort of bridge-transfer mechanism through any of the four coordinating oxygens.

As for Ni²⁺, the relatively small $A'$ seems to indicate that the spin-conversion reaction with Mu probably requires a normal close encounter and is not a long range interaction; this interpretation is in good accord with the observation of Jean et al [24] in which they have studied the spin-conversion of Mu by interaction with paramagnetic ions.

On a larger scale, including all five solutes, one can say that the $A$-factors of all reactions are about the order of $10^{13}$ M⁻¹s⁻¹. The overall picture for these reactions can be summed up qualitatively by Fig. 3.8. The
Figure 3.8: Interpreted Arrhenius plots for reactions of Mu with various solutes in aqueous solutions.
picture groups the diffusion controlled reactions together giving an $E_a$ of about 4 kcal.mole$^{-1}$. This scheme, as drawn, suggests that NO$_3^-$ is activation controlled with an added, largely temperature-independent, process such as tunnelling. The idea is that the observed curvature suggests the reaction is faster at lower temperatures than Arrhenius expressions would predict. A possibility then is that tunnelling contributes and it shows up as the curvature in the direction (sense) seen.

The importance of tunnelling in hydrogen abstraction reactions by muonium has been suggested by Roduner et al [45] for the reaction of Mu with methanol. Although one would not expect to be able to distinguish any curvature in such a small temperature range, the large experimental $E_a$ (as compared to Mu+MeOH, $E_a$ ~2 kcal.mole$^{-1}$) seems to suggest little or no tunnelling contribution for the HC0$_2^-$ reaction from 0 to 92°C. The fact that the zero-point energy of muonium is larger than that of hydrogen would lead one to expect $k_{Mu} < k_H$ (Table 3.3). This is the observed result without any tunnelling considerations. In fact, Table 3.6 has given the relative order of three abstraction reactions in terms of their k values. The observed k order can be explained in terms of their relative endothermicities. To a first order approximation, one can write the enthalpy of the reaction $[\Delta H_{\text{reaction}}]$ as the difference between the broken reactant bond energy and the formed product bond energy; that is,

$$\Delta H_{\text{reaction}} = D_o(\text{broken}) - D_o(\text{formed})$$

(3.4)

where $D_o$ is the bond dissociation energy in kcal.mole$^{-1}$. For example, the enthalpy of reaction (H) in Table 3.6 is

$$\Delta H_{\text{rx(H)}} = D_o(HCO_2^-) - D_o(H_2)$$
TABLE 3.6

Relative reaction rates, bond dissociation energies, and relative endothermicities for abstraction reactions.

<table>
<thead>
<tr>
<th>REACTION</th>
<th>SPECIES</th>
<th>$^*$D&lt;sub&gt;o&lt;/sub&gt;(kcal.mole&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H)</td>
<td>H + HCO&lt;sup&gt;-&lt;/sup&gt; → H&lt;sub&gt;2&lt;/sub&gt; + CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.2x10&lt;sup&gt;8&lt;/sup&gt;</td>
<td>1.00</td>
</tr>
<tr>
<td>(D)</td>
<td>H + DCO&lt;sup&gt;-&lt;/sup&gt; → HD + CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.3x10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>0.50</td>
</tr>
<tr>
<td>(Mu)</td>
<td>Mu + HCO&lt;sup&gt;-&lt;/sup&gt; → MuH + CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.4x10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>0.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>RELATIVE ENDOOTHERMICITIES(kcal.mole&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>RELATIVE RATES</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH&lt;sub&gt;rx(H)&lt;/sub&gt; - ΔH&lt;sub&gt;rx(D)&lt;/sub&gt;</td>
<td>-0.25</td>
<td>k&lt;sub&gt;D&lt;/sub&gt; &lt; k&lt;sub&gt;H&lt;/sub&gt;</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;rx(H)&lt;/sub&gt; - ΔH&lt;sub&gt;rx(Mu)&lt;/sub&gt;</td>
<td>-7.30</td>
<td>k&lt;sub&gt;Mu&lt;/sub&gt; &lt; k&lt;sub&gt;H&lt;/sub&gt;</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;rx(D)&lt;/sub&gt; - ΔH&lt;sub&gt;rx(Mu)&lt;/sub&gt;</td>
<td>-7.05</td>
<td>k&lt;sub&gt;Mu&lt;/sub&gt; &lt; k&lt;sub&gt;D&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

Reactions (H) & (D) are taken from ref. [50].

#<sub>m</sub> is the attacking species and m<sub>2</sub> is the species being abstracted.

* Bond dissociation energies in kcal.mole<sup>-1</sup>

† The absolute values of $D_o$(HCO<sup>-</sup>) and $D_o$(DCO<sub>2</sub><sup>-</sup>) are not known, but their difference should be in the zero point energies of C-H & C-D stretching vibrations, which is ≈1.1 kcal.mole<sup>-1</sup>.
From this table, the relative endothermicities of the three abstraction reactions correlate in the same order as their reaction rates constants, k.

\[ \Delta H_{rx}(\text{Mu}) < \Delta H_{rx}(\text{D}) < \Delta H_{rx}(\text{H}) \]  

\[ k_{\text{Mu}} < k_{\text{D}} < k_{\text{H}} \]

The consideration of relative endothermicities seems to explain why hydrogen abstracts much more efficiently than muonium \((k_{\text{H}} > k_{\text{Mu}}, \text{Table 3.3})\). Also, it should be mentioned in Table 3.6 that there is an interesting correlation in the mass ratio of the attacking species and the species being abstracted \((m_1/m_2)\) and the reaction rate \((k)\). The trend indicates that the probability of a small atom (Mu) abstracting a much larger one (H) is much smaller than that of one atom (H) abstracting an equivalent size atom (H).

As mentioned earlier (Fig. 3.8), the diffusion controlled reactions of \(\text{MnO}_4^-\), \(\text{Ni}^{2+}\), and maleic acid all have comparable \(E_a\)'s and A-factors (within a factor of 2). Here, the rates are determined by diffusion of species in aqueous solutions. There does not seem to be any isotopic effect for \(\text{MnO}_4^-\) and maleic acid with H compared to Mu. (One must note that the hydrogen atom rate constant quoted for \(\text{Ni}^{2+}\) is that of a reduction reaction while the Mu rate constant is that of a spin-conversion process; therefore, the ratio of \(k_{\text{Mu}}/k_{\text{H}} = 4\times10^4\) in Table 3.3 is not a meaningful comparison. The analogous \(k_{\text{H}}\) for spin exchange with \(\text{Ni}^{2+}\) has not been measured.) The lack of an isotope effect for diffusion limited reactions suggests that the diffusion coefficient of H and Mu \((D_H \text{ & } D_{\text{Mu}})\) are virtually the same. Thus the diffusive process does not seem to depend directly on the mean velocity (and thus \(1/\sqrt{\text{mass}}\)) for
these small particles in aqueous solutions. This is in conformity with the Stokes-Einstein relationship, but is surprising for species which are smaller than the natural holes in the liquid.

The most intriguing result is that of $\text{NO}_3^-$. Here, the extremely small $E_a$ coupled with a large isotope effect appears to suggest a contribution of quantum-mechanical tunnelling. Experimentally, the presence of appreciable tunnelling would lead to (a) non-linear Arrhenius plots [55], (b) greatly enhanced isotope effects [55,56], and (c) unexpectedly large differences in effective activation energies for isotope species [55]. The practical observation of one or more of these phenomena will depend on the accuracy of the data, the temperature range studied, and, of course, the magnitude of the tunnelling contribution [57]. Indeed, in this thesis, although a relatively small temperature range of 90 degrees was used, there still seems to be a noticeable consistent trend of curvature demonstrated by the $\text{NO}_3^-$ data points (dotted line of Fig. 3.1). Along with the huge isotope effect ($k_{\text{Mu}}/k_{\text{H}}$) of 156, the $\text{NO}_3^-$ data suggest the influence upon reaction rates by quantum mechanical tunnelling. However, deviations from Arrhenius equations can arise for various reasons quite unconnected with tunnelling. One obvious reason is a change of mechanism at low temperatures; if there are two competing reactions, the one with the higher activation energy will become relatively more dominant as the temperature rises, and the Arrhenius plot will curve in the same direction as found here. For example, the situation could be represented by equation (3.6),

$$
\text{Mu} + \text{NO}_3^- \xrightarrow{k_1} P_1 \quad \xrightarrow{k_2} P_2
$$

(3.6)
in which \( k_1 \) and \( k_2 \) have different Arrhenius parameters \( A_1, E_1 \) and \( A_2, E_2 \) respectively. Specifically, if \( A_1 \sim 3 \times 10^{12} \text{ M}^{-1}\text{s}^{-1} \) and \( E_1 \sim 4.8 \text{ kcal.mole}^{-1} \) then reaction (1) would dominate at high temperatures, and if \( A_2 \sim 6 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \) and \( E_2 \sim 0.8 \text{ kcal.mole}^{-1} \) then reaction (2) would dominate at low temperatures, and \( k_1 \) would be comparable to \( k_2 \) at room temperatures. These values actually correspond to the slopes of the dotted lines drawn through the three highest and three lowest temperature data (see Table 3.3). In fact, Dainton et al [54] have studied the relative rates of abstraction by hydrogen and deuterium atoms from propan-2-ol and \( \left[^2\text{H}_7\right] \text{propan-2-ol} \) as a function of temperature in 6 M \( \text{H}_2\text{SO}_4 \) using both \( \gamma \)-irradiation and photolysis of \( \text{Fe}^{2+} \) as the source of \( \text{H} \). They found that the Arrhenius behaviour changes from the expected activation control limit at high temperatures to the diffusion control limit at lower temperatures. Other reasons [58] for non-linear Arrhenius behaviour include such effects as solvent reorientation when the transition state is formed (this can result in an apparent dependence of the enthalpy of activation on temperature) and a change of solvent structure at low temperatures. These two effects are further possibilities for the explanation of the \( \text{NO}_3^- \) data.

It is interesting to note that the apparent \( E_a \) of \( \text{NO}_3^- \) is similar in magnitude to the \( E_a \) value of 2.3 kcal.mole\(^{-1}\) obtained for the analogous reaction of \( \text{NO}_3^- \) with the solvated electron (\( e^{-}_\text{aq} \)) [59,60], and the tunnelling mechanism is considered to have a significant contribution to ultra-short time electron scavenging reactions in liquids [61]. Overall, it thus seems reasonable to propose that the reaction of \( \text{NO}_3^- \) with Mu occurs through a quantum mechanical tunnelling contribution upon an otherwise activation controlled mechanism.
3.B.2. $\lambda_\mu$ in CS$_2^-$

The observation of muon relaxation in liquid CS$_2$ is a very strange and puzzling phenomena. Its origin could be due to a few possible causes. One possibility is the presence of impurities in liquid CS$_2$ which react chemically with the diamagnetic muonic species. That there is a huge variation in the muon relaxation time ($T_2$, Table 3.7) seems to reflect the possibility of different amounts of impurities in CS$_2$. Invariably, one of the common impurities in liquid CS$_2$ is sulfur (S$_8$). Gurevich et al [62] have observed some very unusual $\mu^+$ behaviour in yellow crystalline sulphur. They found that the $\mu^+$ relaxation time ($T_2$, Table 3.7) in S$_8$ has a small value of only 0.03 $\mu$sec (i.e. $\lambda_\mu = 33 \mu\text{sec}^{-1}$). This means the presence of 1% sulphur in our sample could cause the observed $\lambda_\mu$ in our work. However, the presence of 1% sulphur in our CS$_2$ sample was not very likely since the already spectro-grade liquid was purified by column distillation which should have reduced the sulphur residue down to, at most, 0.002% (manufacturer's sulphur residue content). In the next experimental beamtime it is proposed to add sulphur to CS$_2$ to explore this possibility.

Since CS$_2$ is a good electron scavenger,

$$\text{CS}_2^- + e^- \rightarrow \text{CS}_2^-, \quad (3.7)$$

another possibility for $\lambda_\mu$ is the formation of a long-lived complex (long enough within our experimental time scale of 100 nsec), formed by addition of $\mu^+$ to CS$_2^-$ as in equation (3.8).

$$\mu^+ + \text{CS}_2^- \rightarrow [\mu^+\text{CS}_2^-]^+ \quad . \quad (3.8)$$
### TABLE 3.7
Collected data on CS$_2$ and sulfur.

<table>
<thead>
<tr>
<th>SUBSTANCE</th>
<th>T(°C)</th>
<th>$^\dagger T_2$(usec)</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS$_2$</td>
<td>22</td>
<td>&gt;20</td>
<td>[62]</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>22</td>
<td>&lt;0.05</td>
<td>[71]</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>22</td>
<td>5</td>
<td>[this work]</td>
</tr>
<tr>
<td>sulfur</td>
<td>22</td>
<td>0.03</td>
<td>[1]</td>
</tr>
</tbody>
</table>

$^\dagger T_2$ is the muon relaxation time defined as the reciprocal of $\lambda_\mu$. 
This is similar to the formation of molecular $\mu^+$ ions in noble gas reactions [22,53]. The complex formed in equation (3.8) may cause effective muon depolarization, but it may give rise to Arrhenius behaviour in a temperature investigation of $\lambda_\mu$. However, the extremely small $E_a$ of about 0.4 kcal.mole$^{-1}$ seems to suggest the above explanation is also inadequate.

The muon relaxation observed in liquid CS$_2$ at present is a mystery. However, it is an interesting result and warrants more careful investigation in the immediate future.

3.B.3. $\lambda_0$ in H$_2$O.

The small change of $\lambda_0$ in H$_2$O as a function of temperature is an important result in the study of muonium in liquids. Its interpretation can be used to elucidate the validity of the many possible origins giving rise to the observed $\lambda_0$ in water. One of these is the occurrence of a pseudo-first order chemical reaction between Mu and the solvent water molecule giving diamagnetic species such as MuOH, MuH or MuO [23]. The following are possible reactions.

\begin{align*}
\text{Mu} + H_2O & \rightarrow H + \text{MuOH} & \text{(3.9a)} \\
\text{Mu} + H_2O & \rightarrow OH + \text{MuH} & \text{(3.9b)} \\
\text{Mu} + H_2O & \rightarrow H_2 + \text{MuO} & \text{(3.9c)}
\end{align*}

In equations (3.9) the reactions of Mu with H$_2$O do not involve diffusion of the species (the water molecules are already there, at concentration of 55 M). However, since $k$ is small, as shown in equation (3.10),
\[ \lambda_0 = k[H_2O] \]
\[ 0.25 \times 10^6 \text{ s}^{-1} = k \times 55 \text{ M} \]
\[ k = 5 \times 10^4 \text{ M}^{-1} \text{s}^{-1} \]

if \( A = 10^{13} \text{ M}^{-1} \text{s}^{-1} \), then using the Arrhenius expression, one would get an \( E_a \) of about 12 kcal.mole\(^{-1}\) for the above reactions. Consequently, the small experimental \( E_a \) rules out this possible origin of \( \lambda_0 \). Alternatively, the pre-exponential factor may be unusually small for some unknown reason.

Another possible cause of \( \lambda_0 \) can be some chemical reaction of Mu with impurities such as residual \( O_2 \). But following similar arguments as in the above case, the much smaller value of \( E_a \) of 0.6 kcal.mole\(^{-1}\) again rules out chemical reactions since all the values found are at least 2 kcal.mole\(^{-1}\) (and probably at least 4 kcal.mole\(^{-1}\)).

Two other possibilities are the experimental artifacts of magnetic field inhomogeneities and the physical phenomena of collision broadening or frequency beating [1,46], both of which require further experimental investigations. Yet another possible origin of \( \lambda_0 \) involves intra-spur reactions of Mu with species produced at the end of the \( u^+ \) track. This was eliminated earlier [23] based on arguments that such intraspur processes would not follow first order kinetics [63] nor last longer than \( 10^{-6} \) sec [64]. Also, the radiation dose levels produced within the experimental timescale could not account for sufficient production of \( H_2O_2 \) concentration to give diamagnetic products via reaction of Mu with \( H_2O_2 \).

\[ \text{Mu} + H_2O_2 \rightarrow \text{MuOH} + OH \]  

(3.11)
It was mentioned in section 3.A.3. that a plot of $\ln \lambda_0$ versus $\ln T$ for pure water gave a value of $n=1.5\pm0.3$. This result is not as that found in gas phase studies [53] where a simple velocity dependence would have given $n=\frac{1}{2}$. Perhaps this highlights an important difference between gas phase and liquid phase reactions. For liquid it is unlikely that diffusion is proportional to $\sqrt{v}$ and hence to $T^{1/2}$. Furthermore, liquid phase reactions involve solute-solvent interactions, including caging effects, while such considerations are absent in gases.

At this moment, observation of Mu in non-aqueous media such as methanol, tetramethylysilane (TMS), cyclohexane and n-hexane are extending our investigations of $\lambda_0$ [27]. It is hoped that further studies in these neat liquids will help in the elucidation of the mechanism causing $\lambda_0$, a residual relaxation rate in the absence of added solutes.

3.B.4.a. $P_D$ in $\text{CCl}_4^-$

The muon asymmetry of $\text{CCl}_4$ has a comparable value to that found in simple metals such as copper and aluminum, which strongly implies that $P_D=1$ for $\text{CCl}_4$ and that the process giving rise to the diamagnetic fraction is very efficient [65]. The origin of the diamagnetic/muonium fractions has attracted two models - the 'SPUR' and 'HOT' models. From the viewpoint of intraspur processes [66], one can present two possible mechanisms. One simple mechanism is that since $\text{CCl}_4$ is a very good electron scavenger, it can then capture efficiently spur electrons to give $\text{CCl}_4^-$, which then gives $\text{Cl}^-$ and $\text{CCl}_3$ (as in equation (3.12)).

$$\text{CCl}_4 + e^- \rightarrow [\text{CCl}_4^-] \rightarrow \text{CCl}_3 + \text{Cl}^- \quad (3.12)$$
The \( \text{Cl}^- \) is long lived and consequently could neutralize with \( \mu^+ \) to form the diamagnetic muonic species of \( \text{MuCl} \) (as in equation (3.13)).

\[
\mu^+ + \text{Cl}^- \rightarrow \text{MuCl} 
\]  

(3.13)

The other spur mechanism arises by arguing that the efficient scavenging of spur electrons by \( \text{CCl}_4 \) to give long lived anions in fact prevents the neutralization process of \( \mu^+ \) in the spurs, i.e. all the muons stay in the \( \mu^+ \) diamagnetic state. The fact that the muon asymmetry in \( \text{CCl}_4 \) is observed to not change with temperature merely suggests that the mechanism giving rise to \( P_D \) is already a very efficient process. One can argue that the increase in temperature should have also increased the rate of the mechanism giving rise to \( P_M \) in \( \text{CCl}_4 \). However, it was unfortunate that a search for a trace of muonium in \( \text{CCl}_4 \) was not carried out due to limitation in experimental beam time. Finally, it should be noted that the observed results in \( \text{CCl}_4 \) seem to be in agreement also with the hot model, since one would predict that the hot mechanism is unaffected by temperature (as indeed, the word "hot" implies); therefore one would not expect \( P_D \) to change. This temperature-dependence study therefore does not help to resolve the mechanism by which \( \text{CCl}_4 \) gives \( P_D = 1 \).
3.B.4.b. P_D in H_2O.

The observed small change in the muon asymmetry of water can be interpreted by both the spur and hot mechanisms. From the spur model point of view [32,67], the immediate conclusion from Fig. 1.2 is that the encounter frequency of the \( \mu^+ \) and e\(^-\) decreases as temperature increases. In other words, the probability of these species escaping from intraspur reactions with each other increases with temperature. This idea seems to be in accord with the observed free ion yield \(^{\dagger}G_{fi}\). Since the \( G_{fi} \) values increase by about 10% from 0 to 90°C [68], this means more ions will escape intraspur processes with increasing temperature and consequently lead to an increase of \( P_D \) in this temperature range. One must consider the factors that contribute to \( G_{fi} \). These include the changes in the dielectric constant of the medium, the thermalization distance and the mobility of the electron as a function of temperature. As one increases the temperature of the medium, the dielectric constant of water decreases from 87.7 at 0°C to 58.3 at 90°C [69]. Also, the effective thermalization distance of the electron (related to the time taken for the electron energy to reach ambient temperature) probably should decrease in this range. Both of these factors should effectively increase the encounter frequency of \( \mu^+ \) and e\(^-\). This means that the dominating factor lies with the higher electron mobility giving an overall increase in \( G_{fi} \) with increasing temperature.

\(^{\dagger}\)The free ion yield is defined as the number of ions per 100 eV of energy absorbed which escape geminate recombination. The data are compiled via methods of scavenging, conductivity or charge collection.
However, this apparent agreement of an increasing $P_D$ with $G_{\tilde{f}_1}$ does not necessarily indicate a verification of the spur model because an increase in $P_D$ should also bring about a decrease in $P_M$. At present, this parameter has not been fully investigated although preliminary results seem to show little or no change in the value of $P_M$ with increasing temperature. Furthermore, the observed change in $P_D$ with temperature may be consistent with the hot model. Whereas the ambient temperature change will have little effect on epithermal Mu (or $\mu^+$) it has a considerable influence on the medium, water. In particular, at 2°C, water is some 80% hydrogen-bonded whereas at 95°C it may be only 30% hydrogen-bonded [70]. It is possible therefore that this structural difference leads to a significant change in the fraction of muons emerging from their tracks already incorporated in diamagnetic molecules.
CHAPTER 4

COLLABORATIVE WORKS
4.A. Reaction of muonium with $O_2$ in aqueous solution.

4.A.1. Introduction.

The first detection of muonium in water was by Percival et al [18]. It was suspected then that earlier unsuccessful attempts of observation of muonium in liquids was due to the incomplete removal of oxygen in the samples. This suspicion is now verified by an investigation of the rate at which muonium reacts with molecular oxygen ($O_2$). It was well known that reducing species such as hydrogen atoms, solvated electrons, positronium atoms and free radicals react with extreme rapidity and efficiency with $O_2$ in aqueous solutions. Therefore, before any kinetic investigation can be carried out between these species, a thorough deoxygenation process of the liquid samples must be necessary. A muonium atom reacts chemically with $O_2$ in a similar manner as do the aforementioned species; but because of the presence of (paramagnetic) oxygen in solution, a spin-conversion process can also occur between Mu and $O_2$. Both of these two processes, chemical reaction (removal of Mu atom) and spin-conversion (depolarization of Mu atoms), lead to a decrease of the MSR signal. Unfortunately, these cannot be differentiated in transverse magnetic field studies.
4.A.2. Results.

Experimental details describing how known concentrations of $O_2$ were obtained are given in chapter 2. The raw data of the different oxygen concentrations used are tabulated in Table 4.1 and those of the right side detector for the three oxygen concentrations (including $\lambda_0$) are shown in Fig. 4.1. The resulting $\lambda$'s are plotted against $O_2$ concentration and are shown in Fig. 4.2. As described in chapter 2, the slope obtained from this plot is interpreted as the bimolecular rate constant for the reaction, $k_{obs}$ (i.e. $\lambda = \lambda_0 + k_{obs}[O_2]$). The extracted $k_{obs}$ and $\lambda_0$ have values of $(2.4 \pm 0.5) \times 10^{10}$ M$^{-1}$s$^{-1}$ and $0.28 \times 10^6$ s$^{-1}$, respectively. The fitted value of $\lambda_0$ is in good agreement with that found previously [23,24].


The value of $k_{obs}$ obtained in Fig. 4.2 demonstrates the importance of deoxygenation in liquid muonium studies. For air-saturated water, the $O_2$ concentration is $2.6 \times 10^{-4}$ M, this means $\lambda$ for the muonium signal ($k_{obs}[O_2]$) would be about 6 $\mu$s$^{-1}$. In other words, the mean lifetime of Mu in non-deoxygenated water is only 0.16 $\mu$s and therefore barely observable by the present MSR technique. However, by bubbling with an oxygen-free gas for a few minutes prior to experiment, the $[O_2]$ content in the samples can be reduced to $\approx 1\%$ $O_2$ which would render the contribution of the reactions of $O_2$ toward the rate of Mu depolarization insignificant.

The possible reactions of $O_2$ with Mu can be represented either by a chemical reaction,

$$\text{Mu} + O_2 \xrightarrow{k_{Mu}} \text{MuO}_2 \quad \text{(or } \mu^+ + O_2^- \text{, or MuO} + 0) \quad (4.1)$$
TABLE 4.1

Raw data of different oxygen concentrations used in aqueous solutions.

<table>
<thead>
<tr>
<th>%O₂ in O₂/N₂ mixture</th>
<th>*[O₂]/10⁻⁵ M</th>
<th>λ/10⁶ s⁻¹ left</th>
<th>λ/10⁶ s⁻¹ right</th>
</tr>
</thead>
<tbody>
<tr>
<td>0⁺</td>
<td>0</td>
<td>0.295±0.023</td>
<td>0.277±0.030</td>
</tr>
<tr>
<td>2.8</td>
<td>3.3±1.0</td>
<td>1.94±0.08</td>
<td>1.09±0.12</td>
</tr>
<tr>
<td>5.8</td>
<td>6.9±1.0</td>
<td>1.97±0.14</td>
<td>1.66±0.12</td>
</tr>
<tr>
<td>8.0</td>
<td>9.5±1.0</td>
<td>2.83±0.16</td>
<td>3.01±0.11</td>
</tr>
</tbody>
</table>

* The zero concentration of oxygen is represented by pure N₂-bubbled water.

† The O₂ concentrations are obtained by multiplying %O₂ with the solubility of O₂ in water at 740 mm Hg (1.182 mM).
Figure 4.1: Muonium precession signal in (a) pure water, (b) $3.3 \times 10^{-5}$ M $O_2$, (c) $6.9 \times 10^{-5}$ M $O_2$, and (d) $9.5 \times 10^{-5}$ M $O_2$ in aqueous solution at 295°K. The histograms were obtained by the right side detector, typically collecting 8-10 million events, at a magnetic field of 6 gauss. The constant background and exponential muon decay have been removed leaving the plotted signal:

$$A(t) = A_\mu \cos(\omega_\mu t + \phi_\mu) + A_{Mu} \exp(-\lambda t) \cos(\omega_{Mu} t + \phi_{Mu})$$
Figure 4.2: Plot of the observed decay constant $\lambda$ against $O_2$ concentration. (● Left hand side detector, ▲ right hand side detector.) The line drawn is the least-squares-fit by the computer.
or by a spin-conversion,

\[ \text{Mu}(\uparrow\uparrow) + O_2 \xrightarrow{k_D} \text{Mu}(\uparrow\uparrow) + O_2 \]  \hspace{1cm} (4.2)

where \( k_{\text{Mu}} \) and \( k_D \) are the ordinary chemical reaction and spin conversion rate constants, respectively. With these possibilities, one can write

\[ \lambda = \lambda_0 + (k_{\text{Mu}} + k_D)[O_2] \]  \hspace{1cm} (4.3)

where \( k_{\text{obs}} = k_{\text{Mu}} + k_D \). However, in this case, \( k_{\text{obs}} = 2.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \) is probably at the diffusion controlled limit - as judged by the maximum rate constants found for any Mu reactions, and similar to that for \( e^\text{-aq} \) [72], H [50] and Ps [73]. Therefore, \( k_{\text{obs}} \) can be equated with either \( k_{\text{Mu}} \) or \( k_D \) but not with their sum when they are at the diffusion controlled limit; otherwise one would end up having \( k_{\text{Mu}} + k_D = 2k_{\text{diff}} \) which would be an impossible consequence. In other words, once an encounter has occurred, either of the reactions will occur, and their sum of \( k_{\text{Mu}} + k_D \) equals \( k_{\text{diff}} \) but can never exceed it. Unfortunately, one cannot decide on the relative dominance of reaction (4.1) or (4.2) in this case. In fact by comparing the rate constants of reactions (4.1) and (4.2) with the analogous reactions of \( k(\text{H}+O_2) = 2.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \) [50] and \( k(\text{Mu}+\text{Ni}^{2+}) = 1.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \) [24], respectively, one expects both \( k_{\text{Mu}} \) and \( k_D \) to be \( \approx 2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \). The fact that both \( k_D \) and \( k_{\text{Mu}} \) are the order of \( k_{\text{diff}} \) (diffusion controlled rate constant) suggests that the reaction of Mu with \( O_2 \) in aqueous solution must require a normal encounter, therefore implying that the spin-conversion process is not a long range effect. This interpretation of the \( O_2 \) data is contrary to the idea that the "missing" fraction of muon polarization [32] could arise from an intraspruor spin exchange over considerable distances [66].
In the gas phase, the spin-exchange reaction between Mu and O\(_2\) has been studied [74]. There, a value of \(k_{\text{obs}} = 1.6 \times 10^{11} \text{ M}^{-1} \text{s}^{-1}\) was obtained. More importantly, a hard sphere interaction distance (\(R_{\text{eff}} = 1.6 \times 10^{-8} \text{ cm.}\)) was derived from these results which is in good agreement with the value of \(R_c = 2.3 \times 10^{-8} \text{ cm.}\) obtained from the mass-independent cross section based on a spin-exchange model using the "random-phase" approximation [9,74,75]. These calculations of \(R_{\text{eff}}\) and \(R_c\) are comparable to the sum of the expected hard sphere radii of O\(_2\) (1.5\( \times 10^{-8}\) cm. from viscosity and Van der Waals data [69]) and Mu (Bohr radius \(= 0.5 \times 10^{-8}\) cm. [2]). Therefore, similar to that in liquids, the spin exchange process in the gas phase appears to involve only hard-sphere collisions and consequently does not seem to be a long-range effect.

In the liquid phase, as mentioned in chapter 1, the motions of molecules are largely hindered by the fact that they must squeeze past one another to make any substantial movements, but once the reaction partners encounter, their collision frequency increases due to the caging effect by neighbouring solvent molecules. Using Fick's first law of diffusion and application of steady-state gradients [76], the observed bimolecular rate constant can be represented by:

\[
k_{\text{obs}} = \frac{k_{\text{diff}}}{1 + \frac{k_{\text{diff}}}{k'}}
\]

(4.4)

where \(k'\) is the true "kinetic" rate constant that would describe the reaction if equilibrium distributions of reactants are maintained. Assuming that \(k'\) is given by either the gas phase value of \(1.6 \times 10^{11} \text{ M}^{-1} \text{s}^{-1}\) for Mu [22,74] or
the analogous H-atom value of $2 \times 10^{12}$ M$^{-1}$s$^{-1}$ [77], then $k' \gg k_{diff}$ for either reaction (4.1) or (4.2) which reduces equation (4.4) to $k_{obs} = k_{diff}$.

This can be compared with the H-atom value of $k$ for reaction with $O_2$ (equation (4.1)) is $2.5 \times 10^{10}$ M$^{-1}$s$^{-1}$ [50]. This means that $k_{diff}$ for reaction of $O_2$ with $H$ and with Mu are essentially the same. One can derive via Fick's diffusion laws the following expression for $k_{diff}$,

$$k_{diff} = 4\pi R_{12}^2 D_{12} N_0 10^{-3} \quad (4.5)$$

where $R_{12}$ is the sum of the Mu and $O_2$ interaction radii ($R_{12} = R_{(Mu)} + R_{(O_2)}$), $D_{12}$ is the sum of the diffusion coefficients ($D_{12} = D_{(Mu)} + D_{(O_2)}$), and $N_0$ is Avogadro's number. Since $R_{(Mu)}$ is probably the same as $R_{(H)}$ (both Mu and H have the same Bohr radii), therefore $D_{(Mu)}$ is the same as $D_{(H)}$. This suggests that the diffusion coefficients of Mu and H have no mass dependence in aqueous solution. This result is in accordance with the classical (Stokes-Einstein) formulation of the diffusion coefficient; however, it is surprising to find that it also applies to such small species which are probably much smaller than the "holes" in the liquid. Under these conditions, especially with such a large difference in mass ($m_{Mu} \approx 1/9 m_H$), one might expect the rate of diffusion to depend on the mean velocity with which these species "bounced about" within such a hole, and consequently depend on the inverse of the square root of their masses, in which case one gets $D_{(Mu)} = 3D_{(H)}$.

In the study of hydrated electron reactions, Hart and Anbar [72] have analyzed $k_{diff}$ using equation (4.5) and their data indicated that $D_{(H)} = 5 \times 10^{-5}$ and $D_{(O_2)} = 2 \times 10^{-5}$ cm$^2$ s$^{-1}$. Using these values of diffusion coefficients and
our \( k_{\text{obs}} \), one finds that \( R_{12} = 4.7 \times 10^{-8} \) cm. for both the H+O\(_2\) and the Mu+O\(_2\) reaction. The fact that \( R_{12} \) is, within a factor of two, equal to the sum of "hard-sphere" radii (\( \approx 2 \times 10^{-8} \) cm.) again suggests the reaction with O\(_2\) requires an ordinary bimolecular encounter, irrespective of whether it is a chemical reaction (equation (4.2)), as with H \([50]\), or the spin-conversion reaction (equation (4.1)), as in the gas phase \([9,74]\).
4.B. Chemical reactions between muonium and porphyrins.

4.B.1. Introduction.

The use of the MSR technique as a potentially sensitive and non-destructive probe for biological applications was recognized by Jean et al [24] when they observed that muonium reacts at diffusion-controlled rates with all paramagnetic ions in aqueous solutions. In fact, Bucci et al [78] have recently reported the reaction rate constants of Mu with DNA and its constituents in water solutions. In our investigation, the porphyrin and metalloporphyrin systems are chosen since the reaction with Mu should be sensitive to the spin state (5/2 for "high" spin or 1/2 for "low" spin depending on ligand field energies) of the paramagnetic Fe(III) metal centre in the latter case. The important functions of porphyrins in biochemical transformations are well recognized and reviewed [79,80]. Indeed, even though the electronic configuration of a metalloporphyrin can now be readily determined, the mechanism, or route, of electron transfer by which such systems undergo redox chemistry is still a subject of much speculation with respect to even simple metalloporphyrins, which may be used as models of heme proteins; while the mechanism by which heme proteins themselves transport electrons still remain, in general, largely unexplained [81]. For example, the exceptionally high reaction rates between porphyrin molecules and solvated electrons or the hydrogen atom (k > 10^{11} and > 10^{10} M^{-1}s^{-1}, respectively [82]) suggest our interest in measuring Mu reaction rates with these large molecular systems.
4.B.2. Results.

The solutes studied are protoporphyrin IX and chlorohemin IX.

As shown above, protoporphyrin is a square planar molecule; however, the chlorohemin (we shall refer to chlorohemin as hemin\(^+\) from now on since the Cl group will be replaced by OH in alkaline solution) is a five-coordinate square-pyramidal molecule with Fe\(^{3+}\)-N distance of 2.07 Å [83]. The nomenclature for the side groups are: M, -CH\(_3\); V, -HC=CH\(_2\); p, -CH\(_2\)CH\(_2\)COOH. The range of concentrations investigated are tabulated in Table 4.2. The relaxation rate constant of the background solvent (0.1 M NaCl) was defined as \(\lambda_0\) which has a value of \((3.1\pm0.7)\times10^5\) s\(^{-1}\). This is comparable with typical pure water values found previously [23,24] \((1.8-3\times10^5\) s\(^{-1}\)). The relaxation rate constants, \(\lambda\), are plotted against the porphyrin concentrations (Fig. 4.3) and the resulting slopes interpreted as the second-order rate constants (Table 4.3). It must be noted that the errors used in the plots of \(\lambda\) versus [S] are statistical errors, and the actual experimental errors are presumed to be slightly larger (=30%). Also, the straight lines obtained in Fig. 4.3 indicate that protoporphyrin and hemin remain as homogeneous solutions (i.e., no polymerization or aggregation) in the concentration range studied here (0.2 to 1.5 mM for hemin and 0.2 to 3.9 mM for protoporphyrin).

\(^+\)Hemin is structurally the same as protoporphyrin except in hemin an Fe(III) replaces 2 protons.
### TABLE 4.2

Raw data of protoporphyrin and hemin as solutes in aqueous solutions.

<table>
<thead>
<tr>
<th>SOLUTE</th>
<th>CONCENTRATION/M</th>
<th>$\lambda/10^6$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl*</td>
<td>0.1</td>
<td>0.31±0.07</td>
</tr>
<tr>
<td>Protoporphyrin</td>
<td>$0.213 \times 10^{-3}$</td>
<td>0.33±0.08</td>
</tr>
<tr>
<td></td>
<td>$0.400 \times 10^{-3}$</td>
<td>0.45±0.08</td>
</tr>
<tr>
<td></td>
<td>$1.95 \times 10^{-3}$</td>
<td>1.49±0.13</td>
</tr>
<tr>
<td></td>
<td>$3.90 \times 10^{-3}$</td>
<td>2.65±0.14</td>
</tr>
<tr>
<td>Hemin</td>
<td>$0.207 \times 10^{-3}$</td>
<td>0.62±0.13</td>
</tr>
<tr>
<td></td>
<td>$0.307 \times 10^{-3}$</td>
<td>0.63±0.31</td>
</tr>
<tr>
<td></td>
<td>$0.460 \times 10^{-3}$</td>
<td>0.78±0.40</td>
</tr>
<tr>
<td></td>
<td>$1.03 \times 10^{-3}$</td>
<td>2.74±0.35</td>
</tr>
<tr>
<td></td>
<td>$1.55 \times 10^{-3}$</td>
<td>4.86±0.59</td>
</tr>
</tbody>
</table>

$^\dagger$ Values of $\lambda$ are average of left and right histograms. Uncertainties are given by computer statistical error calculations.

$^*$ 0.1 M NaCl is used as $\lambda_0$ in this case since it is the blank containing everything except the porphyrin solutes.
Figure 4.3: Plot of muonium relaxation rate constant ($\lambda$) versus concentration of porphyrins. The data shown are the average values of left and right histograms with error bars being the average statistical errors. The lines drawn are the best line given by the computer least-squares-fit.
TABLE 4.3

Reaction rate constants (in M$^{-1}$s$^{-1}$) of M* in aqueous solutions at 295°K.

<table>
<thead>
<tr>
<th>SOLUTE</th>
<th>$k_{obs}$</th>
<th>SPIN</th>
<th>REFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protoporphyrin</td>
<td>(6.2±0.5)×10$^8$</td>
<td>0</td>
<td>[this work]</td>
</tr>
<tr>
<td>Hemin</td>
<td>(2.4±1.0)×10$^9$</td>
<td>5/2 or 1/2</td>
<td>[this work]</td>
</tr>
<tr>
<td>Fe$^{3+}$(aq.)</td>
<td>5.5 ×10$^9$</td>
<td>5/2</td>
<td>[24]</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$</td>
<td>2.0 ×10$^{10}$</td>
<td>1/2</td>
<td>[24]</td>
</tr>
<tr>
<td>Benzene</td>
<td>8.0 ×10$^8$</td>
<td>0</td>
<td>[1]</td>
</tr>
<tr>
<td>Pyridazine</td>
<td>-8.7 ×10$^8$</td>
<td>0</td>
<td>(a)</td>
</tr>
</tbody>
</table>

(a) Estimated by multiplying $k_H$ by 3. ($k_H$ from reference [50])

From Table 4.3, one can see that the rate constant for protoporphyrin \(6.2 \times 10^8\) is comparable to that of benzene \(8 \times 10^8\) while the rate constant for hemin \(2.4 \times 10^9\) is slightly smaller than that of Fe\(^{3+}\) \(5.5 \times 10^9\) (high spin). Essentially, for the protoporphyrin molecule, the most likely reaction for Mu should be that of a Mu addition to the unsaturated bonds. It should be noted that although the addition reaction rate constant between Mu and a single double bond is very large (i.e. \(k_{\text{Mu}}\) for maleic acid is \(-1 \times 10^{10}\) \(\text{M}^{-1}\text{s}^{-1}\) [22]), the analogous rate constant for a conjugated double bond is of much lower value (i.e. \(k_{\text{Mu}}\) for benzene is \(-8 \times 10^8\) \(\text{M}^{-1}\text{s}^{-1}\) [1]). This is presumably due to the delocalization of \(\pi\)-electrons which has the effect of strengthening the skeletal periphery of the unsaturated molecule. The two carboxylic groups (designated as the P side chains) on the periphery probably react with Mu at a relatively slower rate (as compared with the expected double bond addition reaction) since the formate reaction rate constant is only about \(10^7\) \(\text{M}^{-1}\text{s}^{-1}\) [67]. Therefore, the value of \(k_{\text{obs}} = 6.2 \times 10^8\) \(\text{M}^{-1}\text{s}^{-1}\) obtained for the reaction between Mu and protoporphyrin suggests that the mechanism involves addition of Mu to a large conjugated aromatic molecule. It also seems to suggest that \(k_{\text{obs}}\) is independent of the size of the molecule since the result obtained here is very similar to that of benzene, which is a much smaller molecule compared to protoporphyrin.

The rate constant obtained for hemin is about 4 times larger than that of protoporphyrin. This result must be due to the presence of the ferric ion in the centre of the porphyrin molecule. From structure (c), one can
see that if Mu can always attack the paramagnetic ferric ion in an axial position (below the plane of the square-pyramidal metalloporphyrin), the expected rate constant should be faster \( k_{\text{Mu-Fe(III)}} = 5.5 \times 10^9 \text{ (spin=5/2)} \) or \( 2 \times 10^{10} \text{M}^{-1}\text{s}^{-1} \text{(spin=1/2)} \) due to a direct spin conversion process \[18\]. Therefore, the somewhat smaller \( k_{\text{obs}} \) of \( 2.4 \times 10^9 \text{M}^{-1}\text{s}^{-1} \) seems to suggest either (i) that Mu does not attack the hemin in an axial position or (ii) there is an orientational (steric) factor in the Arrhenius pre-exponential term \( A \). In either case the Mu spin conversion process is inhibited by the porphyrin sheath, which in turn agrees with the previous conclusion that spin conversion is not a long-range effect in aqueous solution \[18\]. Furthermore, it suggests that the \( \pi \)-peripheral ring of the metalloporphyrin plays an important role in shielding the Fe\(^{3+}\) spin force from Mu such that Mu does not always attack Fe\(^{3+}\) directly from an axial position but involves the peripheral substituents as well.

As with the \( O_2 \) case in the previous section, there are two possible mechanisms leading to the depolarization of Mu and the resulting \( k_{\text{obs}} \). These are the spin conversion process as represented by

\[
\text{Mu}(\pi\pi) + \text{Fe}^{3+} \xrightarrow{k_D} \text{Mu}(\pi\pi) + \text{Fe}^{3+} \quad (4.6)
\]
or the reduction process as depicted by

\[
\text{Mu} + \text{Fe}^{3+} \xrightarrow{k_{\text{Mu}}} \mu^+ + \text{Fe}^{2+} \quad (4.7)
\]

With the present transverse MSR technique, one cannot distinguish whether \( k_{\text{obs}} \) of \( 2.4 \times 10^9 \) for hemin is due to reaction (4.6) or (4.7). The electron
transfer process from Fe$^{3+}$ to Fe$^{2+}$ has been observed in porphyrins [50, 73] induced by solvated electrons or by hydrogen atoms, with very high rate constants. For example, they are $10^{11}$ and $10^{10}$ M$^{-1}$s$^{-1}$, respectively, in the case of cytochrome-c [73]. However, relative to the hydrogen atom value for cytochrome-c, the Mu value seems to be smaller by a factor of 4. In the case of DNA and its substituents, $k_{Mu}$ is always greater than $k_{H}$ by at least a factor of 16 [78].

From these MSR measurements of porphyrins one can conclude that: (i) the reactions of Mu with porphyrins occur at a rate less than expected if there was always uninhibited axial attack; (ii) the ferric spin state is partially screened by the peripheral $\pi$-electrons; (iii) the larger conjugation of double bonds does not increase the Mu reaction rate; and (iv) the reaction mechanism between Mu and protoporphyrin is probably an addition process at the double bond while that of hemin is either a reduction of Fe$^{3+}$ or a spin conversion process for Mu. Further MSR studies at high magnetic fields in a search for $\pi$-cation or $\pi$-anion muonic radical intermediates [20] and the use of longitudinal magnetic fields may be useful in elucidating the mechanism of electron transfer reaction between Mu and metalloporphyrins and further our understanding of porphyrin chemistry.
CHAPTER 5

CONCLUSION
From these temperature dependence studies it was shown that Mu reacted at diffusion-controlled rates with MnO$_4^-$, maleic acid and Ni$^{2+}$, and at an activation-controlled rate with HCO$_2^-$. On the other hand, the strange result for NO$_3^-$ was explained via quantum mechanical tunnelling contributions or alternative reaction paths. Perhaps one can perform an indepth and systematic temperature-dependence study for the different reaction types to further elucidate those mechanisms giving rise to occasional large kinetic isotope effects involving Mu and H. The muon relaxation observed in CS$_2$ was very intriguing and warrants future investigations. Studies with other sulphur containing liquids and measurement of the possible muon reaction rate constant ($k_\mu$) with CS$_2$ as a solute in various solvents will probably give insights into this strange phenomena. Results for P$_D$ and P$_M$ in CCl$_4$ and H$_2$O are fundamental to muon chemistry. However, more data at different magnetic fields and temperatures are needed to determine the correct model(s) (Hot, Spur or 'others') for muonium formation in liquids.

In the study of Mu reaction with O$_2$ in aqueous solution, it was shown that the reaction did not involve any long range encounter. However the nature of the reaction, spin conversion or chemical reduction, was not determined using the transverse field technique. It is hoped that future investigations with other gases such as NO and NO$_2$ in both transverse and longitudinal fields can distinguish between these two mechanisms. For the study of Mu with porphyrins, it was found that the MSR technique was sensitive to the presence of the Fe$^{3+}$ in the porphyrin molecule. This sensitivity suggests that one can employ Mu as a nuclear probe (perhaps of the spin state of metal...
ions) in large molecular systems such as biological and polymeric materials. Perhaps the latter might lead to applications in catalysis-related industries.

At present, the apparatus and set-up for liquid chemistry has many problems. Effects such as unstable cell geometry, magnetic field inhomogeneity and small positron solid angle detection all contribute to uncertainties in both μSR and MSR measurements. Of course, the make-shift modification of the gas-cart apparatus further compounds these problems. Therefore, it is hoped that an all-purpose liquid chemistry apparatus employing a He-gas-flow and cryostat situated between a pair of "tip-pole" magnets (range ~5 kG) will be built in the near future to not only remedy the above problems but also to facilitate the study of Mu-substituted radicals. With the incorporation of such an apparatus, one can be assured that the μSR/MSR technique will be both a productive and useful tool in this field of scientific research.
REFERENCES


