

# Leptons in Chemistry

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Continuing reclassifications of "elementary particles" is the delight of high-energy physicists and the despair of most other physical scientists. The major classification at the moment is the division into "leptons" and "quarks". Of the three particles, three antiparticles, and six neutrinos that constitute the lepton family (see Table I), only the electron ( $e^-$ ) and the muon ( $\mu^-$ ) and their antiparticles ( $e^+$  and  $\mu^+$ ) have any chemical importance at present. The tauon ( $\tau$ ) has not yet been directly detected but apparently will have a mass about twice that of a proton and a lifetime of  $\sim 5 \times 10^{-13}$  s so it has no obvious special chemical interest. And the three generations of neutrinos are all too elusive and noninteracting for chemistry.

The stable lepton is the electron, the very cornerstone of chemistry, being its internuclear "binding" component and its "reactivity" component. But it will be discussed here only as a free species in solution or in association with other leptons. Electrons are probably the only stable particles of matter with nonzero mass and the most abundant. By contrast, the positron's existence in nature is extremely rare, because of the unequal particle/antiparticle distribution and the positron's annihilation by  $e^-$ .

Muons also occur extremely rarely, being mere transitory intermediates in the decay of cosmic pions (see Table I). However, they can be produced artificially from high-energy proton beams, via pions, and exist as  $\mu^+$ , which takes on a "nuclear" role (superlight proton)<sup>1</sup> or  $\mu^-$  with an "orbital" role (superheavy electron). It is through their radioactive decay, their characteristic magnetic moments and mass, and their initial spin polarization that muons find particular use as analogues of proton and electron properties.

Our involvement with leptons can be classified into three areas: (i) as high-energy particles, resulting from radioactive decay, which interact with the medium by radiation-chemical processes, (ii) as free charged particles, reacting as thermalized chemical species with the medium and its additives, and (iii) as neutral "atoms", after combining with other leptons.

## Leptons as Polarized Radiation Sources

The four leptons are each generated as high-energy ionizing radiations ( $\sim 10^6$  eV of kinetic energy) in the decay processes shown in column 5 of Table I. Yet none of these (even  $^{90}\text{Sr}$ -Y as a 2.2-MeV  $\beta^-$  source) is used much nowadays for general radiolysis purposes because they have been usurped by machine-made beams. Linear and van de Graaf accelerators have the enor-

mous advantage of providing very short, high flux pulses of particles for in situ study of radiation-produced transient species by the various detection methods of pulse radiolysis.<sup>2</sup> It is only in specialized areas, such as the need for spin-polarized particle beams or circularly polarized  $\gamma$ -radiation, that these radioactive sources of leptons hold a clear advantage. The decay schemes (column 5, Table I) leading to leptons are governed by the "weak interaction", with its breakdown of the parity-invariance principle as a result of the specific helicities of neutrinos that are produced concurrently.<sup>3</sup> These decays give rise to a predominance of left-handed (negative polarization)  $e^-$  and  $\mu^+$  beams and right-handed  $e^+$  and  $\mu^-$  beams, in the parent particle's frame of reference.<sup>4</sup>

Such spin-polarized particles have been utilized in two kinds of chemical studies. The first involves a test of the question posed by Vester and Ulbricht:<sup>5</sup> Is there a connection between the specific chirality (handedness) of the molecular constituents of life and the inherent asymmetry of naturally occurring leptons? Although originally framed with circularly polarized bremsstrahlung as the source (polarized  $\beta$ -particles  $\rightarrow$  circularly polarized bremsstrahlung  $\rightarrow$  stereoselective photochemical resolution), which was shown to be too small to appear in a laboratory test,<sup>6</sup> the question soon became: Could the polarization of the particles themselves be responsible for the fact that biological matter utilizes only L-amino acids and D-sugars and not their mirror images? If one could show in the laboratory that spin-polarized electrons or muons show a *slight* preferential decomposition of the *unnatural* stereoisomer of a racemic mixture, then the connection would be established as feasible—because even a miniscule initial preponderance of one enantiomer at the prebiotic stage would be expected to lead to complete optical purity, by the autocatalytic and self-replicative processes of biology.

Several such tests have been made.<sup>7</sup> Electrons in the form of  $^{40}\text{K}$   $\beta$ -particles constitute some 25% of the high (>5 eV) energy sources to which primitive earth was

(1) (a) V. G. Nosov and I. V. Yakovleva, *Nucl. Phys.*, **68**, 609 (1965); (b) J. H. Brewer and K. M. Crowe, *Annu. Rev. Nucl. Part. Sci.*, **28**, 239 (1978); (c) see *Hyperfine Interact.* **8** (1981) and 17-19 (1984).

(2) (a) M. S. Matheson and L. M. Dorfman, "Pulse Radiolysis", M.I.T. Press, Cambridge, MA, 1969; (b) J. W. Hunt *Adv. Radiat. Chem.*, **5**, 185; (1976); (c) see "The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis", J. H. Baxendale and F. Busi, Eds., Reidel Publishing Co., Dordrecht, the Netherlands, 1981; (d) S. C. Wallace and D. C. Walker, *J. Phys. Chem.*, **76**, 3780 (1972).

(3) T. D. Lee and C. N. Yang, *Phys. Rev.*, **104**, 254 (1956).

(4) (a) C. S. Wu, E. Amber, R. W. Hayward, D. D. Hopper, and R. P. Hudson, *Phys. Rev.*, **105**, 1413 (1957); (b) R. L. Garwin, L. M. Lederman, and M. Weinrich, *Phys. Rev.*, **105**, 1415 (1957).

(5) (a) F. Vester, Seminar Yale University, 1957; see *J. Mol. Evol.* **4**, 1 (1974); (b) T. L. V. Ulbricht, *Q. Rev., Chem. Soc.*, **13**, 48 (1959).

(6) D. C. Walker, *Origins Life*, **7**, 383 (1976).

(7) (a) A. S. Garay, *Nature (London)* **219**, 338 (1968); (b) W. A. Bonner, in "Origin of Optical Activity in Nature", D. C. Walker, Ed., Elsevier, Amsterdam, 1979, p 5; (c) W. A. Bonner, N. E. Blair, and F. M. Dirbas, *Origins Life*, **11**, 119 (1981); (d) D. W. Gidley, A. Rich, J. Van house, and P. W. Zitzewitz, *Nature (London)*, **297**, 629 (1982).

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Table I  
Leptons and Some of Their Properties

lepton	mass ( $M_e$ )	charge	spin	formation from hadrons	intrinsic lifetime	decay
electron ( $e^-$ )	1	-	$1/2$	$n \rightarrow p^+ + e^- + \bar{\nu}_e$	$\infty$	$\{ e^+ + e^- \rightarrow 2\gamma$ (annihilation)
positron ( $e^+$ )	1	+	$1/2$	$p^+ \rightarrow n + e^+ + \nu_e$	$\infty$	
muon ( $\mu^-$ )	207	-	$1/2$	$\pi^+ \rightarrow \mu^- + \bar{\nu}_\mu$	$2.2 \times 10^{-6}$ s	$\mu^- \rightarrow e^- + \bar{\nu}_e + \nu_\mu$ $\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$
positive muon ( $\mu^+$ )	207	+	$1/2$	$\pi^+ \rightarrow \mu^+ + \nu_\mu$	$2.2 \times 10^{-6}$ s	
tauon ( $\tau^-$ )	$\sim 3500$	-	$1/2$	?	$\sim 5 \times 10^{-13}$ s	
positive tauon ( $\tau^+$ )	$\sim 3500$	+	$1/2$	?	$\sim 5 \times 10^{-13}$ s	
neutrinos ( $\nu_e, \nu_\mu, \nu_\tau$ )	$\approx 0$	0	$1/2$	(see above)		
antineutrinos ( $\bar{\nu}_e, \bar{\nu}_\mu, \bar{\nu}_\tau$ )	$\approx 0$	0	$1/2$	(see above)		

<sup>a</sup> From a proton within a neutron-deficient nucleus.

subject<sup>8</sup> and are therefore of particular interest, but muons of cosmic origin and positrons from minerals make finite contributions too. There have also been studies of a possible preferred stereoselective reactivity of chiral solvated electrons toward the *R* or *S* enantiomers of a chiral solute<sup>9</sup> and of the formation probability of muonium from polarized muons<sup>10</sup> and positronium from <sup>22</sup>Na  $\beta^+$ -particles<sup>11</sup> in chiral media. Most of these results were negative and even the positive ones were tentative, so a connection has not been established.

These tests, for one reason or another, were not particularly sensitive. Most of them involved irradiating a racemic mixture in order to search for any induced net chirality.<sup>7</sup> Yet 80–90% of the radiation chemical effects of a high-energy particle are induced by secondary electrons ( $\delta$  rays) that do not carry the polarization of the primary particle. Consequently, there was a potential 5–10-fold “dilution” factor. This problem was averted<sup>12</sup> by using a 50–50% mixture of pure *D* and *L* crystals (rather than a racemic mixture at the molecular level) where the crystal size exceeded the  $\delta$ -ray range, so that each time a primary interaction occurred with the polarized particle, its entire effect would be deposited in that same enantiomer. So far the results have indicated that any overall stereoselectivity that exists is beyond the accuracy of the measurements (i.e., <2%),<sup>12</sup> although the best polarized source ( $\mu^+$ ) has still not reached the necessary flux for an ideal test. That an electron or muon of negative polarization interacts differently with the *D* compared to the *L* enantiomer is not questioned, nor that “electro-weak” theory has established a different energy level with respect to the two enantiomers.<sup>13</sup> The only question is whether these differences are large enough to cause observable chemical or biological effects.

A second way polarized leptons are used in chemistry is in spin-polarized beams of muons for the  $\mu$ SR techniques (muon spin rotation, relaxation, or resonance).<sup>1</sup> These techniques are based on the fact that as a muon decays (see Table I) the emitted electron is given off

preferentially along the instantaneous muon spin direction, another consequence of the “weak interaction”<sup>4b</sup> The  $\mu$ SR techniques are able to monitor the muon’s spin vector at its moment of decay through the use of electron telescopes. When the sample in which an originally polarized muon beam comes to rest is in a transverse magnetic field, the muon’s spin precesses. A lifetime histogram of the muon has the precession signals imposed upon it. These signals are analyzed by computer fitting to a multiparameter equation that gives amplitudes (yields), frequencies (identifying the magnetic state), and relaxations (providing rate constant data).<sup>14,15</sup>

These  $\mu$ SR studies require polarized muons in order that they precess coherently. Three distinct chemical states of  $\mu^+$  are regularly studied: free muonium atoms, muon-containing free radicals, and diamagnetic species. The  $\mu^-$  lepton can be studied by equivalent  $\mu^-$ SR techniques, although the polarization is much smaller due to muonic atom formation.

### Free Leptons as Chemical Species

Of the four particles,  $e^-$  is the most important as a free thermalized ionic species, because it is liberated from the medium by ionization and is inherently stable. The others occur fleetingly at the very end of the tracks in which they were injected as high-energy particles. Bare positrons have subnanosecond lifetimes due to quasi-free annihilation<sup>16</sup> and have been seen only in association with anions as in  $e^+F^-(PsF)$ . Negative muons do not even reach thermal energy before being caught in high Rydberg states of the molecules or atoms of the medium. Bare or solvated  $\mu^+$  ions undoubtedly do survive for their full 2- $\mu$ s lifetime in certain media, such as metals, noble gases, and possibly strongly-dipolar aprotic liquids. However, free  $\mu^+$  cannot be distinguished from a muon incorporated in a diamagnetic molecule such as  $MuH$  or  $MuOH$  until “chemical shifts” of 10 ppm or so are available in  $\mu$ SR. Electric field gradients at 20  $kV\ cm^{-1}$  were found to have no effect on diamagnetic signals in nonpolar liquids like hexane,<sup>17</sup> which suggests that free neutralization, if it occurs, does not take place on the  $\mu$ SR time scale of  $10^{-9}$ – $10^{-5}$  s.

Free electrons are liberated by ionization of the molecules of a medium by high-energy radiations, or by photolysis, electrolysis, or alkali-metal reduction.<sup>18</sup>

(8) M. Calvin, “Molecule Evolution”, Oxford University Press, London, 1969.

(9) M. M. Ulrich and D. C. Walker, *Nature (London)*, **258**, 418 (1975).

(10) (a) R. M. Lemmon, K. M. Crowe, F. N. Gygas, R. F. Johnson, B. D. Patterson, J. H. Brewer, and D. G. Fleming, *Nature (London)*, **252**, 692 (1974); (b) D. P. Spencer, D. G. Fleming, J. H. Brewer, and R. J. Mikula in “Origins of Optical Activity in Nature”, D. C. Walker, Ed., Elsevier, Amsterdam, 1979, p 87.

(11) (a) A. S. Garay, L. Keszthelyi, I. Demeter, and P. Hrasco, *Chem. Phys. Lett.*, **23**, 549 (1973); (b) Y. C. Jean and H. J. Ache in “Origins of Optical Activity in Nature”, D. C. Walker, Ed., Elsevier, Amsterdam, 1979, p 67.

(12) T. Q. Nguyen, L. D. Hayward, and D. C. Walker, unpublished data.

(13) (a) D. W. Rein, R. A. Hegstrom, and P. G. H. Sanders in “Origins of Optical Activity in Nature”, D. C. Walker, Ed., Elsevier, Amsterdam, 1979, p 21. (b) T. P. Emmons, J. M. Reeves, and E. N. Fortson, *Phys. Rev. Lett.*, **52**, 86 (1984); (c) S. F. Mason, *Nature (London)*, **311**, 19 (1984).

(14) D. C. Walker, “Muon and Muonium Chemistry”, Cambridge University Press, London 1983.

(15) D. C. Walker, *J. Phys. Chem.*, **85**, 3960 (1981).

(16) V. I. Goldanskii, *Acc. Chem. Res.*, **10**, 153 (1977).

(17) Y. Ito, B. W. Ng, Y. C. Jean, and D. C. Walker, *Hyperfine Interact.*, **8**, 355 (1981).

(18) (a) E. J. Hart, *Acc. Chem. Res.*, **2**, 161 (1969); (b) E. J. Hart and M. Anbar, “The Hydrated Electron”, Wiley-Interscience, New York, 1970; (c) D. C. Walker, *Q. Rev., Chem. Soc.*, **21**, 79 (1967).

**Table II**  
**Comparison of Reaction Rate Constants for Hydrated Electrons ( $k_e$ ), Positronium ( $k_p$ ), Muonium ( $k_M$ ), and Hydrogen ( $k_H$ ) in Dilute Aqueous Solution at  $\sim 295$  K: A Small Selection Demonstrating Several Reaction Types, Presented as Ratios, with  $k_M$  Given<sup>a</sup>**

rxn type	solute	$k_M/k_e$	$k_M/k_p$	$k_M/k_H$	$k_M/(M^{-1} s^{-1})$
reduction	MnO <sub>4</sub> <sup>-</sup>	1	1	1.0	$2.5 \times 10^{10}$
	Ag <sup>+</sup>	0.5	$>10^3$	0.5	$1.6 \times 10^{10}$
	Tl <sup>+</sup>	0.03	$>8$	7	$8 \times 10^8$
addition	acrylamide	1	1	1	$1.9 \times 10^{10}$
	<i>p</i> -nitrophenol	0.3	1	2.7	$8 \times 10^9$
abstraction	phenol	400	$>70$	3.5	$7 \times 10^9$
	methanol	$>3$		0.01	$3 \times 10^4$
acid-base	HCO <sub>2</sub> <sup>-</sup>	800		0.03	$8 \times 10^6$
	OH <sup>-</sup>	$>10^3$		1.0	$1.7 \times 10^7$
others	NO <sub>3</sub> <sup>-</sup>	0.15		155	$1.5 \times 10^9$
	I <sub>2</sub>	1	1	1	$1.7 \times 10^{10}$
	O <sub>2</sub>	1	1	2	$2.4 \times 10^{10}$

<sup>a</sup> Data taken from ref 14. Some indication of the probable error is shown, but original data should be consulted.

They form a variety of localized states, from quasi-free to fully relaxed, depending on the medium's polarity, solvating power, and trapping ability. In a strongly polar fluid like water, the electron rapidly ( $<10^{-12}$  s)<sup>19</sup> reaches the fully equilibrated solvated state ( $e_{aq}^-$ ) where it takes on kinetic and thermodynamic characteristics of an ordinary chemical species.<sup>18</sup> Most solvated or trapped electrons show broad, structureless optical absorption bands in the red (710 nm for H<sub>2</sub>O) or near-infrared (1750 nm for NH<sub>3</sub>) which are largely resistant to bleaching or hole burning. The energy of the band maxima reflect the electron-well depth and are much better measures of the solvating power of a solvent for negative ions than is the dielectric constant. This was quite evident from the infrared band ( $>1500$  nm) found for the highly polar aprotic solvent dimethyl sulfoxide.<sup>20</sup> Pulse radiolysis studies based on optical absorption, paramagnetism, and conductivity have made the hydrated electron into the most exhaustively studied reactive chemical species, with over 400 reaction rate constants known. A handful of these are presented in Table II for comparison with positronium, muonium, and hydrogen. H and  $e_{aq}^-$  constitute a conjugate acid-base pair, where reaction of H can give a different product to that obtained from  $e_{aq}^-$  followed by protonation.<sup>18b</sup> A great deal is known about electrons localized in other media, and their physical properties continue to intrigue theorists and experimentalists alike.<sup>21</sup> Perfectly stable solutions of solvated electrons in liquid ammonia can be made,<sup>22</sup> this being impossible in water because of the bimolecular reaction to form H<sub>2</sub>.

### Atoms Composed of Leptons

The predictions of the Bohr atomic model of one-electron systems in eq 1 show that the mean orbital radius of principal quantum number  $n$  is inversely proportional to the reduced mass,  $m^*$ , while its binding energy is directly proportional to that mass. The ap-

$$r_n \propto n^2/Zm^* \text{ and } E_n \propto Z^2m^*/n^2 \quad (1)$$

propriate quantities are given in Table III for the atoms of interest here. For tritium and hydrogen,  $m^*$  is seen to be essentially equal to the electron mass, and for muonium it is within 0.5% of the electron mass. Thus all three have nearly identical Bohr radii and ionization energies and differ only by virtue of their actual mass. So in the accepted chemical sense,<sup>15</sup> Mu is also an "isotope" of H, which provides a unique opportunity to study mass-dependent effects.

In the case of positronium (Ps), its constituent particles  $e^+$  and  $e^-$  are of equal mass, so they oscillate about their mutual center of mass, with twice the mean separation and half the ionization energy of Mu, <sup>1</sup>H, and <sup>3</sup>H. This confers on Ps totally different chemical properties and it is not an isotope of H. Instead, its miniscule mass ( $1/900$ th) and large atomic volume (some 8 times) compared to <sup>1</sup>H provide it with a totally different set of quantum mechanical parameters for comparison purposes.

Muonic hydrogen ( $p^+\mu^-$ ) is at the other extreme. Here the reduced mass is close to that of the muon with the result that the Bohr radius is 186 times less and the binding energy 186 times larger than those of Mu, <sup>1</sup>H, and <sup>3</sup>H. This extremely small tightly bound atom resembles a free neutron.

Muonic helium, on the other hand, has the properties of a heavy hydrogen isotope. This is because the ground-state orbital of  $\mu^-$  (1s) is so close to the <sup>4</sup>He<sup>2+</sup> nucleus that it merely reduces the effective nuclear charge by one unit. Consequently, the electron in its 1s orbital experiences a net nuclear charge of 1 rather than 2, and it behaves as an isotope of hydrogen with a mass equal to that of (<sup>4</sup>He +  $\mu$ ) = 4.11 amu. Furthermore, it has a spin- $1/2$  pseudonucleus with a magnetic moment equal to that of muonium;<sup>23</sup> therefore, <sup>4</sup>He<sup>2+</sup> $\mu^-e^-$  and Mu are superideal isotopes for comparison.

It is impractical with present muon fluxes to make an atom in which two muons replace two electrons to go to the Z-2 atom. Indeed, all species involving two rare particles can probably be ignored from a practical chemical point of view; and in any event, there does not seem to be a purely leptonic atom on the horizon to match the potential interest of Ps and Mu.  $\mu^-e^+$  is just antimuonium, and  $\mu^+\mu^-$  (mumuonium) can be anticipated to have mass, Bohr radius, and binding energy within the ranges already covered (see Table III).

In summary, Mu, <sup>1</sup>H, <sup>3</sup>H, and <sup>4</sup>He<sup>2+</sup> $\mu^-e^-$  constitute an isotope series, with masses of 0.11, 1, 3, and 4, respectively. Ps is unique and requires its own spot in the periodic table—indeed, its own column and row. The muonic atoms are of interest due to their formation probabilities and decay modes, explored further on.

### Positronium (Ps, $e^+e^-$ )

Positronium is the bound quantum state of a positron-electron pair, appearing as singlet (<sup>1</sup>S<sub>0</sub>, p-Ps) or triplet (<sup>3</sup>S<sub>1</sub>, o-Ps) in a 1:3 ratio. The spin-paired p-Ps undergoes spontaneous annihilation by emission of two 180°-correlated 0.51-MeV photons, with a mean lifetime of 0.125 ns, which is too short-lived to be of much chemical interest at present. The ortho species is re-

(19) J. M. Wiesenfeld and E. P. Ippen, *Chem. Phys. Lett.*, **73**, 47 (1980).

(20) D. C. Walker, N. V. Klassen, and H. A. Gillis, *Chem. Phys. Lett.*, **10**, 636 (1971).

(21) (a) D-F. Feng and L. Kevan, *Chem. Rev.*, **80**, 1 (1980); (b) B. Webster, *J. Phys. Chem.*, **84**, 1070 (1980); (c) G. R. Freeman, *Ann. Rev. Phys. Chem.*, **34**, 463 (1983); (d) T. R. Tuttle, S. Golden, S. Lwenje, and C. M. Stupak, *J. Phys. Chem.*, **88**, 3188 (1984).

(22) J. Belloni, private demonstration.

(23) (a) P. A. Souder, et al., *Phys. Rev. A*, **22**, 33 (1980); (b) H. Orth, *Hyperfine Interact.*, **17-19**, 829 (1983).

Table III  
Properties of Positronium, Muonium, and various Atomic Systems for Comparison

name	composition	$M_e$		Bohr radius/pm	ionization (or binding) energy/eV
		actual mass	reduced mass		
positronium	$e^+e^-$	2	0.5000	106	6.8
muonium	$\mu^+e^-$	208	0.9952	53.15	13.54
hydrogen (protium)	$p^+e^-$	1837	0.9995	52.92	13.60
tritium	$2n\ p^+e^-$	5498	0.9998	52.90	13.60
muonic hydrogen	$p^+\mu^-$	2043	186	0.28	2530
muonic helium	${}^4\text{He}^{2+}\mu^-e^-$	7497	0.9999	52.9	13.6
muoniumium	$\mu^+\mu^-$	413	103.5	0.51	14.10

Table IV  
Selection of Positronium Yields (Fraction of Total  $e^+$ )

gases <sup>a</sup>	Ps	liquids <sup>b</sup>	Ps
He	0.23	H <sub>2</sub> O	0.36
Ne	0.26	D <sub>2</sub> O	0.29
Ar	0.33	aliphatic alcohols	0.28–0.36
Kr	0.11 (0.38) <sup>c</sup>	aliphatic ethers	0.33–0.49
Xe	0.03 (0.44)	(CH <sub>3</sub> ) <sub>2</sub> CO	0.24
N <sub>2</sub>	0.19–0.4 <sup>e</sup>	linear saturated hydrocarbons	0.55–0.60
H <sub>2</sub>	0.35–0.5 <sup>e</sup>	spherical compounds <sup>d</sup>	0.73–0.78
		aromatic hydrocarbons	0.50–0.55
SF <sub>6</sub>	0.3–0.6 <sup>e</sup>	CS <sub>2</sub>	0.55
		CH <sub>3</sub> CN	0.20
C <sub>2</sub> H <sub>6</sub>	0.5–0.8 <sup>e</sup>	CCl <sub>4</sub>	0.01

<sup>a</sup> From T. C. Griffith, et al., in "Positron Annihilation", P. G. Coleman, et al., Ed., North-Holland Publishing Co., Amsterdam, 1982, p 61. <sup>b</sup> Sum of o-Ps plus p-Ps, from O. E. Mogensen, et al., in footnote a, p 809. <sup>c</sup> Theoretical estimates, footnote a. <sup>d</sup> C(CH<sub>3</sub>)<sub>4</sub> and Si(CH<sub>3</sub>)<sub>4</sub>. <sup>e</sup> Pressure dependent.

stricted in accordance with symmetry rules to 3 $\gamma$ -annihilation, with a mean lifetime of 140 ns. Such a long life can only be realized in vacuo, however, because in a condensed medium the density of other electrons leads to positron "pick-off" reactions that convert o-Ps within a few nanoseconds to p-Ps (or other short-lived states), resulting in prompt 2 $\gamma$ -annihilation.<sup>24</sup> In pure water, the mean lifetime of o-Ps is  $\sim$ 1.8 ns.<sup>25</sup> When solutes that react specifically with o-Ps are added to the water, the o-Ps lifetime is reduced further. It is the direct measurement of this lifetime reduction, the "quenching" of o-Ps, that provides most of the reaction rate constant data.

Positrons are created with  $\sim$ 10<sup>6</sup> eV of kinetic energy from radioactive  $\beta^+$  sources such as <sup>22</sup>Na. When injected into a medium, they transfer energy by ionization and excitation, eventually reaching thermal energy as free positronium atoms or in captured states of neutral molecules or anions, or they undergo quasi-free annihilation.<sup>24</sup> The fraction yielding Ps changes with the chemical and physical properties of the medium. A selection of yields is given in Table IV.

The most commonly used method for determining reaction rates and yields of o-Ps is the positron-annihilation-lifetime technique. One counter sees a start- $\gamma$  associated with  $\beta^+$  emission and another sees an annihilation- $\gamma$ , so the time elapsed represents one data point in a lifetime histogram, typically composed of 10<sup>8</sup> events. Computer analysis of this gives two or more components of amplitude and mean lifetime. o-Ps is usually the longest lived component. In  $\gamma$ -irradiated aqueous glasses at 77 K o-Ps was seen to localize in two

distinct types of traps from which it has two different decay rates.<sup>26</sup> Due to the ever improving response time of detectors and electronics, faster reactions and greater resolutions become possible each year. The chemical state of  $e^+$  at its moment of annihilation can also be studied through momentum distribution, by measuring the Doppler broadening of the width of the lifetime spectrum or from precise measurements of the 2 $\gamma$ -angular correlation.<sup>27</sup>

Positronium shows reactions of "association", "electron transfer", "spin exchange", "positron pick-off", etc., and some examples appear in Table II. Quantum theorists have an intriguing particle for study.<sup>28</sup> Calculations have been performed for mixed positron-electron molecules, including PsH, PsF – PsI, PsOH, and higher polyleptons such Ps<sup>-</sup> and Ps<sub>2</sub>, all of which have also been detected experimentally,<sup>29</sup> except for the first and last mentioned.

The advent of positron emission tomography (PET) in medicine has broadened the interest in positrons. In PET, all signals are rejected other than a coincident pair of 180°-correlated annihilation  $\gamma$ s, which then define a line through the patient on which the positron appeared. But, so far, there does not seem to have been interest in exploiting the fact that o-Ps will be the precursor of some 50% of the observed annihilations. If the o-Ps lifetime were also measured, then extra information about the chemical environment of the positron would be available.

#### Muonium Atoms (Mu, $\mu^+e^-$ )

During the last 10<sup>4</sup> eV of its radiation track, an energetic muon undergoes a sequence of "charge-exchange" cycles in which it picks up an electron from a molecule of the medium to become Mu\* and then loses it again to return to  $\mu^{*+}$ . As it slows down, it spends progressively less time in the charged state where it produces most radiation damage. While in the hot neutral state, Mu\* can undergo a variety of hot-atom reactions in molecular systems (abstraction, substitution, or insertion) that result in some muons becoming incorporated in diamagnetic molecules. Or they may reach thermal energy ( $k_B T$ ) to become free thermalized muonium atoms. Either of these events ends the track in a relatively low density of ionization and

(26) (a) M. Eldrup, *J. Chem. Phys.*, **64**, 5283 (1976); (b) Y. C. Jean, B. W. Ng, J. M. Stadlbauer, and D. C. Walker in "Positron Annihilation", P. G. Coleman, S. C. Sharma, and L. M. Diana, Eds., North-Holland Publishing Co., Amsterdam, 1982, p 836.

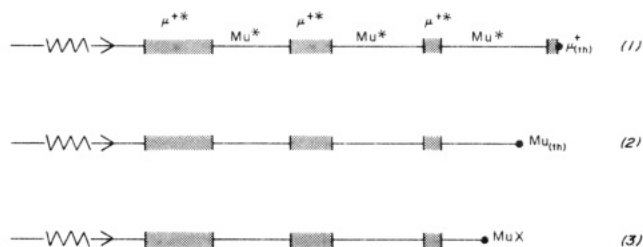
(27) R. N. West, *J. Phys. Chem.*, **84**, 1286 (1980).

(28) (a) A. Ore, *Phys. Rev.*, **83**, 665 (1951); (b) D. M. Schrader in "Positron Annihilation", P. G. Coleman, S. C. Sharma, and L. M. Diana, Eds., North-Holland Publishing Co., Amsterdam, 1982, p 71; (c) P. E. Cade and C.-M. Kao in ref 28b, pp 799, 800, and 802.

(29) (a) S. J. Tao and J. H. Green, *J. Phys. Chem.*, **73**, 882 (1969); (b) O. E. Mogensen, *Chem. Phys.*, **37**, 139 (1979); (c) J. R. Andersen, N. J. Pedersen, O. E. Mogensen, and P. Christensen, *Chem. Phys. Lett.*, **63**, 171 (1979); (d) A. P. Mills, Jr., *Phys. Rev. Lett.*, **46**, 717 (1981).

(24) (a) See J. Green and J. Lee, "Positronium Chemistry", Academic Press, New York, 1964; (b) V. I. Goldanskii and V. P. Shantarovich, *Appl. Phys.*, **3**, 335 (1974); (c) H. J. Ache, *Adv. Chem. Ser.*, **175**, 1 (1979).

(25) J. Ch. Abbé, G. Duplatre, A. Haessler, A. M. Netto, and D. P. Veloso, *J. Phys. Chem.*, **88**, 2071 (1984).



**Figure 1.** Charge exchange cycles ( $\mu^{+*} \rightarrow \text{Mu}^* \rightarrow \mu^{+*}$ ) and possible end-of-track events (last  $10^3$  eV) for a positive muon. While it is a hot charged particle ( $\mu^{+*}$ ), it creates a track of ionizations and excitations (collection of spurs) as depicted by the shaded areas, but while it is the neutral hot muonium atom ( $\text{Mu}^*$ ) little ionization occurs (represented by the lines). As the particle slows down it spends a larger fraction of its time in the  $\text{Mu}^*$  state (hence the changing lengths). Line 1 represents the muon reaching thermal energy while it is in the charged state, thereby forming  $\mu^{+}_{(\text{th})}$  in the track of ionization. Line 2 shows it reaching thermal energy as a neutral muonium atom,  $M\mu_{(\text{th})}$ . Line 3 depicts the track ending when  $\text{Mu}^*$  undergoes a hot atom reaction with a molecule of the medium to form a molecule  $\text{MuX}$ .

**Table V**  
Selection of Muonium Yields<sup>a</sup> (Fraction of Incident Muons  
observed  $10^{-7}$  to  $10^{-5}$  s)

compd	$P_M$		
	gas	liquid <sup>b</sup>	solid
He	0.0	0.0	
Kr	1.0	0.57	0.71
N <sub>2</sub>	0.84	0.2 <sup>c</sup>	0.2 <sup>c</sup>
CH <sub>4</sub>	0.88	0.2 <sup>c</sup>	0.2 <sup>c</sup>
H <sub>2</sub> O	0.93	0.20	0.52
C <sub>6</sub> H <sub>14</sub>	0.81	0.13	0.2
C(CH <sub>3</sub> ) <sub>4</sub>	0.8 (SiMe <sub>4</sub> )	0.18	0.19
CCl <sub>4</sub>	0.5	0.0	0.0
Al			0.0
quartz			0.71

<sup>a</sup> Most data taken from appendix of ref 14. <sup>b</sup> Many of these values are low by a factor up to 2 due to depolarization on the time scale  $10^{-9}$ – $10^{-7}$  s. <sup>c</sup> Tentative data from Y. C. Jean, et al. (to be published).

excitation. Sometimes, however, the muon will reach thermal energy as  $\mu^+$ . An attempt to visualize these alternative track-ends is presented in Figure 1. Whether the thermal chemistry starts with  $\text{Mu}$  or  $\mu^+$  depends precisely on which leg of the charge-exchange cycle happened last. That in turn depends on the ionization energy of the medium relative to the 13.5 eV of  $\text{Mu}$ , as with the change across the noble gases.<sup>14</sup> It also depends whether a hot-atom reaction occurred during a  $\text{Mu}^*$  period, which depends on the chemical composition of the medium.

A variety of muonium yields is therefore to be expected and has been found. A small selection is given in Table V. They are seen to be quite different to Ps yields (Table IV). Saturated molecules apparently undergo hot-atom reactions much less readily in the gas phase than as liquids or solids, and whenever fast thermal reactions of  $\text{Mu}$  occur—as with  $\pi$ -bonded, halogenated, or paramagnetic compounds—then no muonium is observable on the  $\mu\text{SR}$  time scale. Small yields of muonium are readily observable and quite long lived in common solvents like water, alcohols, and hydrocarbons.<sup>30</sup> Their reactivity toward additives can be

(30) (a) P. W. Percival, H. Fischer, M. Camani, F. N. Gyax, W. Ruegg, A. Schenck, H. Schilling, and H. Graf, *Chem. Phys. Lett.*, **39**, 333 (1976); (b) P. W. Percival, E. Roduner, and H. Fischer, *Adv. Chem. Ser.*, **175**, 335 (1979); (c) Y. Ito, B. W. Ng, Y. C. Jean, and D. C. Walker, *Can. J. Chem.*, **58**, 2395 (1980).

studied by  $\mu\text{SR}$  under high sensitivity and ideal pseudo-first-order conditions.

Many kinetic isotope effects have been seen by comparing reaction rates of  $\text{Mu}$  with those of  $\text{H}$  ( $k_M/k_H$ ) in gases<sup>31</sup> and in solution.<sup>14,15,30</sup> The 9-fold smaller mass of  $\text{Mu}$  reduces its rates, by increasing the activation barrier of its reaction because of an increase in the zero-point vibrational energy of the activated complex and product. This is seen in reaction with  $\text{H}_2$ .<sup>32</sup> On the other hand, it increases the rate by greatly enhancing the rate of quantum mechanical tunneling, as in reaction with  $\text{F}_2$ .<sup>33</sup> It also confers a 3-fold higher mean thermal velocity. This increases the encounter frequency (though not in aqueous solution), but it then decreases the duration of collisions, thereby causing orientational limitations.<sup>14</sup> Such effects have been subject to theoretical studies of elementary  $\text{Mu}$  reactions based on semiempirical interaction potentials (ab initio only for the  $\text{H}_2$  reaction) and using various semiclassical and quantum mechanical approaches for the dynamics.<sup>34</sup> Another consequence of the exceptionally low mass of  $\text{Mu}$  has resulted in theoretical predictions for “vibrationally bonded” molecules such as  $\text{IMu}$ .<sup>24d,e</sup> These will have unique  $\mu\text{SR}$  precession frequencies and a search for them experimentally is planned.

Bimolecular rate constants,  $k_M$ , have been determined for more than 60 solutes in dilute aqueous solution,<sup>14</sup> for more than 15 additives in  $\text{N}_2$  or Ar gases,<sup>31</sup> and for a few compounds in organic media including solutes encapsulated in micelles, cyclodextrins, and porphyrins.<sup>35</sup> A few of the aqueous solution values are compared with  $\text{H}$ ,  $\text{Ps}$ , and  $e_{\text{aq}}^-$  in Table II. The  $k_M/k_H$  isotope effect can be seen to range from  $\sim 10^{-2}$  to  $10^2$ , depending on the type of reaction. Abstraction is strongly favored by the heavier isotope, whereas special reactivity is shown by  $\text{Mu}$  toward some solutes, such as nitrate. In  $\text{H}^+$  (or  $\mu^+$ ) transfer reactions there is no isotope effect even with an activation energy of  $\sim 40$  kJ mol<sup>-1</sup>,<sup>36</sup> and Hammett  $\rho$  factors are comparable for addition reactions to the benzene ring.<sup>37</sup> In solution there is always the natural upper limit to reaction rate constants set by the diffusion-limited encounter frequency, which is the order of  $2 \times 10^{10}$  M<sup>-1</sup> s<sup>-1</sup> in water. The fastest reactions of  $\text{Mu}$  show activation energies of  $17 \pm 2$  kJ mol<sup>-1</sup>, equal to the energy barrier to viscous flow ( $\Delta E_{\text{vis}}$ ) of water, with  $k_M/T$  being inversely proportional to the viscosity.<sup>38</sup> This implies that the diffusion of  $\text{Mu}$  and

(31) (a) V. W. Hughes, *Ann. Rev. Nucl. Sci.*, **16**, 445 (1966); (b) D. M. Garner, Ph.D. Thesis, University of British Columbia, 1979; (c) D. G. Fleming, D. M. Garner, and R. J. Mikula, *Hyperfine Interact.*, **8**, 337 (1981).

(32) D. M. Garner, et al., unpublished data.

(33) (a) D. M. Garner, D. G. Fleming, and J. H. Brewer, *Chem. Phys. Lett.*, **55**, 163 (1978); (b) J. N. L. Connor, W. Jakubetz, and J. Manz, *Chem. Phys.*, **28**, 219 (1978).

(34) (a) J. N. L. Connor, W. Jakubetz, and J. Manz, *Chem. Phys. Lett.*, **45**, 265 (1977); (b) J. N. L. Connor, *Hyperfine Interact.*, **8**, 423 (1981); (c) D. K. Bondi, D. C. Clary, J. N. L. Connor, B. C. Garrett, and D. G. Truhlar, *J. Chem. Phys.*, **76**, 4986 (1982); (d) J. Manz, R. Meyer, E. Pollak, and J. Romelt, *Chem. Phys. Lett.*, **93**, 184 (1982). (e) D. C. Clary and J. N. L. Connor, *J. Phys. Chem.*, **88**, 2758 (1984).

(35) (a) C. Bucci, G. Guidi, M. Manfredi, R. Tedeschi, P. R. Crippa, G. M. de Munari, A. Vecchi, and P. Podini, *Hyperfine Interact.*, **6**, 425 (1979); (b) Y. C. Jean, B. W. Ng, and D. C. Walker, *Chem. Phys. Lett.*, **75**, 561 (1980). (c) Y. C. Jean, B. W. Ng, J. M. Stadlbauer, and D. C. Walker, *J. Chem. Phys.*, **75**, 2879 (1981); (d) Y. C. Jean, B. W. Ng, Y. Ito, T. Q. Nguyen, and D. C. Walker, *Hyperfine Interact.*, **8**, 351 (1981).

(36) B. W. Ng, J. M. Stadlbauer, and D. C. Walker, *J. Phys. Chem.*, **88**, 857 (1984).

(37) J. M. Stadlbauer, B. W. Ng, R. Ganti, and D. C. Walker, *J. Am. Chem. Soc.*, **106**, 3151 (1984).



H follow the Stokes–Einstein relationship governing bulk hydrodynamic properties rather than diffusing in proportion to their mean velocities.<sup>14</sup> This has been explained through computer simulation studies as due to the considerable van der Waals radii of Mu and H<sup>39</sup> and their enclathration by 23 and 18 H<sub>2</sub>O molecules, respectively.<sup>40</sup> It remains to be seen whether a kinetic isotope effect greater than unity emerges in much less structured solvents at the diffusion-controlled limit. (A muonium–radical reaction rate has been observed to be 75 000 times that of its H analogue.<sup>41</sup> Here the higher zero-point energy of Mu compared to H lies with the reactants, so it favors the Mu reaction.)

Electron-spin-exchange interactions between paramagnetic species are of growing general interest.<sup>42</sup> Such reactions of Mu (and by implication H) can readily be followed because a spin conversion from “triplet” Mu to “singlet” Mu registers as an enhanced relaxation due to hyperfine depolarization and therefore is seen as a rate constant when a solute is present. Such reactions have been reported for NO and O<sub>2</sub> in gases<sup>43</sup> and for paramagnetic ions in solution.<sup>44</sup> Nickel cyclam [(1,4,8,11-tetraazacyclotetradecyl)nickel(II)] was particularly interesting because interconversion between paramagnetic (octahedral-axial H<sub>2</sub>O ligands) and diamagnetic (square planar) states was achieved merely by addition of inert salt, without changing the transition-metal ion, its oxidation state, or its major ligands.<sup>44b</sup> There was at least a 100-fold difference in the rate constant for Mu reacting with the paramagnetic compared to the diamagnetic state. For H to H spin exchanges in solution it has been predicted that a long-range interaction occurs,<sup>45</sup> which is interesting in view of the  $k_M$  values<sup>44</sup> and the lack of an observable ionic strength effect on electron-exchange Mu reactions.<sup>46</sup>

Free radicals are recognized as important reactive intermediates in many chemical or biological processes and are generally studied by ESR. But when one of the nuclei is  $\mu^+$ , then the muon spin precession frequencies observed by  $\mu$ SR can be used to identify the radical's structure, and also to determine its yield and rate of reaction.<sup>47</sup> Here the muon is a distinguishable passive nuclear probe. It also reveals dynamic isotope effects stemming from the higher zero-point vibrational energy and smaller moment of inertia associated with Mu compared to H.

(38) (a) B. W. Ng, Y. C. Jean, Y. Ito, T. Suzuki, J. H. Brewer, D. G. Fleming, and D. C. Walker, *J. Phys. Chem.*, **85**, 454 (1981); (b) J. M. Stadlbauer, B. W. Ng, Y. C. Jean, and D. C. Walker, *J. Phys. Chem.*, **87**, 841 (1983).

(39) J. S. Tse and M. L. Klein, *J. Phys. Chem.*, **87**, 5055 (1983).

(40) B. De Raedt, M. Sprik, and M. L. Klein, *J. Chem. Phys.*, **80**, 5719 (1984).

(41) E. Roduner, and K. Munger, *Hyperfine Interact.*, **17–19**, 793 (1984).

(42) Yu. N. Molin, K. M. Salikhov, and K. I. Zamaraev, “Spin Exchange”, Springer-Verlag, West Berlin, 1980.

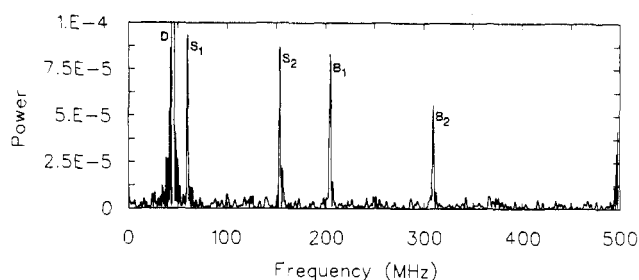
(43) (a) R. M. Mobley, J. M. Bailey, W. E. Cleland, V. W. Hughes, and J. E. Rothberg, *J. Chem. Phys.*, **44**, 435 (1966); (b) D. G. Fleming, R. J. Mikula, and D. M. Garner, *J. Chem. Phys.*, **73**, 2751 (1980).

(44) (a) Y. C. Jean, J. H. Brewer, D. G. Fleming, and D. C. Walker, *Chem. Phys. Lett.*, **60**, 125 (1978); (b) J. M. Stadlbauer, B. W. Ng, Y. C. Jean, and D. C. Walker, *J. Am. Chem. Soc.*, **105**, 752 (1983).

(45) B. Brocklehurst, *Radiat. Phys. Chem.*, **23**, 187 (1984).

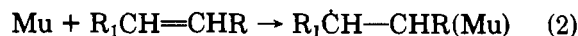
(46) Y. C. Jean, J. H. Brewer, D. G. Fleming, D. M. Garner, and D. C. Walker, *Hyperfine Interact.*, **6**, 409 (1979).

(47) (a) E. Roduner, P. W. Percival, D. G. Fleming, J. Hochmann, and H. Fischer, *Chem. Phys. Lett.*, **57**, 37 (1978). (b) E. Roduner and H. Fischer, *Chem. Phys.*, **54**, 261 (1981); (c) E. Roduner in “Muons and Pions in Materials Research”, J. Chappert and R. I. Grynspan, Ed., Elsevier, Amsterdam, 1984, p 209; (d) H. Fischer, *Hyperfine Interact.*, **17–19**, 751 (1984).



**Figure 2.** FT spectrum of 20% styrene by volume in benzene, obtained from a 3.4-kG  $\mu$ SR histogram. Peak D represents the diamagnetic signal (13.6 kHz/G), S<sub>1</sub> and S<sub>2</sub> (sum = 214 MHz) are from the Mu radical in styrene, while B<sub>1</sub> and B<sub>2</sub> (sum = 514 MHz) come from the Mu radical in benzene. [Power is proportional to amplitude squared.] (Figure from ref. 50b.)

So far the free radicals studied have  $\mu^+$  as a muonium atom bonded by an ordinary  $\sigma$  bond to C or O atoms that are one to three bonds removed from the center of free-electron density. Such a radical may be formed by addition of Mu to a  $\pi$  bond (as in eq 2). It should also be possible to study  $\mu^+$  radical cations or, indeed, anions, biradicals, and paramagnetic complexes containing muons.



Mu radicals are generally studied in the high-field limit of  $\mu$ SR where other nuclear interactions are decoupled. They are presented as precession frequencies in Fourier transform. The muon spin polarization is distributed over a pair of frequencies, separated from each other by twice the diamagnetic frequency, whose vector sum equals the isotropic muon–electron hyperfine coupling constant ( $A_\mu$ ), which is field independent.  $A_\mu$  values have invariably been observed to be larger than the proton equivalent by more than the nuclear magnetic moment ratio of 3.18, resulting in “dynamic” isotope effects of 10–20% for aromatics (attributed to out-of-phase deformations) and 15–70% for aliphatics (due to incomplete conformational averaging).<sup>48</sup> Already more than 200 Mu radicals have been studied. Sometimes there is great intra- and intermolecular specificity. For instance, in pure styrene only one of six possible radicals is observed,<sup>49</sup> and in styrene–benzene mixtures<sup>50</sup> the radical from styrene forms about 7 times as frequently as that from benzene, as indicated in Figure 2. Primary competition for the precursor is suggested here by the linearity of inverse-yield vs. inverse-concentration plots.<sup>50</sup> However, the mechanism of Mu radical formation is not yet settled, with thermal Mu challenged by hot Mu, free  $\mu^+$ , and  $\mu^+$  cations as primary species.<sup>14,50,51</sup>

(48) (a) E. Roduner, *J. Mol. Struct.*, **60**, 19 (1980); (b) M. J. Ramos, D. McKenna, B. C. Webster, and E. Roduner, *J. Chem. Soc., Faraday Trans. 1*, **80**, 267 (1984).

(49) J. M. Stadlbauer, B. W. Ng, D. C. Walker, Y. C. Jean, and Y. Ito, *Can. J. Chem.*, **59**, 3261 (1981).

(50) (a) S. F. J. Cox, A. Hill, and R. De Renzi, *J. Chem. Soc., Faraday Trans. 1*, **78**, 2975 (1982); (b) B. W. Ng, J. M. Stadlbauer, Y. Ito, Y. Miyake, and D. C. Walker, *Hyperfine Interact.*, **17–19**, 821 (1984); (c) B. W. Ng, Ph.D. Thesis, University of British Columbia, 1983.

(51) (a) E. Roduner, G. A. Brinkman, and P. W. F. Louwrier, *Chem. Phys.*, **73**, 117 (1982); (b) A. Hill, G. Allen, G. Stirling, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, **78**, 2959 (1982); (c) E. Roduner and B. C. Webster, *J. Chem. Soc., Faraday Trans. 1*, **79**, 1939 (1983); (d) E. Roduner, *Hyperfine Interact.*, **17–19**, 785 (1984); (e) E. Roduner, G. A. Brinkman, and P. W. F. Lowier, *Chem. Phys.*, **88**, 143 (1984).

### Muonic Atoms

The basic properties resulting from exchange of an orbital electron of an atom by a negative muon have already been outlined. Although not yet developed,<sup>14</sup>  $\mu^-$  capture has the potentiality of becoming an analytical and diagnostic tool, because the muon's capture probability and its lifetime (or muonic X-ray spectrum) can be directly correlated with the chemical composition of the medium.

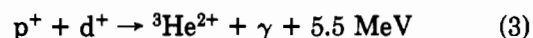
The capture of  $\mu^-$  by a molecule is characterized by four stages.<sup>14,52</sup> First is the localization of a "sluggish"  $\mu^-$  (10–20 eV) in a high Rydberg state of the molecule. This overlaps the electronic molecular orbitals and is therefore quite sensitive to them. Second, the muon localizes from this molecular orbital onto an atom (often the highest Z). Third, is the cascading of  $\mu^-$  to its lowest (1s) atomic orbital, which causes Auger electron loss and characteristic Lyman X-ray emission. Fourth, the  $\mu^-$  lifetime is reduced by coulombic nuclear capture. This lifetime complements the X-ray spectrum in characterizing the capturing nucleus. The atoms present are identified from the muonic X-ray spectrum, the Auger emission, or the distribution of  $\mu^-$  lifetimes. And the structure is correlated to the initial molecular capture cross sections and relative yields of muonic atoms.

Finally, muonic molecules are possible: the most interesting of which are those without any electrons. In the molecular ion ( $p^+-\mu^-d^+$ ), the two nuclei are drawn together by the enormous binding energy of  $\mu^-$  (see eq 1), such that the proton and deuteron have a mean separation of only  $\sim 2 \times 10^{-13}$  m.<sup>53</sup> At this distance there is significant tunneling, which leads to nuclear fusion, as in eq 3. Whether this, or its d-t counterpart,

(52) (a) L. I. Ponomarev, *Ann. Rev. Nucl. Sci.*, **23**, 395 (1973); (b) T. Yamazaki in "Muons and Pions in Materials Research", J. Chappart and R. I. Grynspan, Eds., Elsevier, Amsterdam, 1984, p 241; (c) Y. Sakai, T. Tominaga, K. Ishida, and K. Nagamine, *Radiochem. Radioanal. Lett.* **58**, 285 (1983).

(53) L. W. Alvarez, et. al., *Phys. Rev.*, **105**, 1127 (1957).

can be utilized in a controlled and economical way remains to be seen.<sup>54</sup>



### Concluding Comments

An attempt is being made to see how exotic species can be used for insights into natural atoms. The series of species  $e_s^-$ , Ps, Mu, and H make an excellent test pattern for basic physicochemical properties, particularly the transition from classical to quantum mechanical effects. Their intercomparison in aqueous solution is useful because of the range of reaction types that they undergo: spin exchange, charge transfer, "pick-off", "addition" with different Hammett  $\rho$  factors, and others. Their diffusion-controlled rates, their enclathration or solvation, and their trapping are all interesting because of the range of masses, radii, and effective charges shown. The Mu-H comparison is perfect for studying isotope effects; the Ps-Mu comparison is ideal for spin-exchange studies and quantum effect;  $e_s^-$ -Ps offer unusual charge effects;  $e_s^-$ -H distinguish acid-base processes, etc. There is interest too in the bond energy of  $\text{Mu}_2$  and  $\text{Ps}_2$ , in the solvation energy of  $\mu^+$  and  $e^+$ , and in the  $pK_a$  and  $E^0$  values of Mu and Ps.

Great potential exists in the further development of  $\mu\text{SR}$  studies of Mu-containing free radicals. In addition it should be possible to distinguish diamagnetic  $\mu^+$  environments through chemical shifts; to apply muonic X-ray or lifetime studies to analytical chemistry; and to utilize o-Ps lifetimes in positron emission tomography.

*Gratitude is extended to the Directors and staff of TRIUMF, my colleagues in  $\mu\text{SR}$ , the many collaborators I have enjoyed working with over the years, and NSERC of Canada for financial support.*

(54) (a) Yu. V. Petrov, *Nature (London)*, **285**, 466 (1980); (b) S. E. Jones, et al., *Phys. Rev. Lett.*, **51**, 1757 (1983).