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Muonium Addition to Cyanides

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ABSTRACT

Muonium, the light radioactive isotope of hydrogen, was found to add
to the $C\equiv N$ bond of acetonitrile, cyanoacetate, cyanide and tetracyano-
cadmate(II) with room temperature rate constants, k_M, of 5.1×10^7,
7.7×10^7, 3.0×10^9, and 1.7×10^{10} (all $M^{-1}s^{-1}$), respectively. While
$Cd(CN)_4^{-2}$ is diffusion controlled with an activation energy of ~ 15 kJ/mole
the others appear to be activation controlled as with cyanoacetate's acti-
vation barrier of ~ 35 kJ/mole. Kinetic isotope effects range from 0.7
to 24.

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INTRODUCTION

Muonium (Mu) is an atom-like particle consisting of a positive muon nucleus (μ^+) with a bound electron. Though the mass of Mu is 1/9 that of H the reduced masses are nearly equal giving Mu an ionization potential and Bohr radius similar to H. Because the muon nucleus is a radioactive particle with an intrinsic lifetime of 2.2×10^{-6}s, muonium can be used as a probe to directly observe hydrogen-atom reactions. Due to the factor of 9 between the masses of Mu and H, Mu should be an excellent particle to study kinetic isotope effects.

Muonium is formed when an energetic muon (4.1 to 28 MeV) enters the target and abstracts an electron from the stopping medium into a bound state. The muon itself is a product of a positive pion (π^+) decay which in turn is a product of a proton capture by ^{9}Be. When the muon decays it ejects a positron which can be easily observed and counted using nuclear physics counting techniques. More detailed descriptions of the particles and techniques are available elsewhere[1,2].

Muonium was originally observed to form in gases[3]. Later, pure liquids such as water[4], alcohols[5,6], and certain hydrocarbons[7,8] were found to produce usable amounts of muonium with long enough lifetimes (up to 20μs in water[9]) to be useful as solvents to study a diverse number of solutes more reactive toward muonium. In water such reactions as addition, abstraction, oxidation-reduction, and spin conversion can be observed and measured[2]. When analogous hydrogen atom reactions have been measured the kinetic isotope effect can be calculated.

In a previous study we observed the addition reactions of Mu with several vinyl monomers[10] reporting isotope effects of 1.1 and 2.8 for acrylamide and acrylonitrile, respectively. In an effort to obtain a

better understanding of muonium addition reaction isotope effects we selected cyanide, both organic and inorganic forms, as the reactive solute. ESR studies[11,12] have established that both organic and inorganic cyanides undergo addition by H; therefore Mu should also add across the C≡N bond of cyanide.

EXPERIMENTAL

A. Chemicals. The cyanoacetic acid used was 98% pure while the acetonitrile was spectroscopic grade. Certified A.C.S. KCN was used directly and with reagent grade $3CdSO_4 \cdot 8H_2O$ in the preparation of aqueous $K_2Cd(CN)_4$ following the standard procedure[13]. However, since K^+ and $SO_4^=$ do not react appreciably with Mu^{14}, dilutions of the prepared $K_2Cd(CN)_4$ solution were used directly without first recrystalizing the cadmium complex as a further purification step. With an overall formation constant of $\beta_4 = 1.5 \times 10^{18}$, the tetrahedral $Cd(CN)_4^{-2}$ was the predominant structure. The water used throughout was de-ionized and doubly distilled from chromic acid and potassium permanganate solutions.

B. MSR: Muonium Spin Rotation Measurements. Under a transverse magnetic field the so-called 'triplet' Mu (both particle spins parallel) has a precession frequency of 1.39 MHz/G while the free muon and other diamagnetic muonic species have a precession frequency of 13.6 kHz/G. It is, therefore, relatively easy to distinguish Mu from other muonic species in solution. When the muon decays the decay positron is ejected in the direction of the muon spin. The data is collected in a muon lifetime histogram with the muonium precession signal superimposed on the muon signal. Figure 1(a) shows a typical data histogram for water. These histograms are computer analyzed using a floating parameter χ^2-minimization program (MINUIT) to fit Eq. (1).

$$N(t) = N_0\exp(-t/\tau_\mu)[1+A_D\cos(\omega_Dt+\phi_D)+A_M\exp(-\lambda t)\cos(\omega_Mt-\phi_M)]+BG \ , \qquad (1)$$

where $N(t)$ is the signal amplitude at time t, N_0 a normalization factor, τ_μ is the muon lifetime, A_D and A_M are the diamagnetic muon and muonium signal amplitudes, ω_D and ω_M their precession frequencies, ϕ_D and ϕ_M their initial phases, λ is the muonium decay constant, and BG is the background count rate. This decay constant is a measure of the damping of the Mu precession signal as Mu reacts with the selected concentration of solute. Having obtained values for λ for several concentrations of solute, [S], the Mu bimolecular rate constant, k_M, can be calculated from

$$\lambda = \lambda_0 + k_M[S] \ , \qquad (2)$$

where λ_0 is the observed decay constant for the pure solvent ($\lambda_0 = 2.4\pm0.6)\times10^5s^{-1}$ at TRIUMF[14,15]. The slope of the best straight line in a plot of λ vs. [S] is taken as k_M.

To obtain these data a 4.1 MeV muon beam from the M20 channel at TRIUMF (Tri University Meson Facility in Vancouver) was made to strike a shallow Teflon cell (with thin mylar windows) containing approximately 80 ml of sample solution. Target solutions were bubbled with high purity He before and during the experiment to remove dissolved oxygen. Water prebubblers were used to wet the gas and in the case of acetonitrile the prebubbler contained a portion of the working solution to minimize loss of solute through volatilization. Magnetic field coils, held trans-verse to the beam and centered on the target provided an external field of 8G to give a Mu precession frequency of 11.1 MHz. A schematic of the experimental set up is given in Fig. 2. The temperature dependence studies of cyanoacetate and tetracyanocadmate(II) were done in a simi-lar manner using a copper-backed temperature cell as described elsewhere[15].

RESULTS

Table I lists the solutes studied, their concentrations, decay constants (λ), and calculated rate constants (k_M). With two separate sets of positron detectors, left and right, each particular experiment yields two data histograms and hence two decay constants. The decay constants listed in Table I are the average of the separate left and right values obtained for each solute concentration. Statistically the errors on k_M values average $\pm10\%$, but because MSR measurements are subject to experimental irreproducibilities (from beam structure and electronics to target concentrations and geometries) a more realistic error of ⁺25% is reported[15].

From collision theory the frequency factor, B, in the modified Arrhenius equation [Eq. (3)] has a temperature

$$k = B(T^{1/2})\exp(-Ea/RT) \tag{3}$$

dependence of $T^{1/2}$. Therefore, in determining the activation energies and frequency factors for the reactions of Mu with cyanoacetate and tetracyanocadmate(II) $\ln(k_M/T^{1/2})$ was plotted against 1/T (see Fig. 3) to fit Eq. (4). The activation energy for cyanoacetate was

$$\ln(k_M/T^{1/2}) = \ln B - E_a/RT \tag{4}$$

found to be 35 ± 2 kJ/mole and that for the cadmium cyanide complex to be 15 ± 2 kJ/mole. This latter value, being close to the diffusion energy of water, suggests a diffusion-controlled reaction. However, because water structure and diffusion energy vary with temperature, it is necessary to examine the effect of viscosity on the rate constant as demonstrated by Lazzarini[16]. From Smoluchowski's equation below, where κ is the Boltzman constant, T is absolute temperature, n is viscosity, and r_A and r_B are the effective radii of the reacting species, it can

be seen that for a diffusion-controlled process the plot of k/T vs. $1/\eta$ should be a straight line.

$$k = \frac{\kappa T}{3\eta} \times \frac{(r_A + r_B)^2}{r_A \, r_B} \; . \tag{5}$$

Figure 4 shows such a straight line for the observed muonium rate data for tetracyanocadmate(II). Table II lists the parameters used in Figs. 3 and 4 as well as the calculated activation energies, E_a, and frequency factors, B. Table III lists the room temperature rate constants for the Mu and H reactions with the four cyanides and the calculated kinetic isotope effects, k_M/k_H. Also listed here are the k_M blank values for acetic acid and $CdSO_4$[17] and previously examined hexacyanoferrate(II)[18].

The earlier esr studies[11,12] reported that the hydrogen-atom radicals in cyanides were weak and broad in nature with very large coupling constants, $\alpha_H \sim 80G$ for cyanoacetate and acetonitrile. In an attempt to observe the muonium containing radical product for the Mu addition to acetonitrile we examined the neat solute at a field of 3 kG. No radical frequencies were observed in the FFT (Fast Fourier Transform) spectra of the data. However, it is likely that the resolution and range of the current experimental equipment is incapable of observing weak radical frequencies. The expected muonium hyperfine coupling constant, α_μ, is >710 MHz.

DISCUSSION

Unlike the vinyl monomers[10], which reacted with Mu at or near the diffusion-controlled limit of $2 \times 10^{10} M^{-1} s^{-1}$, the cyanides studied give rate constants ranging from $5.1 \times 10^7 M^{-1} s^{-1}$ to $1.7 \times 10^{10} M^{-1} s^{-1}$ (see Table I). Because the C≡N bond system is stronger than the C=C double bond of the monomers, with more electron density to shield the nucleophilic Mu from the target C atom, we expected the cyanide rate constants

to be smaller than those for the monomers. The range of these cyanide rate constants suggested that for the organic nitriles and cyanide the reaction is activation-controlled while the $Cd(CN)_4^{-2}$ reaction is diffusion-controlled. The activation energies for cyanoacetate and $Cd(CN)_4^{-2}$ were found to be 35 kJ/mole and 15 kJ/mole, respectively. The latter, being close to the diffusion energy of water, indicated diffusion-control and this was confirmed by the straight line plot of k_M/T vs. $1/\eta$ in Fig. 4. Assuming that acetonitrile and cyanide are similar to cyano-acetate in their activation energy barriers, why does the tetracyano-cadmate complex exhibit diffusion-control and not the others? One possible explanation is that because of its larger size and the fixed proximity of available cyanides in the complex the cage effect increases the collision and reaction probability for each Mu encounter. Another possibility is that the cadmium complex stabilizes the radical product to a much higher degree than the other cyanide reactants. The complex could be undergoing a number of different Mu reactions, but the isotope effect for abstractions is usually 10^{-2} and the standard reduction poten-tial for $Cd(CN)_4^{-2} + 2e^- \rightarrow Cd + 4CN^-$ is -1.09 V. This fast reaction of Mu with $Cd(CN)_4^{-2}$ seems peculiar to this complex in that no such reaction rate was observed for hexacyanoferrate(II) listed in Table III[18]. Further examination of transition metal cyanide complexes for which there are hydrogen atom reaction rate constants is needed.

From the data in Table III it can be seen that the organic nitriles react with Mu in the same order as they do with H, only somewhat faster with Mu. The inorganic cyanides, on the other hand, appear to be reversed in their reaction order. However, with the k_H of $Cd(CN)_4^{-2}$ reported only as $>2.4 \times 10^9 M^{-1}s^{-1}$ it is possible that the H-atom and Mu reactivi-ties of these two reactants do indeed follow the same trend.

Also listed in Table III are the kinetic isotope effects, k_M/k_H, for the studied reactants. The inorganic cyanides as aqueous CN^- and $Cd(CN)_4^{-2}$ show isotope effects of 0.7 and <7, respectively. These data (especially if k_M/k_H is truly ~1 for $Cd(CN)_4^{-2}$) tend to support the idea that addition reactions, being primarily electronic in nature, should have little if any mass effect; as exemplified by the isotope effects of 1.1, 2.8, and 1.4 for acrylamide, acrylonitrile, and maleic acid, respectively[10,15]. On the other hand, both the organic nitriles react much faster with Mu than with H giving isotope effects of 24 for cyanoacetate and 19 for acetonitrile. The only other addition reaction to date showing a similar isotope effect, $k_M/k_H = 40 \pm 10$, is that of acetone in water[5]. These data, rather than clearing up the question of Mu addition isotope effects, point toward the need for more kinetic information; especially activation-controlled addition reactions with organic solutes.

ACKNOWLEDGEMENTS

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Table I. Reaction rate data for the addition of muonium to organ-
ic and inorganic cyanides.

Solute	[S]/mM	$\lambda/10^6 s^{-1}$ [a]	$k_M/M^{-1}s^{-1}$ [b]
Cyanoacetate	17.0	1.26	
$N\equiv CCH_2COO^-$	19.7	1.93	7.7×10^7
	25.2	2.70	
Acetonitrile	10.0	0.81	
$N\equiv CCH_3$	18.0	1.18	5.1×10^7
	24.0	1.29	
Cyanide	0.23	0.81	
$N\equiv C^-$	0.46	1.85	3.0×10^9
	0.69	2.40	
Tetracyanocadmate(II)	0.05	0.92	
$Cd(C\equiv N)_4^{-2}$	0.10	1.90	1.7×10^{10}
	0.21	3.18	
	0.30	5.96	

[a] Statistical errors on these decay constants are 10% or less.

[b] Realistic error on reported rate constants is ±25%.

Table II. Temperature and viscosity parameters for Mu addition to cyanoacetate and tetracyanocadmate(II).

Solute	T/°C	T/°K	$k_M/M^{-1}s^{-1}$	$\ln(k_M/T^{1/2})$	$(k_M/T)/M^{-1}s^{-1}K^{-1}$	$(1/\eta)/10^{-2}$ poises	$E_a/kJmole^{-1}$	$B/M^{-1}s^{-1}$
Cyanoacetate	0	273	6.7×10^7	14.62	0.25×10^6	0.56		
	23	296	7.7×10^7	15.31	0.26×10^6	1.07		
	62	335	5.4×10^8	17.20	1.62×10^6	2.21	$15 \cdot 2$	3.1×10^{11}
	80	353	1.6×10^9	18.25	4.65×10^6	2.82		
$Cd(CN)_4^{-2}$	0	273	1.0×10^{10}	20.22	0.37×10^8	0.56		
	23	296	1.7×10^{10}	20.71	0.57×10^8	1.07		
	71	344	3.8×10^{10}	21.44	1.11×10^8	2.51	$35 \cdot 2$	1.0×10^{13}
	80	353	5.6×10^{10}	21.82	1.59×10^8	2.82		

Table III. Muonium and hydrogen rate constants with calculated
kinetic isotope effects and some associated muonium rate constants.

Solute	$k_M/M^{-1}s^{-1}$	$k_H/M^{-1}s^{-1}$ [a]	k_M/k_H
Cyanoacetate	7.7×10^7	3.2×10^6	24
Acetonitrile	5.1×10^7	2.7×10^6	19
Cyanide	3.0×10^9	4.1×10^9	0.7
Tetracyanocadmate(II)	1.7×10^{10}	$>2.4 \times 10^9$	<7
Acetic acid	$\sim 3.8 \times 10^6$		
Cadmium(II)	8.5×10^5		
Hexacyanoferrate(II)	3×10^8		

[a]Hydrogen rate constants taken from ref. 19.

FIGURE LEGENDS

Fig. 1. Typical MSR histograms: (a) raw data for pure water in an 8G
field; (b) the data in (a) fitted to Eq. (1) with muon decay
and background subtracted out; (c) and (d) are the data for
0.23 mM and 0.46 mM CN⁻ fitted to Eq. (1) as in (b).

Fig. 2. Schematic diagram of the MSR experimental apparatus. A and B
are lead shielding and collimation for the muon beam. C is a
thin scintillator muon (start) counter. D represents the
shallow Teflon target in which the sample is bubbled contin-
uously with high purity He. E and E, separated by a carbon
absorber (F), represent one set of two positron telescopes
which provide a stop signal when a decay positron is emitted
in their direction. G indicates a set of Helmholtz coils which
provide a field perpendicular to the paper causing the muon to
precess in the plane of the paper.

Fig. 3. Modified Arrhenius plots of Eq. (4) for tetracyanocadmate(II)
(△) and cyanoacetate(O). Large error in temperature value at
85°C for the cadmium cyanide complex is due to thermocouple
failure during that experiment.

Fig. 4. Inverse viscosity plot showing diffusion-control for tetra-
cyanocadmate(II) (△) and nondiffusion-control for cyanoacetate
(O). Left vertical scale used for the cadmium complex data
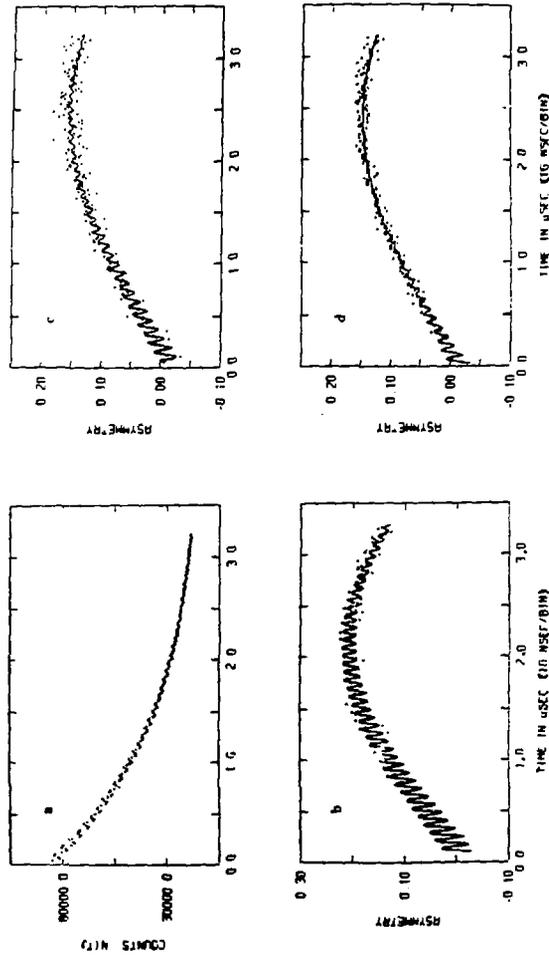while the right vertical scale is used for the cyanoacetate
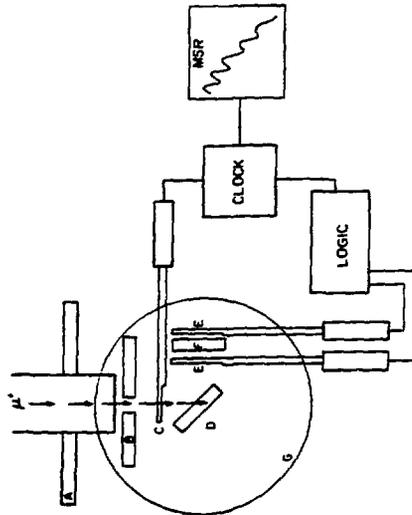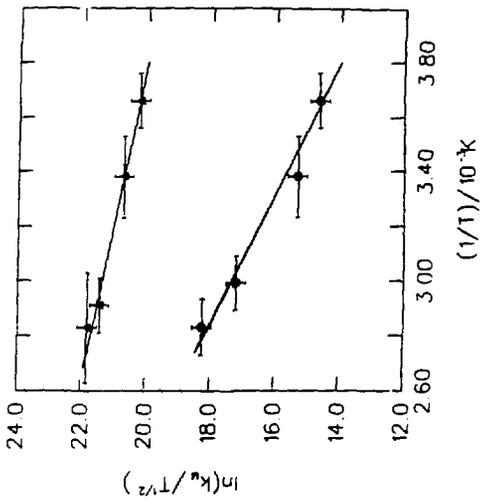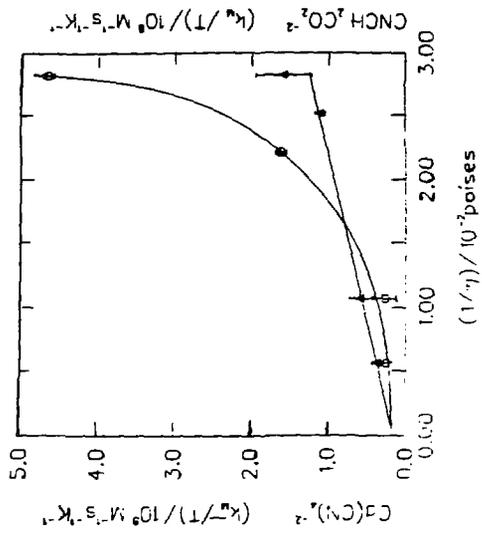data.

Fig. 1

COUNTS N(T)

ASYMMETRY

TIME IN uSEC (10 NSEC/BIN)

TIME IN uSEC (10 NSEC/BIN)

Fig. 2

MSR

CLOCK

LOGIC

μ^+

$\ln(k_u/T^{1/2})$

$(1/T)/10^{-3}$ K

Fig. 3

$CNCH_3CO_2^{-2}$

$(k_u/T)/10^8 \ M^{-1}s^{-1}K^{-1}$

$(1/\eta)/10^{-2}$ poises

$Cd(CN)_4^{-2}$

$(k_u/T)/10^9 \ M^{-1}s^{-1}K^{-1}$

Fig. 4