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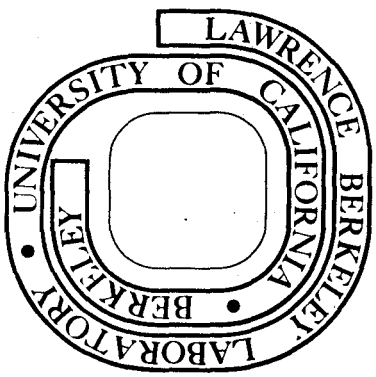

DISCLAIMER

Search for Selectivity Between Optical Isomers in Reactions of Polarized Positive Muons with Alanines and Octanols

One of the most intriguing problems in chemical evolution is the origin of optical asymmetry in biopolymers. The easiest way to state the problem is: why are proteins made almost exclusively of L-amino acid optical isomers and natural sugars of D-optical isomers?[1] That proteins must be made of only one kind of optical isomer is understandable on the basis of their need for precise three-dimensional conformations in order to perform their catalytic roles as enzymes. However, is it just a matter of chance, as suggested in Ref. 2, that our proteins are L-, or is there (was there) some asymmetric agent on our planet that made the protein L-configuration the one upon which life is based?

One possible "non-chance" explanation is the slight degree of circularly- and elliptically-polarized light in sunlight that is reflected and/or refracted in the Earth's magnetic field.[3] Laboratory experiments have indeed shown that circularly polarized light causes unequal decompositions of optical isomers[4]. In light-mediated reactions, it also causes the appearance of optical activity (excess of one optical isomer) in products obtained from optically-inactive starting materials[5,6]. It is thus possible that a slight excess (never actually measured) of right-circularly polarized light in reflected sunlight could produce overall optical asymmetries. However, because of the large intensities of circularly polarized light needed to produce detectable optical asymmetries in laboratory experiments, this hypothesis has been seriously questioned as an explanation for the origin of optical asymmetry in biological molecules[7].

A second possible "non-chance" explanation invokes spin-polarized beta particles, and their associated Bremsstrahlung, that are emitted by certain natural radioactive nuclides[8]. One report claims that in aqueous solution D-tyrosine is decomposed by ^{90}Sr betas faster than L-tyrosine[9]. However, this report has been seriously questioned by later papers[10,11], and must be considered as quite unsubstantiated.

These are all fascinating and unresolved questions. This paper is concerned with a further, and heretofore untried, search for optical selectivity in a direct interaction of a well understood agent with organic molecules--the polarized muon. Longitudinally polarized muon beams, both positive (μ^+) and negative (μ^-), have been produced from decaying pions (see later discussion) for some time now[12,13]. The degree of polarization is large, typically 80% or better. As far as we are aware, this is a higher degree of polarization than that of any particles yet used in the search for selectivity of interactions with optical isomers. Since polarized muons are known components of cosmic rays[14], a selective interaction, possibly leading to selective destruction of one optical isomer, might provide another "non-chance" explanation for the particular appearance of L-amino acids and D-sugars in living cells. Moreover, observation of such an interaction would, by analogy, support the above-mentioned concept of selective decomposition by beta particles.

The interactions of positive and negative muons with matter proceed by very different mechanisms--both of which, because of the high inherent polarization of the muon, might lead to optically selective interactions. Negative muons are initially captured into high-lying muonic orbits[12,15],

where, conceivably, the spin of the μ^- might be sensitive to the valence electron distribution of the molecule. Positive muons, upon slowing down, form the neutral atom "muonium" (μ^+,e^-) which, except for its mass, is analogous to the hydrogen atom[16]. Because of the high degree of polarization of the μ^+ "nucleus", the formation of the muonium atom and/or its subsequent chemical reactions might also be sensitive to optical isomers. This latter supposition is the subject of the present paper. However, as reported below, we have been unable to detect any "optical selectivity" in the interactions of positive muons with either (1) solid D- and L-alanine or (2) liquid D- and L-2-octanol.

The μ^+ beam of the Berkeley 184-inch cyclotron[13] was used in these experiments. The quantity actually measured was the "residual polarization" of muons stopped in the various substances. Although the muons enter the "target" with a well-defined spin polarization in a direction opposite to their momentum (longitudinal polarization), their polarization after stopping is dramatically dependent upon the chemical properties of the medium in which they come to rest, as will be explained later.

The spin polarization of the muons is easily detected through their decay products: the muon decays via

$$\mu^+ \rightarrow e^+ \nu_e \bar{\nu}_u$$

with a mean lifetime of 2.2 μsec; the positron (e^+) from the decay is, on the average, about twice as likely to be emitted in the direction of the μ^+ spin as in the opposite direction[12,13,17]. An ensemble of polarized positive muons thus broadcasts its polarization in a shower of fast (up to 50 Mev) positrons. By detecting these positrons in scintillation counters, we monitor the magnitude of the μ^+ polarization. The neutrino (ν_e) and

antineutrino ($\bar{\nu}_\mu$) go undetected, as usual.

The problem of detecting positrons in many different directions at once is avoided by letting the muon's magnetic moment do the work for us: a magnetic field is applied perpendicular to the muon polarization, causing the muon spin to precess at the μ^+ Larmor frequency,

$$\omega_\mu = \gamma_\mu B, \text{ where } \frac{\gamma_\mu}{2\pi} = 13.55 \text{ MHz/kG}.$$

A single counter telescope in the plane of precession is most likely to detect a positron if the muon decays when its spin points towards the telescope; thus the e^+ detection probability in that telescope will rise and fall as the muon polarization sweeps past it[13].

It is not possible to place the entire muon ensemble in the sample at once and observe the actual positron counting rate as a function of time; instead, we perform an equivalent experiment using one muon at a time. A digital clock is started when a μ^+ enters the target and stopped when the e^+ is detected. The time intervals measured in this way are binned into a histogram such as that shown in Fig. 1. This time histogram [N(t)], which is equivalent to the positron counting probability as a function of the time after the muon stops, is fitted to the functional form

$$N(t) = N_0 \left\{ e^{-t/\tau_\mu} \left[1 + A \exp(-t/T_2) \cos(\omega_\mu t + \phi) \right] + BG \right\},$$

where

N_0 = Normalization factor (counts/bin);

τ_μ = Mean muon lifetime (2.2 μsec);

A = Residual asymmetry;

T_2 = Transverse relaxation time;

ω_μ = Muon Larmor precession frequency;

ϕ = Apparent initial phase of the precession;

BG = Constant background (usually a few percent).

A maximum-likelihood fitting program extracts the best values for all of the parameters listed above, as well as an estimate of the uncertainty in the determination of each.

The extracted value of the asymmetry A is proportional to the residual polarization of the μ^+, P_{res}:

$$A = A_0 P_{res} .$$

The constant of proportionality A_0 is an empirical constant unrelated to the chemical properties of the medium, so that comparing the residual asymmetries in two media is the same as comparing their residual polarization values, as long as they have the same gross physical properties. The values of P_{res} obtained in the present experiment are given in Table 1. Since water has been thoroughly studied[18], the value of $P_{res}(H_2O) = 0.55 \pm 0.03$ from Ref. 18 is used to calibrate the results listed in Table 1. A more detailed technical description of the apparatus and experimental technique can be found in Refs. 13 and 18.

Each target consisted of about 500 g of the substance under study. The solid alanines ("A grade") were obtained fro... Calbiochem, La Jolla, Calif., and the liquid octanols from Norse Laboratories, Santa Barbara, Calif. All samples were used without further purification.

In most condensed media, any residual polarization observed through muon precession is due to chemical reactions of positive muons with molecules of the medium; in the absence of such reactions, all the muon polarization is lost within a few nanoseconds via the so-called "muonium mechanism". This depolarization mechanism arises from the tendency of the μ^+ to capture an electron in the process of slowing down in the medium. In the resulting muonium atom, (Mu) the contact hyperfine interaction

between μ^+ and e^- magnetic moments couples the two spins together so as to reverse the μ^+ spin within $\sim 10^{-10}$ sec. Fast precession of muonium in the external magnetic field conspires with this hyperfine coupling to completely depolarize the μ^+ in muonium within $\sim 10^{-9}$ sec. The only way a muon can be spared this fate is if the Mu atom which it forms reacts chemically with a molecule of the medium to incorporate the μ^+ into a diamagnetic molecule. The chemical behavior of the Mu atom is perfectly analogous to that of the H atom, except that the muon is lighter than the proton by a factor of about 9.

For a rigorous theoretical description of the muonium mechanism of μ^+ depolarization, the reader should consult Refs. 18 and 19. Briefly, there are two sorts of chemical reactions of Mu which prevent complete depolarization of the μ^+: (1) "normal" thermal reactions, which occur after the Mu atom has thermalized and started depolarizing the μ^+; and (2) epithermal or "hot atom" reactions, which occur while the Mu atom is still slowing down, long before any depolarization has taken place. The latter reactions are assumed to be important in the energy region from $\sim$ 10 eV down to thermal energies, and are usually the dominant channel for reactions of Mu in all but the most reactive substances. In water or methanol, for instance, the residual polarization is believed to be due exclusively to "hot atom" reactions[18]. Large hot atom fractions have also been reported in liquid hydrocarbons[18]. Indeed, with particular reference to 2-octanol, it was our hope that the hot atom reaction probability would be particularly sensitive to the hydroxyl group which is located on the asymmetric carbon atom.

As can be seen from Table 1, the residual polarization in a 0.67 M solution of racemic alanines in water is the same, within experimental

uncertainties, as that observed in pure water. We conclude that there is little, if any, thermal reaction of Mu with alanine molecules, at least in solution[18]. Taken with the observation that Mu has a large epithermal reaction probability in most organic substances, this suggests that the residual polarization in the solid alanines is due primarily to hot atom reactions of muonium. The same assumption can be made for the octanols, on the somewhat weaker grounds that Mu has a large, purely epithermal reaction probability with methanol.

The data in Table 1 show that there is no significant difference between the reaction probabilities of polarized Mu atoms with enantiomers of alanine and 2-octanol. The errors given are derived from the fitting procedure previously referred to. While it is statistically possible that a few percent difference could be realized ($\Delta A/A = 0.0 \pm 0.05$ for alanine and $\Delta A/A = 0.0 \pm 0.03$ for 2-octanol), this difference could only be accurately determined on the basis of many more measurements. Remembering that it is the μ^+ nucleus of the Mu atom which is polarized (negligible polarization is transmitted to the electron in the time of $\sim 10^{-12}$ sec which muonium takes to thermalize), it is perhaps not surprising, in retrospect, that the hot atom reactions are optically indiscriminate.

A more sensitive test of optical selectivity may be possible with polarized μ^+ if muonium precession can be observed directly in these substances. Apparently, recent results using positrons[20] suggest that electrons "picked off" by muons to form Mu atoms might be expected to have an optically-influenced polarization. This effect would be reflected in first order in the amplitude of muonium precession signals. The feasibility of such studies is now being considered.

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Table 1 Residual Muon Polarization in Various Media

Target	Residual Asymmetry (A)	Residual Polarization* (P_{res})
Distilled water	0.153 ± 0.003	0.55 ± 0.03 (def.)*
0.67 M racemic alanine in water	0.151 ± 0.004	0.54 ± 0.03
Solid L-alanine	0.089 ± 0.003	0.32 ± 0.02
Solid D-alanine	0.089 ± 0.003	0.32 ± 0.02
Liquid L-2-octanol	0.140 ± 0.003	0.50 ± 0.03
Liquid D-2-octanol	0.140 ± 0.002	0.50 ± 0.03

* Residual polarization derived from $P_{res} = A/A_o$, where $A_o = 0.278 \pm 0.016$ is calculated by comparing $A(H_2O)$ with the independently determined residual polarization in water, $P_{res}(H_2O) = 0.55 \pm 0.03$ [18].

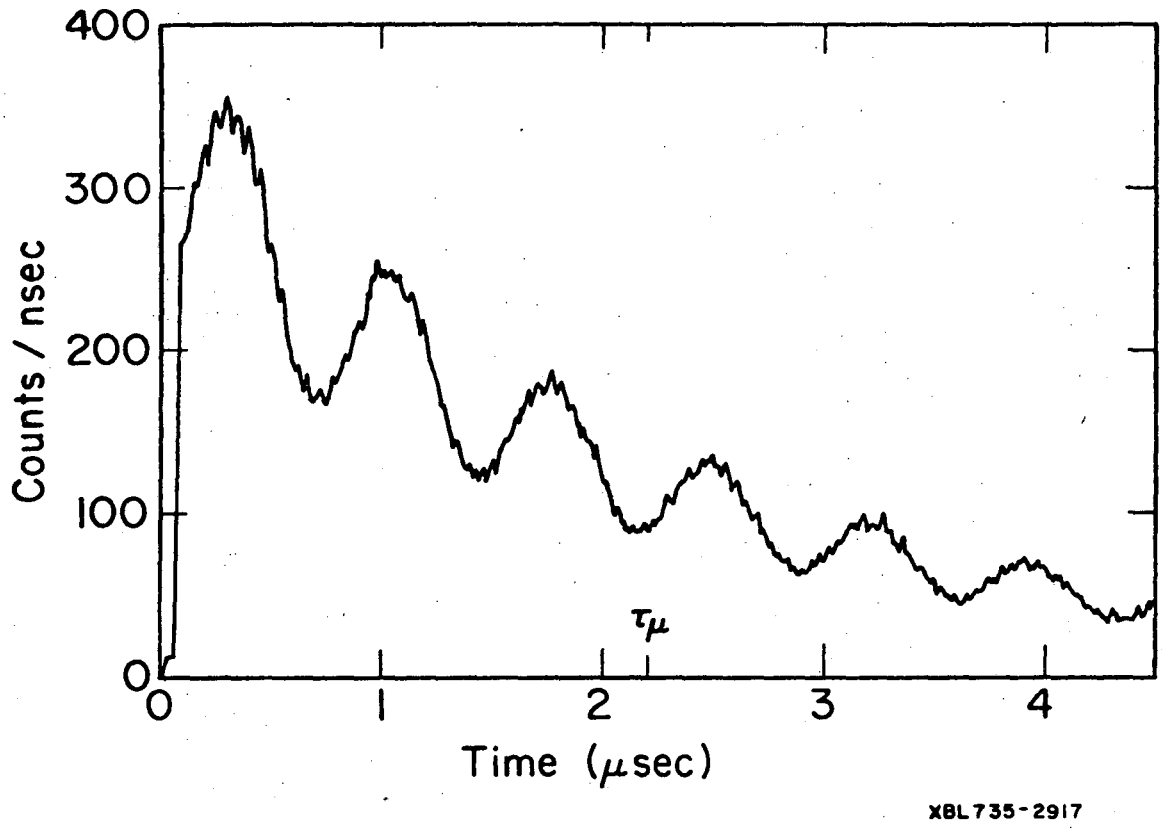

Fig. 1 Typical experimental time histogram showing μ^+ precession in 100 G external field. Data is collected into 10 nsec bins for graphical clarity; for fitting, 0.5 nsec bins were used.

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