Fast Muonium Reactions in Solution: An Electron Spin Exchange Interaction with $Cr(NCS)_6^{3-}$ in Water and Reaction with Iodine in Organic Solvents

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Two reactions of muonium atoms close to the diffusion-controlled limit were analyzed as a function of solute size and solvent viscosity. With $Cr(NCS)_6^{3-}$ as solute in water, the reaction is an electron spin-conversion process, and the observed rate is taken to be half of the actual encounter rate, because of the quantum mechanical statistical factor and the occurrence of multiple collisions due to the solvent cage effect. The encounter rate deduced is 6.2×10^{10} M^{-1} s^{-1}, which implies a large cross section for the Cr complex. In a second series of experiments, the rate of reaction of muonium with I_2 was compared in water, methanol and *n*-heptane. The bimolecular rate constants determined are (1.7 ± 0.3), (7.0 ± 1.2), and (57 ± 22) × 10^{10} M^{-1} s^{-1}, respectively, in these three solvents. This ∼30-fold change in rate is not matched by the change in the inverse of the solvents' viscosities, which changed overall by a factor of only 2.4. It looks as if quantum tunneling dominates over classical diffusion in less polar media where muonium is unencumbered by solvent clathration.

Introduction

Muonium atoms[19] (Mu) have been shown to react with solutes in water with rate constants ranging from $\ll 10^5$ to a maximum approaching 2.5×10^{10} M^{-1} s^{-1}.[1,2] The latter probably represents the diffusion-controlled limit for those reactions. For reactants that obey classical diffusion kinetics, the maximum encounter-rate k_d for a homogeneous bimolecular reaction is given by eq 1:[3]

$$k_d = a(R_M + R_S)(D_M + D_S) \tag{1}$$

where *R* and *D* are the interaction radii and diffusion constants, respectively, for Mu (subscript M in the equations) and solute (S). The constant $a = 4 \times 10^3 \pi N_{(\text{Avogadro})} = 7.6 \times 10^{27}$ mol^{-1} with *D* and *R* in kms units for k_d in M^{-1} s^{-1}. This equation should apply even with charged solutes because Mu is neutral and not readily polarizable for ion−dipole interactions.

If Mu and S both diffuse as Stokes−Einstein particles ($D = k_B T / 6\pi\eta r$),[20] then eq 1 leads to eq 2:

$$k_d = b(R_M + R_S)(r_M^{-1} + r_S^{-1})/\eta \tag{2}$$

where η is the solvent's viscosity and $b = ak_BT/6\pi$. Here r_M and r_S are the "physical contact" radii of Mu and S governing drag in a viscous medium, to be distinguished from the "chemical interaction" radii R_M and R_S. However, if one does make the approximation that $R \simeq r$ for both S and Mu, then eq 2 simplifies to eq 3:

$$k_d = \frac{b}{\eta}\left(2 + \frac{R_S}{R_M} + \frac{R_M}{R_S}\right) \tag{3}$$

For water at 295K, $b/\eta = 0.2 \times 10^{10}$ M^{-1} s^{-1}. The factor in parenthesis equals 4 when $R_M = R_S$ and is progressively greater than 4 the more dissimilar in size they are. To account for $k_d \simeq 2.5 \times 10^{10}$ M^{-1} s^{-1} requires $R_S/R_M \sim 10$.

Whereas the application of the Stokes−Einstein relationship and the $R \simeq r$ approximation may be appropriate for large solutes, they seem rather questionable for a quantum particle like Mu. Yet there are several reactions close to the diffusion limit in water where the observed rate constants for Mu and ^1H are essentially equal and equal to those of hydrated electrons and positronium atoms. This has been interpreted to mean that, in water, diffusion of very light species is governed largely by the solvent through its fluctuating structures and cavity migration.[2] This may still allow the diffusion of a solute to appear to exhibit an inverse radius and viscosity dependence. Furthermore, even Mu and H are "wetted" by water, as suggested by a molecular dynamics calculation.[5] In fact, the extent of clathration of Mu and H by water proved to be rather similar, with Mu higher than H, but only in the ratio 23:18.[5] In unstructured nonpolar solvents the situation may be totally different.

The simple equations above are tested here with respect to fast reactions of Mu by measurement of the absolute bimolecular rate constants for first, an electron-spin-conversion interaction in water, reaction 4,

$$\mathrm{Mu}(\dagger\!\uparrow) + \mathrm{Cr(NCS)}_6^{\;3-} \rightarrow \mathrm{Mu}(\dagger\!\downarrow) + \mathrm{Cr(NCS)}_6^{\;3-} \tag{4}$$

where this Cr(III) complex was predicted to have a particularly large cross section,[6,7] and second, comparison of the rate constants of reaction 5,

$$\mathrm{Mu} + \mathrm{I}_2 \rightarrow \mathrm{Mu}^+ + \mathrm{I}_2^- \qquad \text{(or, MuI + I)} \tag{5}$$

in solvents of different viscosities and dielectric constants.

Experimental Section

Beams of high-energy positive muons in "backward" spin orientation and continuous wave mode were utilized for these experiments on beamline M9B at the TRIUMF cyclotron in Vancouver. The time-differential muon-spin-rotation technique (μSR) was employed, as fully described previously.[8] It used

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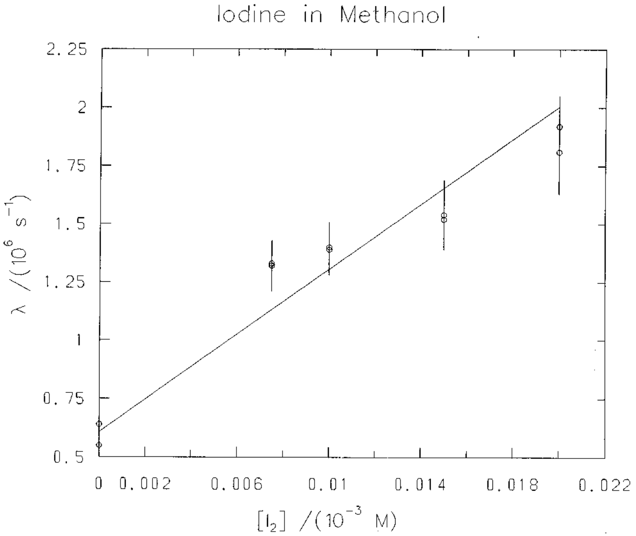

Figure 1. A plot of λ versus solute-concentration, I_2 as solute, for reaction with Mu in methanol at ~295 K.

the SFUMU-counting equipment with transverse magnetic fields of ~8 G, and data were analyzed by MINUIT χ-squared minimization fitting to the conventional semiempirical equation.[8] The bimolecular rate constant (k_M) comes from the fitted Mu decay constant λ in the presence of a reactive solute (S) through the relationship $k_M = (\lambda - \lambda_o)/[S]$, where λ_o is the background value of λ observed in the solvent with $[S] = 0$. Only Mu atoms in a triplet state (↑↑) are observable by μSR, so any electron spin-exchange/spin-conversion/spin-flip process, such as reaction 4, which leads to the spin-paired (↑↓) state, registers as a Mu "reaction".

These experiments were conducted at room temperature (295 ± 2 K) on solutions made from reagent-grade I_2, methanol, and *n*-heptane and from freshly prepared crystalline $K_3Cr(NCS)_6 \cdot 4H_2O$ and triply distilled water. All solutions were adequately deoxygenated by bubbling with pure N_2 immediately prior to study.

Results

Figure 1 shows a typical plot of λ versus [S] for the case of I_2 in methanol. The slope of such plots equals k_M. Counters on opposite sides of the reaction target collected data independently and were analyzed separately, so that two values of λ were determined for each solution studied. I_2 was chosen as solute in the solvent-viscosity study because its k_M is thought to be close to the diffusion-controlled limit in water, and it is sufficiently soluble in this broad range of solvent polarities. *n*-Heptane was chosen as a representative saturated hydrocarbon solvent because our commercial supply showed its λ_o-background to be $<1 \times 10^6$ s^{-1}. [Many liters of solvent were required to complete an experiment. Neopentane is a potentially more interesting solvent, but it was found to have too large a λ_o-background to permit k_M to be determined, probably because of impurities. In a μSR experiment, the chemical lifetime of Mu, with respect to the particular reaction under study, must be changed by altering the solute concentration until the Mu-lifetime is comparable to the timescale over which the muon in muonium itself decays, *i.e.*, in the neighborhood of 10^{-6} s.]

The relevant results for this study are reported in Table 1 as k_M values. Overall experimental uncertainties in k_M are typically ±15–20%, but in *n*-heptane they were much larger on account of the higher λ_o. In *n*-heptane, only micromolar concentrations of I_2 were finally involved because of its very high reaction rate.

TABLE 1: Values of k_M Obtained from the Slope of Plots of λ versus Solute Concentration: for $Cr(NCS)_6^{3-}$ and I_2 in Water, Methanol, and *n*-Heptane, All at ~295 K. The Solvents' Viscosities Are Given in Parenthesis in Centipoise

solute	solvent (η/cP)	$k_M/10^{10}$ M^{-1} s^{-1}
$Cr(NCS)_6^{3-}$	water	3.1 (±0.4)
I_2	water (0.955)	1.7 (±0.3)
I_2	methanol (0.570)	7.0 (±1.2)
I_2	*n*-heptane (0.399)	57 (±~22)

Discussion

(a) Water as Solvent. The observed k_M for $Cr(NCS)_6^{3-}$ is 3.1×10^{10} M^{-1} s^{-1} (Table 1), which makes reaction 4 about the fastest Mu reaction in water recorded (except for solutes localized in micelles[9]) and comparable to the fastest found for H.[10] This reaction between Mu and the Cr^{3+} complex is an electron spin-conversion (spin-flip or catalyzed spin-exchange) interaction, as in reaction 4[6], and for such reactions, the probability that a collision leads to loss of (↑↑)-Mu is less than unity by a statistical angular momentum weighting factor. So the actual encounter rate (k_d) is even higher than the observed Mu decay rate (k_M) by the inverse of this probability factor.

According to theory,[11] this factor will be $^5/_8$ for a spin-$^3/_2$ system like Cr(III) for a polarized muon source on a single collision. But in solution, the spin-flip probability should depend on the "contact time" as well as the instantaneous overlap of spin densities. Previously[6] it was argued that this could be regarded as applying to each collision, and for a reaction in solution there are many "collisions" (10^2 or more[12]) for each "encounter", due to the caging effect of the solutes by the solvent. With a spin-flip probability of $^5/_8$ on each of these many collisions during the contact time, there will quickly become a 50:50% mixture of (↑↑)- and (↑↓)-Mu atoms. The latter will not be significantly depolarized during the encounter (~30 ps[12]), because the hyperfine oscillation period leading to depolarization of the muon's spin in (↑↓)Mu is much longer (224 ps[8]). Thus, spin-flipping goes back and forth during an encounter in solution resulting in equal numbers of (↑↑)- and (↑↓)-Mu states emerging from such encounters. Those with antiparallel spins are subsequently depolarized and "lost" to detection by μSR within a nanosecond or two as they diffuse away. The encounter rate (k_d) should thus be twice the observed reaction rate (k_M). For reaction 4, this makes $k_d = 6.2 \times 10^{10}$ M^{-1} s^{-1}.

What radius does one apply to Mu for eqs 1–3: its Bohr radius (0.05 nm[8]), the van der Waals radius of H (0.12 nm[13]), or Mu's de Broglie wavelength (0.45 nm[2])? Only the very small Bohr radius for r_M, through the Stokes–Einstein relationship, is consistent with a diffusion constant for Mu of $D_M \simeq 5 \times 10^{-9}$ m^2 s^{-1}, which is roughly what is expected, similar to H.[14] For R_M, it seems preferable to take the van der Waals radius of H. Via eq 1 and neglecting D_S relative to D_M, the deduced value of $k_d = 6.2 \times 10^{10}$ M^{-1} s^{-1} then results in $R_S = 1.5$ nm. As an interaction radius this is more than twice the geometric radius of the $Cr(NCS)_6^{3-}$ ion, which is 0.66 nm, as calculated from the crystallographic Cr–N–C–S internuclear distance of 0.476 nm plus the van der Waals radius of sulfur (0.185 nm[13]). This suggests that a large polarized water solvation sheath is also involved in localizing Mu for this spin-flip interaction. If the de Broglie wavelength of Mu were used instead of the van der Waals' radius of H, then R_S would drop to 1.2 nm, but this is still well above the physical dimension of the anion. Alternatively, one can assume $R_M = r_M$ and then use eq 3. This results in $R_S/R_M = 29$, so that even with R_M at the smallest possible value (the Bohr radius), R_S again comes out to be about

TABLE 2: Dependence of k_M on the Number of NCS^- Ligands Attached to Cr^{3+} (NH_3 Making Up the Octahedral Complex) and on the Electron Delocalization Parameter β

complex	$k_M/10^{10}$ M^{-1} s^{-1}	β[a]
$Cr(NH_3)_6^{3+}$	0.9[b]	0.68
$Cr(NCS)_4(NH_3)_2^-$	2.7[b]	0.24
$Cr(NCS)_6^{3-}$	3.1	0.01

[a] Data from Lazzarini.[7] [b] Published data from ref 6.

1.5 nm. Either way, the encounter cross section is seen to be very high for this type of interaction.

No data on spin-exchange interactions for ^1H atoms with Cr complexes seems to be available to compare with Mu, but these types of reactions have been extensively studied with positronium (Ps, e^+-e^-). In fact this led to the prediction by Lazzarini that k_M for $Cr(NCS)_6^{3-}$ would exceed all others.[7] The data in Table 2 confirm a monotonic increase in rate with the number of NCS^- ligands present, thus adding credence to the "mean environmental rule".[7,15,16] Table 2 also indicates that an increasing k_M accompanies a decreasing β factor, which is a measure of the ligands' effect on delocalization of chromium's d electrons. These few data parallel findings for Ps spin-conversion reactions with Cr(III) and other 3d ions.[15,16]

The observed spin conversion rate of $Cr(NCS)_6^{3-}$ with Ps is $k_{Ps} = 8.15 \times 10^9$ M^{-1} s^{-1}.[7] Mu is thus seen to react 3.8 times faster than Ps with this ion, which is close to the average value of 4.3 for the weighted mean for k_M/k_{Ps} for all Cr^{3+} complexes,[7] but somewhat smaller than the mean value of 5.6 from single ratios reported previously.[6] In the case of ortho-Ps, its spin state has been taken as a triplet, so when it interacts with a quartet Cr(III) ion, only $^1/_{12}$ of the interactions lead to spin flips.[15,17] When one now includes the multiple exchanges caused by the cage effect and the fact that the positrons are not of fixed polarization, in contrast to the muons, then $^3/_4$ of the Ps atoms emerge as ortho states, on average, from each multiinteractive encounter. So $^1/_4$ of the original ortho-Ps atoms are converted to singlet para-Ps which annihilate too fast to observe (<1 ns). On this basis, $k_d = 4(8.15 \times 10^9\ M^{-1}\ s^{-1}) = 3.3 \times 10^{10}\ M^{-1}\ s^{-1}$ for the Ps encounter rate, which leaves k_d for Ps 1.9 times smaller than that of Mu. The latter may reflect Mu's better penetrating power through the negative ligands, for better spin−spin coupling with chromium's 3d electrons, due to its considerably lower polarizability than Ps.[6]

(b) Reaction of Mu with I_2 in Water, Methanol and *n*-Heptane. Table 1 shows there to be a ∼4-fold increase in k_M for reaction 5 on changing solvents from water to methanol and a ∼30-fold increase on changing from water to *n*-heptane. In water, this reaction is almost exactly half that found for H in acid solution,[18] yet it seems to be close to the diffusion-controlled limit, because its k_M fits k_d in eqs 1 and 2 with $R_S = 0.33$ nm (estimated van der Waals radius of I_2), $r_M = 0.05$ nm (Bohr radius), $R_M = 0.12$ nm (van der Waals radius of H), and $D_M \simeq 5 \times 10^{-9}$ m^2 s^{-1} (as before).

According to eq 1, any solvent dependence would stem from changes in diffusion coefficients, which, with the Stokes−Einstein law approximation, implicates the inverse solvent viscosity effect of eqs 2 and 3. But, in fact, there is only a 2.4-fold decrease in viscosity in going from water through methanol to *n*-heptane (see Table 1), so the simple form of these equations does not account for the observed changes in rates. An activation barrier to the reaction itself, or the changed solvation of the transition state, might have changed with solvent to account for this change in rate, but at the diffusion limit, the major energy barriers (those due to viscous flow in the solvents) are already entrenched in the solvents' viscosity coefficients.[4]

How does one explain k_M in methanol and *n*-heptane being much faster than expected from the bulk viscosity effect? Three possibilities deserve mention: (i) Perhaps substantially different interaction cross sections apply in less polar liquids compared to water, due to the different degree of solvation or clathration. An argument against this is that for water, where the solvation should be strongest because of its highly polar nature, we have just seen that the small unclathrated radii used (Bohr and van der Waals) fit eqs 1 and 2 well with $k_M \simeq k_d$. (ii) Perhaps the Stokes−Einstein relationship fails for Mu atoms in organic solvents, particularly hydrocarbons. Just on the basis of eq 1 and using the same values of R as above, then the sum of the diffusion constants to get $k_d = 6 \times 10^{11}$ M^{-1} s^{-1} must be ∼2 × 10^{-7} m^2 s^{-1}. Almost all of this will correspond to D_M, which means that Mu is extraordinarily mobile in heptane. Nonclassical behaviour would be clearly indicated. (iii) Following on from this last point, perhaps the true quantum character of the superlight Mu atom manifests itself in motion which is strongly augmented by quantum mechanical tunneling, especially in hydrocarbon solutions. As this is not the case in water and is of marginal significance in methanol, which still has significant hydrogen bonding as a relatively high dielectric polar alcohol, we suggest that tunneling is efficient only in nonpolar media like hydrocarbons. Only there is Mu unencumbered by solvation and able to truly behave as a quantum particle of very small mass (0.114 amu).

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(20) There is a 33% error on this because it is 6 ± 2, depending on the solute/solvent radii ratio (ref 4). k_B is Boltzmann's constant.