MUON DEPOLARIZATION AND THE CHEMISTRY OF FREE RADICALS *

J.H. Brewer, K.M. Crowe, and R.F. Johnson

Lawrence Berkeley Laboratory, University of California

Berkeley, California, USA

A. Schenck

University of Heidelberg

Heidelberg, Germany

Polarized positive muons were stopped in solutions
of bromine and iodine in benzene, and the precession
of their polarization in a 200 gauss transverse magnetic
field was observed via their asymmetric decay. The
magnitude and apparent initial direction of the pol-
arization depended strongly upon the $Br_2$ or $I_2$ conc-
entration. The details of this behavior strongly in-
dicate that muonium is formed and subsequently reacts
with benzene to form the radical $C_6H_6Mu^\cdot$, which later
reacts with the dissolved reagent to form a diamagnetic
compound. Chemical rate constants and other relevant
parameters are extracted.

When polarized positive muons are stopped in condensed media,
the apparent initial magnitude and direction of their polarization can
be measured by observing their asymmetric decay as they precess in a
transverse magnetic field. It has long been known[1] that this apparent

initial polarization ("residual polarization") depends strongly upon the chemical properties of the medium, and in particular that positive muons are strongly depolarized by inert media. In a liquid consisting of a reagent dissolved in a relatively inert solvent, the muons experience less and less depolarization as more and more reagent is added.

In the simplest situations, this phenomenon is explained by the "muonium mechanism", formalized by Ivanter and Smilga[2]: incoming muons capture electrons to form muonium (analogous to atomic hydrogen) in which the hyperfine interaction causes rapid depolarization of the muon until the muonium reacts (either epithermally or thermally) to place the muonium in a diamagnetic compound, where depolarization ceases. The validity of this model has been borne out in several cases[3], and may be accepted for solutions of most reagents in water or methanol.

However, when benzene is used as a solvent, the experimental results are in strong disagreement with the specific behavior predicted by the simple muonium mechanism. As can be seen in Fig. 1, the muonium mechanism unambiguously predicts a "plateau" in the polarization as a function of reagent concentration, and such behavior is markedly absent in benzene. The initial phase also behaves quite differently from the predictions of the simple model.

We have, however, obtained good agreement with the data by assuming a more complicated situation, involving a second strongly depolarizing influence: the muonium adds to the benzene to form the radical $C_6H_6Mu^{\cdot}$, analogous to cyclohexadienyl[4], in which the hyperfine coupling of the muon spin with that of the unpaired electron causes depolarization of the muon in much the same manner as in free muonium, though more slowly.[5]

The radical subsequently combines with the reagent to form a diamagnetic compound, at which point the depolarization ceases. Meanwhile, of course, a competing reaction of the muonium with the reagent may be placing some of the muonium directly into diamagnetic compounds.

Fig. 2 shows schematically the various paths a muon may follow in such a solution. Muonium which escapes epithermal reactions may react either with the solvent to form a radical or with the reagent to form a diamagnetic compound; in any event only those muons which emerge eventually into diamagnetic compounds contribute to the observed polarization. The possibility of reactions of muonium with the reagent to form radicals is excluded here, but in other solutions may well be a significant process.

To calculate the predictions of this generalized mechanism, we adapt the formalism developed by Ivanter and Smilga[2,6]. The fraction h reacting epithermally to form a diamagnetic compound gives a constant, unrotated contribution to the residual polarization; the muonium reacting with the reagent to form diamagnetic compounds gives a contribution predicted by the usual muonium mechanism[6]. The fraction r which react epithermally to form a radical may be thought of as a weaker version of the muonium mechanism, since they are depolarized in the radical until it reacts to place them in diamagnetic compounds; in fact, the contribution from this fraction can be obtained from the same formulas, provided one substitutes $\omega_r$ for $\omega_o$ everywhere. Here $\omega_o$ is the hyperfine frequency in muonium, and $\omega_r$ the analogous hyperfine frequency in the radical.

This leaves only the contribution to the residual polarization from muons which proceed through thermalized muonium into a radical and then into a diamagnetic compound, all via normal chemical reactions.

Since in this case the muon polarization will have evolved for an unspecified time in muonium before beginning to evolve in the radical, the Laplace transform technique employed by Ivanter and Smilga[2] is unfortunately useless for this calculation; the explicit time dependence must be solved.[7]

The result depends on the following empirical parameters:

h = fraction of "hot" muonium atoms reacting epithermally to form diamagnetic compounds.

r = fraction reacting epithermally to form radicals containing muonium.

$k_{mr}$ = chemical rate constant for the reaction Mu + Solvent → Radical.

$k_{md}$ = chemical rate constant for the reaction Mu + Reagent → Diamagnetic Compound.

$k_{rd}$ = chemical rate constant for the reaction Radical + Reagent → Diamagnetic Compound.

The predictions of the theory[7] were fitted to the data for $I_2$ and $Br_2$ in benzene by varying these parameters and the phenomenological parameters describing the magnitude and direction of beam polarization; consistency in the latter parameters was required between fits for the two reagents. Results are shown in Table 1. All errors are approximate.

Table 1.  Chemical rate constants in liters/mole-sec $\times 10^{10}$.

| h | r | $k_{mr}$ | $k_{md}(I_2)$ | $k_{rd}(I_2)$ | $k_{md}(Br_2)$ | $k_{rd}(Br_2)$ |
|---|---|---|---|---|---|---|
| $.13 - .02$ | $0 \pm .1$ | $.1 \begin{smallmatrix} + .20 \\ - .05 \end{smallmatrix}$ | $4.5 \begin{smallmatrix} + 4 \\ - 2 \end{smallmatrix}$ | $.8 \begin{smallmatrix} + .5 \\ - .3 \end{smallmatrix}$ | $11 \begin{smallmatrix} + 8 \\ - 5 \end{smallmatrix}$ | $.6 \begin{smallmatrix} + .5 \\ - .3 \end{smallmatrix}$ |

The value obtained for $k_{mr}$ corresponds[8] to a rate constant of $\sim 3 \times 10^8$ liters/mole-sec for the reaction H· + $C_6H_6$ → $C_6H_7$·, consistent with the value of $5.88 \times 10^8$ measured by Melville and Robb[9].

The generalized model used to fit this data has three more parameters than the simple "muonium mechanism", and consequently produces less precise results when fitting comparable data, which is evident from the size of the errors quoted. This is not to say that the model is less powerful, but only that one needs more experimental information to extract more parameters from the fits. It should be an easy matter to take more data at different concentrations, with higher statistics and better phase resolution, and thereby obtain much more precise information about rate constants and hot chemistry. The phase data cannot be over-emphasized; while the polarization data quickly gives us a qualitative appreciation of the dominant processes at work, it is not nearly as sensitive to the exact ratios of rate constants as the phase data.

The real significance of the results shown here is that they unambiguously confirm the formation of radicals containing muonium, and thus predict the possibility of studying much more intricate processes than could be observed assuming only the pure muonium mechanism.

## REFERENCES

*Work done under the auspices of the U.S. Atomic Energy Commission.

[1] A.O. Weissenberg, Muons, North-Holland Publishing Company: Amsterdam, 1967. Ch. 6.

[2] I.G. Ivanter and V.P. Smilga, Soviet Phys. JETP 27, 301 (1968).

[3] J.H. Brewer, K.M. Crowe, R.F. Johnson, A. Schenck, and R.W. Williams, Phys. Rev. Lett. 27, 297 (1971).

[4] G.S. Forbes and J.E. Cline [J. Am. Chem. Soc. 63, 1713 (1941)] found evidence for the reaction of atomic hydrogen to form the radical cyclohexadienyl, $C_6H_7\cdot$.

[5] Using the value quoted by H. Fischer [Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology, Ed. K.H. Hellwege, Group II: Atomic and Molecular Physics, Vol. I: Magnetic Properties of Free Radicals: Springer-Verlag, Berlin, Heidelberg, and New York, 1965; p. 40], and the ratio $\mu_\mu/\mu_p = 3.18$, we estimate the hyperfine frequency in the radical (neglecting isotopic effects) to be $\omega_r = 0.104\ \omega_o$, where $\omega_o$ is the hyperfine frequency in muonium. A survey of fits showed best agreement with the data for $\omega_r/\omega_o$ between .1 and .2, consistent with this value.

[6] I.G. Ivanter and V.P. Smilga, Soviet Phys. JETP 28, 796 (1969).

[7] J.H. Brewer, K.M. Crowe, R.F. Johnson, and A. Schenck, to be published. Title: "Generalized Mechanism for $\mu^+$ Depolarization in Solutions".

[8] Assuming that the only chemical distinction between Mu and H atoms is their mass difference, simple kinetic theory predicts $k(Mu)/k(H) \simeq 3$. See refs. 3 and 10.
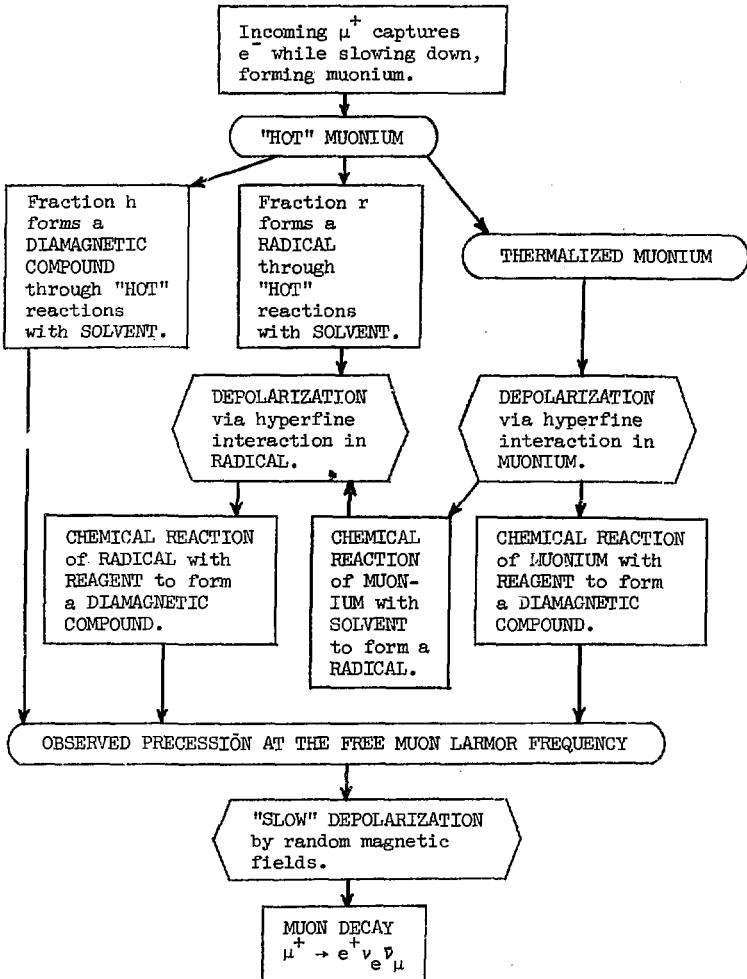
[9] H.W. Melville and J.C. Robb, Proc. Roy. Soc. A202, 181 (1950).

[10] V.G. Firsov and V.M. Byakov, Soviet Phys. JETP 20, 719 (1965).
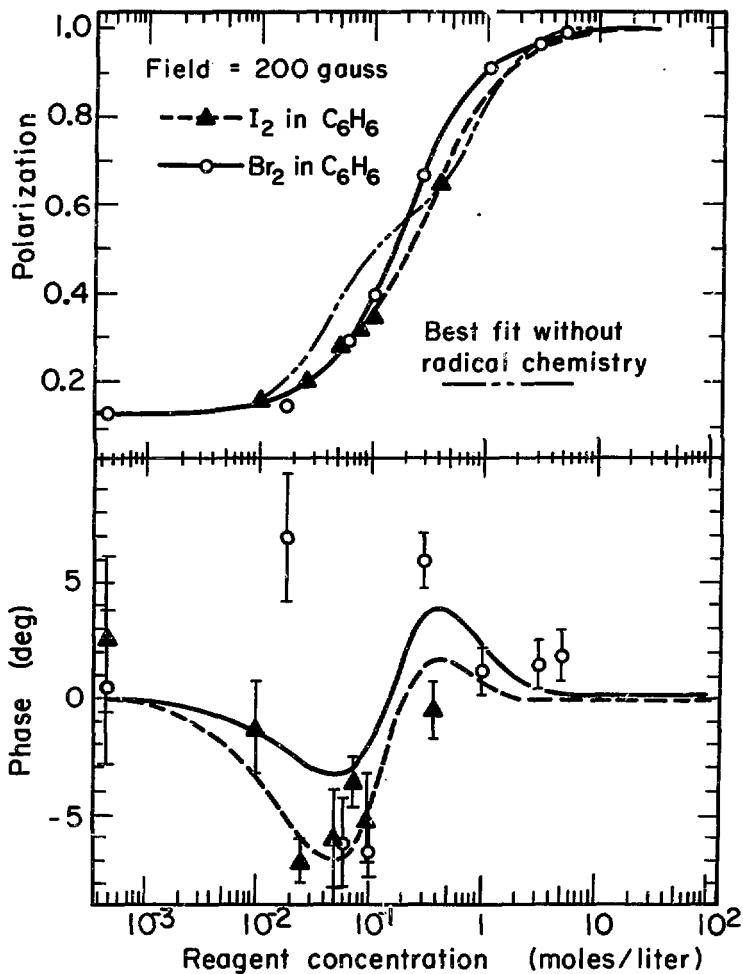
XBL718-4148

Fig. 1

XBL 718-1294

Fig. 2