PHYSICAL REVIEW A VOLUME 9, NUMBER 1 JANUARY 1974

Muonium chemistry in liquids: Evidence for transient radicals*

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(Received 13 July 1973)

Polarized positive muons are stopped in solutions in magnetic fields transverse to their polarization. Positrons from the asymmetric decay are detected as the muons precess, allowing measurement of the magnitude and direction (phase) of the apparent initial polarization P_{res}. Variations of P_{res} with reagent concentration are compared with theoretical predictions. Measurement of both magnitude and phase of P_{res} allows sensitive tests of the mechanism of "fast" μ^+ depolarization. Evidence is found for both epithermal "hot-atom" reactions and chemical reactions of muonium involving formation of rapidly reacting radicals. Chemical rate constants are extracted and compared with rates for analogous reactions of atomic hydrogen.

I. INTRODUCTION

When a positive muon stops in matter, it virtually always captures an electron to form the atom μ^+e^-, called muonium.[1] This atom, herein denoted Mu, is analogous to the hydrogen atom, the principle difference being in the masses ($m_{\text{H}} \approx 9 m_{\text{Mu}}$). Thus Mu and H may be expected to participate in similar chemical reactions, and in many cases it should be instructive to compare their chemical properties. For instance, differences in reaction rates provide valuable new data on kinetic isotope effects. It is possible to infer the chemical properties of muonium atoms by studying the "fast" depolarization of positive muons in media. In particular, the reaction rates of muonium atoms with various reagents in solution can be extracted from experimental measurements of muon depolarization by fitting the data to the predictions of a suitable theory of the depolarizing mechanism. This procedure was first suggested by Firsov and Byakov.[2,3] We present here the results of such an interpretation of data on depolarization of muons in liquids. The theory is described in detail in an earlier paper,[4,5] but a brief review is appropriate.

In an experiment in which muons are initially polarized, the formation of muonium results in their depolarization, the extent of which depends upon the length of time muonium remains free before reacting chemically. This effect is due to the hyperfine interaction in muonium which couples the muon and electron spins; in concert with an external magnetic field perpendicular to the initial muon polarization, the hyperfine coupling causes rapid motion of the muon spin. When the Mu atom reacts chemically to place the muon in a diamagnetic environment, this motion stops and is replaced by the comparatively slow Larmor precession of the muon in the applied field. Much later, the muon decays. Since each Mu atom reacts at a different time, each muon "emerges" from the muonium environment with a different spin direction, so that the "residual" polarization P_{res} of the muon ensemble is reduced and rotated with respect to its initial magnitude and direction. The reaction times are distributed exponentially, so that the probability of a Mu atom remaining free until time t is e^{-t/τ_m}, where τ_m is the "chemical lifetime" of free muonium atoms. If τ_m is much shorter than the period of a hyperfine oscillation in muonium (2.24×10^{-10} sec), the muon spins will not have moved appreciably before the muonium reacts and there is no depolarization. A sufficiently rapid relaxation of the spin of the muonium electron by the medium can also prevent depolarization of the muon, but this effect is probably not significant in liquids.[4]

This simple model embodies the essential features of the depolarizing mechanism as envisioned by Nosov and Yakovleva[6,7] and formalized by Ivanter and Smilga.[8] Although qualitatively correct, it is incomplete. Several related phenomena must be included before the model is sufficiently general to describe physical reality, and permit a practical study of the chemical properties of muonium by measurements of muon depolarization.

First, as noted by Ivanter and Smilga,[9] "hot-atom chemistry" must be included: Incoming muons capture electrons to form muonium while still energetic (typically at kinetic energies ~200 eV),[10] and the "hot" Mu atoms thermalize by collisions with molecules of the medium within about 10^{-11} sec.[11] During these epithermal collisions the Mu atoms may react chemically in ways forbidden to thermalized muonium. These processes are analogous to those studied in hot-tritium chemistry.[12] The fraction "h" of muons entering diamagnetic compounds in this way, virtually at $t=0$, experience no depolarization.

With the inclusion of hot-atom chemistry, the model[9] can be used to interpret experimental results for muon depolarization in solutions,[13] as long as chemical reactions leave muons only in diamagnetic compounds. In this form, the model is referred to as the "proper muonium mechanism." It is still incomplete, however; a second additional process must also be taken into account:

As noted by Firsov and Byakov[2] as well as by Ivanter and Smilga,[9] muonium is apt to react with many substances to form free radicals (paramagnetic molecules) incorporating muons. In a radical, as in muonium, there is a hyperfine interaction between the muon and the unpaired electron; though always weaker than that in muonium, it causes similar rapid evolution of the muon spin and leads to further depolarization of the muon ensemble.

Unfortunately, while the theory constructed by Firsov and Byakov incorporated radical formation, it had serious shortcomings. First, they failed to include hot-atom chemistry, and have subsequently treated it as incidental.[14] Second, their treatment of the depolarizing effect of the hyperfine interaction in muonium is oversimplified, particularly in the presence of applied magnetic fields. Depolarization via radicals is even less adequately treated. Finally, they do not consider rotations of the muon's residual polarization due to precession of "triplet" states of muonium and radicals, and thereby omit a dramatic experimental test of the mechanism: variation of the apparent initial direction (phase) of the residual polarization with the chemical properties of the medium. In light of these deficiencies, we must regard their interpretation of experimental results[14,15] as questionable.[9,13]

The formalism developed by Ivanter and Smilga in Ref. 9 is an elegant description of a very general mechanism; however, like Firsov and Byakov, they assume that the radicals formed by reactions of muonium are stable, leading to complete depolarization of those muons that end up in radicals. The experimental results presented here indicate the necessity of taking into account the formation of radicals which subsequently react in very short times, ultimately leaving the muons in diamagnetic environments. In addition, the consistently important role of hot atom reactions is firmly established.

Finally, the chemical rate constants and epithermal reaction efficiencies extracted from the data exemplify the sort of detailed quantitative information about muonium chemistry that can be obtained by studies of muon depolarization.

II. EXPERIMENTAL TECHNIQUE

The apparatus used in this experiment is essentially the same used by Crowe *et al.* to measure the magnetic moment of the muon.[10] The general technique and some details distinguishing this experiment are outlined below.

A polarized beam of positive muons is produced by momentum selection of a decaying π^+ beam, taking muons from forward π decay. The resultant stopping μ^+ beam is on the order of 80% polarized. About 1500 muons/sec are stopped in a thin-walled Mylar and Teflon cube 3-in. on a side, filled with solution. This target is in a uniform magnetic field perpendicular to the muon polarization; the field strength is typically 100 G. The field is produced by a large Helmholtz coil with several trim coils to allow adjustment of the field homogeneity to the order of $\pm 0.1\%$. Within a few nsec after stopping, the muons form muonium, are partially depolarized, and react chemically to end up in diamagnetic environments. After this effectively discontinuous depolarization process, they precess in the applied field at essentially their free Larmor frequency $\omega_\mu = 0.85 \times 10^5 \times B$ (gauss) rad/sec until they decay (an average of 2.20 μsec later). Any muons still in muonium or radicals after the first few nsec appear completely depolarized, since in this experiment we look only for precession at the free muon Larmor frequency.

In the decay $\mu^+ \to e^+ \nu_e \bar{\nu}_\mu$ the positron (which we detect) is emitted preferentially along the muon spin direction. More precisely, the dependence of the decay probability upon the angle θ between the muon spin and the positron direction is given by $dW \approx 1 + a\cos\theta$, where a is the asymmetry parameter, a function of positron energy.[16] Thus a counter telescope mounted in the plane of precession of the muon polarization is more likely to detect the decay positron at times when the muon spin has precessed until it points toward the telescope.

The arrangement of scintillation counters around the stopping target is shown conceptually in Fig. 1. The signature of a stopping muon is logically defined as

$$\mu = B \cdot M \cdot S1 \cdot \overline{S2X}, \quad \text{where } B = B1 + B2, \qquad (1)$$

and the signature of a positron exiting from μ^+ decay is

$$e=\overline{(B1+M+S1)}\circ S2X\circ S2\cdot E\cdot S3\,. \tag{2}$$

The pulses "μ" and "e" are used as gates in coincidence with timing pulses from counters M and E to form starting and stopping pulses for a Hewlett-Packard type 5360A computing counter, used in its time interval measuring mode. This "clock" digitizes the time interval between the starting and stopping pulses with a nominal resolution of 0.1 nsec and an interval range (in this experiment) from ~50 nsec to ~20 μsec. The actual time resolution of the entire system is on the order of 1 nsec.

The digitized time interval is sent to an on-line PDP-15 computer along with a number of diagnostic logic bits whose functions are to eliminate spurious events or ambiguities and to monitor the equipment functions. These functions are described in detail in Refs. 5 and 10. The time intervals are binned in a 16 000-bin histogram of 0.5 nsec per bin. A run of about 6 h yields on the order of a million events, giving ~230 counts/bin in early bins. Time zero is defined for each run by taking a few thousand events with vetoes removed from the coincidences, allowing both "μ" and "e" to be triggered by a single particle passing through the whole counter array without stopping. The experimental distribution of events per bin as a function of time interval between "μ" and "e" is equivalent to the positron detection probability as a function of the time since the muon stopped. This probability is enhanced when the muon spin points toward the positron telescope; thus, the distribution has a component which oscillates with time as the muon precesses in the plane of the telescope. An example of such an experimental histogram, taken in an applied field of 100 G, is shown in Fig. 2.

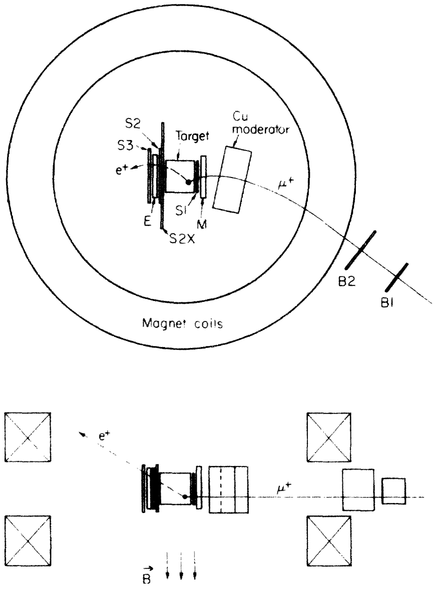

FIG. 1. Top and side views of stopping target, counter arrangement, and magnet coils. Not to scale.

Histograms are compared with the following distribution:

$$N(t)=N_0\{B+e^{-t/\tau_\mu}[1+Ae^{-t/T_2}\cos(\omega_\mu t+\phi)]\}\,, \tag{3}$$

where N_0 = a normalizing factor (counts/bin); B = time-independent background (random events); τ_μ = the mean muon lifetime, 2.20 μsec; A = "asymmetry" (relative amplitude of the precession); T_2 = transverse relaxation time (usually $\gtrsim$ a few μsec); ω_μ = muon Larmor frequency, 0.85×10^5 rad/sec per gauss; ϕ = phase of the precession at $t=0$.

A χ^2-minimization computer program determines the best values of all the parameters except τ_μ (which is known), and the uncertainty in the determination of each. The capability of the apparatus to record a very large range of time intervals with great accuracy makes possible a particularly precise determination of ω_μ and ϕ. The earlier experiment[10] used ω_μ to determine the muon magnetic moment to 2.6 ppm. In the present study, the measurement of ϕ is of special importance, since the behavior of the initial phase is very sensitive to the details of the depolarizing mechanism.[4]

III. FITS TO THE DATA

For each target, a histogram of times is accumulated and fitted as described above to yield values for A and ϕ. This procedure is repeated for a series of targets consisting of varying

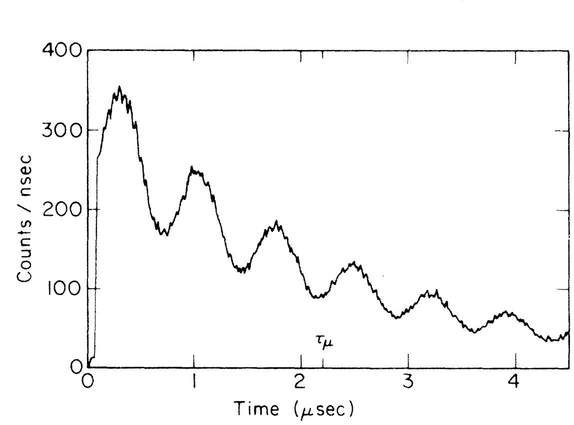

FIG. 2. Typical experimental histogram. Carbon tetrachloride at 100 G. The data is binned into 10-nsec bins for clarity; for fitting, 0.5-nsec bins were used. The mean muon lifetime τ_μ = 2.20 sec is indicated.

amounts of a given reagent "X" dissolved in a given solvent "S". Such a "titration technique" was first applied in an earlier study[17] as an important improvement upon the "method of competing acceptors" used by Babaev *et al.*[15] The concentration of the reagent is written $[X]$, and is usually expressed in moles/liter.

The resultant experimental dependence of A and ϕ upon $[X]$ is then compared with the predictions of the theory of the depolarizing mechanism, derived in Ref. 4. In fitting the data to this theory, two empirical parameters are introduced. First, the experimental asymmetry A is taken to be the product of the residual polarization $|P_{\text{res}}|$ and A_0, the limiting value of the asymmetry corresponding to no depolarization in the target. The quantity A_0 depends upon the beam polarization, counter geometry, target density, and the details of the weak decay; its fitted value is typically ~0.28. Second, the experimental phase includes the average angle ϕ_0 between the polarization direction of muons in the stopping beam and the axis of symmetry of the positron telescope. Thus, in the figures below showing best fits to the data, the quantities plotted against reagent concentration are $|P_{\text{res}}| = A/A_0$ and "phase" $= \phi - \phi_0$.

The theory-fitting program minimizes χ^2 to find the best values for the empirical parameters A_0 and ϕ_0 simultaneously with the following parameters of theoretical interest: h is the fraction of muonium atoms reacting epithermally to place the muon in diamagnetic compounds; k_{mxd} is the chemical rate constant for the reaction $\text{Mu} + X \rightarrow D$, where "$D$" is a diamagnetic molecule incorporating the muon; k_{msr} (or k_{mxr}) is the chemical rate constant for the reaction $\text{Mu} + S$ (or X)$\rightarrow R$, where "R" is a radical incorporating the muon; k_{rxd} is the chemical rate constant for the reaction $R + X \rightarrow D'$, where D' is a second diamagnetic species incorporating the muon, probably different from D.

The general theory derived in Ref. 4 has been restricted in these fits by several simplifying assumptions. First, "hot" reactions are presumed to lead only to diamagnetic compounds incorporating muons; radicals are assumed to form only in thermal chemical reactions. Second, relaxation of the spin of the muonium electron is assumed to be slow by comparison with the electron Larmor frequency, and is therefore neglected. This assumption is supported by ESR data on hydrogen atoms in solution.[18] Relaxation of the unpaired electron in radicals is likewise presumed to be negligible. Third, it is assumed that only one species of radical incorporating the muon is present in a given type of solution and that it is formed by chemical reaction with either the reagent ($k_{msr} = 0$) or the solvent ($k_{mxr} = 0$), but never both in the same solution. Finally, neither muonium nor the radical is presumed to react thermally with the solvent to form a diamagnetic species incorporating the muon, except at negligible rates ($< 10^7$ liter/mole sec). These assumptions give the simplest form of the theory which permits a good fit to all our data. Justifications and possible exceptions will be presented along with the results.

When the radical species "R" is assumed to be known, the hyperfine frequency ω_r in the radical is obtained by multiplying the ratio $\mu_\mu/\mu_p = 3.18$ of muon and proton magnetic moments into the measured value of the hyperfine frequency for the analogous radical in which the muon is replaced by a proton; these values are obtained from Landolt and Börnstein.[19] When the radical species is unknown, ω_r is fitted by trial and error, and the optimal value is used to make the best determinations of the parameters described above. In such cases, the choice of ω_r will dramatically affect the fitted values of the rate constants. This is because ω_r sets the time scale for depolarization in the radical, while the rate constants determine the duration of that chemical state. In general, when fitting data in which the radical stage plays an important role, we find that if we change ω_r by some factor, the resultant change in the fitted value of a given rate constant is never more than a similar multiplicative value. In the cases where ω_r is chosen by trial and error, the specified uncertainties in the rate constants shown below present only the tolerance of the fits for the specified choice of ω_r. An additional uncertainty, which could in some cases be as large as an order of magnitude, is implicit in the crude determination of ω_r. However, this degree of accuracy is still sufficient to allow many interesting comparisons with H-atom chemistry, as will be seen later. Most importantly, the qualitative conclusion that a radical depolarization mechanism is involved remains unaffected by these uncertainties. Further experiments may allow positive identification of the radical species or direct measurement of ω_r, thereby eliminating these ambiguities.

IV. RESULTS

A. Example of proper muonium mechanism: I_2 in CH_3OH

Figure 3 shows the observed dependence of residual polarization and phase upon the concentration of iodine in methanol solution in a magnetic field of 102 G. The leftmost point in this and all such graphs corresponds to the result for the pure solvent; owing to the log scale of the concentration,

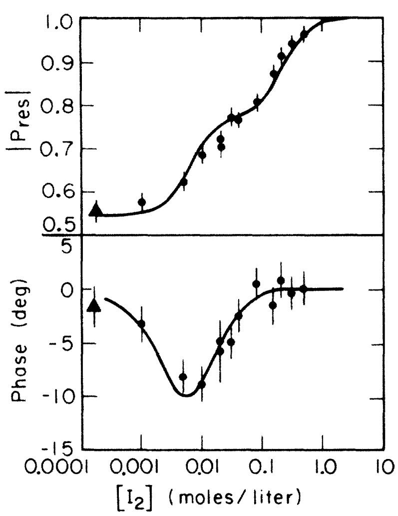

FIG. 3. Residual muon polarization in methanol as a function of the concentration of dissolved iodine. Best fit of the data to the proper muonium mechanism.

the point is actually infinitely far off scale to the left. The curve through the points is the best fit to the theory,[4] assuming that the muons are depolarized by the proper muonium mechanism (i.e., that no radical formation is involved). The chemical reaction involved is presumed to be

$$\mathrm{Mu} + \mathrm{I}_2 \xrightarrow{(k_{mxd})} \mathrm{MuI} + \mathrm{I}. \qquad (4)$$

The fraction of muonium atoms reacting epithermally with CH_3OH is $h \approx \frac{1}{2}$. The phase variation is striking, and the "plateau" in $|P_{res}([I_2])|$ is noticeable. Both of these phenomena are due to the coherent precession of free muonium atoms in the magnetic field, as explained in detail in Ref. 4, and constitute proof of the central role of muonium in the depolarization mechanism. If a substantial number of muons were placed in radical molecules, the effect (as will be seen later) would be to decrease the amplitude of the phase dip and to destroy the plateau. There does in fact seem to be a slight lessening of the plateau effect, and this may be due to a small but finite probability of reaction of muonium with CH_3OH to form a radical containing the muon, probably in epithermal collisions. This would constitute an exception to the assumption that hot-atom reactions lead only to diamagnetic muon environments. The quality of the fit is improved slightly by allowing some radical formation, but the correction is so small that the result is insensitive to the source, type, and fate of the radicals involved. Thus, since the mechanism is clearly dominated by reaction (4), this case may be practically considered to be an example of the proper muonium mechanism.

In an earlier paper[13] we reported similar results for I_2 in CH_3OH at fields of 1000 and 4500 G. The 100-G results are consistent with the earlier ones, but are much more conclusive, since the phase dip and plateau are most evident at low fields (see Ref. 4). The numerical results of these and other fits are listed in Tables I and II.

B. Evidence for radical formation in benzene

The muon asymmetry in benzene (C_6H_6) has long been known[20] to be exceptionally low, implying a hot fraction $h \approx \frac{1}{8}$, as compared to $h \approx \frac{1}{2}$ for methanol or water. This property makes benzene an attractive solvent for studies of muonium chemistry, since the range $(1-h)$ through which $|P_{res}|$ can be varied by chemical means is near maximum, and the amplitude of the phase dip is increased accordingly. Bromine was chosen as a muonium scavenger because of its virtually unlimited solubility in benzene and because of the analogy with iodine; the expected reaction in this case is

TABLE I. Asymmetry normalization and comparison of fit quality with and without radicals.

Solvent	Reagent	Field (G)	A_0	χ^2/degree of freedom No radicals	With radicals
CH_3OH	I_2	103	0.25 ±0.01	0.8	0.4
		1000	0.27 ±0.01	1.1	Same
		4500	0.27 ±0.01	0.6	Same
C_6H_6	Br_2	200	0.271±0.005	27	2.3
	I_2	200	0.272±0.03	11	0.4
H_2O	H_2O_2	100	0.26 ±0.01	7.4	0.8
	HNO_3	100	0.277±0.01	11	1.0
		4500	0.30 ±0.01	1.9	Same
	$FeCl_3$	4500	0.31 ±0.01	0.6	Same
	$Fe(ClO_4)_3$	100	0.29 ±0.03	8.3	0.6
		4400	0.30 ±0.02	0.6	Same
	$Fe(NO_3)_3$	11 000	0.35 ±0.02	7.7	Same

TABLE II. Results of best fits. Errors are approximate.

Solvent	Reagent	Field (G)	Radical	ω_r/ω_0	h	Rate constants (liter/mole sec)× 10^{-10} k_{mxd}	(Z)	k_{mzr}	k_{rxd}
CH_3OH	I_2	103	None	⋯	0.54 ± 0.02	13.4 ± 2	⋯	⋯	⋯
		1000	None	⋯	0.51 ± 0.02	13 ± 3	⋯	⋯	⋯
		4500	None	⋯	0.53 ± 0.02	13.4 ± 2	⋯	⋯	⋯
C_6H_6	Br_2	200	$C_6H_6Mu\cdot$	0.095	0.134 ± 0.01	9.4 ± 0.3	S	0.125 ± 0.05	0.36 ± 0.1
	I_2	200	$C_6H_6Mu\cdot$	0.095	0.133 ± 0.07	5.7 ± 1	S	0.054 ± 0.03	0.2 ± 0.1
H_2O	H_2O_2	100	$MuO\cdot$	0.083	0.59 ± 0.01	0.24 ± 0.05	X	0.85 ± 0.1	0.14 ± 0.02
	HNO_3	100	?	0.125 ± 0.05	0.545 ± 0.01	3 ± 1	X	10 ± 5	0.1 ± 0.01
	$Fe(ClO_4)_3$	100	?	$0.010^{+0.040}_{-0.005}$	0.52 ± 0.03	$0.57^{+0.8}_{-0.4}$	X	3.8 ± 0.8	0.02 ± 0.002
	$FeCl_3$	4500	None (?)	⋯	0.51 ± 0.02	2.1 ± 0.2	⋯	⋯	⋯

$$\mathrm{Mu} + \mathrm{Br}_2 \xrightarrow{(k_{mxd})} \mathrm{MuBr} + \mathrm{Br}\,. \tag{5}$$

Data were taken in a 200-G magnetic field so that the "plateau" would be visible.

However, as can be seen in Fig. 4, the results are in strong disagreement with the predictions of the proper muonium mechanism, the best fit for which is indicated by the dashed lines. There is no discernible plateau, and the phase variation is much less sharp than predicted by the simple theory. The results in fact resemble the predictions of the proper muonium mechanism in a stronger magnetic field. Since the criterion for a "strong" field is that it be comparable with the effective hyperfine field (see Ref. 4), this observation led to consideration of environments similar to muonium but with lower values of the effective hyperfine field (e.g., radicals).

On the basis of other chemical studies,[21,22] we make the following assumptions about the chemical processes involved: First, that the reaction

$$\mathrm{Mu} + \mathrm{C}_6\mathrm{H}_6 \xrightarrow{(k_{msr})} \mathrm{C}_6\mathrm{H}_6\mathrm{Mu}\,\cdot \tag{6}$$

(where the dot after the symbol designates a free radical), forming the muonium analog of the radical cyclohexadienyl ($C_6H_7\cdot$), is in competition with reaction (5) for muonium. Second, the radical is presumed to react subsequently with bromine to place the muon in a diamagnetic compound, according to

$$\mathrm{C}_6\mathrm{H}_6\mathrm{Mu}\cdot + \mathrm{Br}_2 \xrightarrow{(k_{rxd})} D\ (\text{unidentified})\,. \tag{7}$$

The isotropic average effective hyperfine field at the unpaired electron due to the extra proton in cyclohexadienyl is 47.71 G,[19] as compared with 1588 G in muonium; thus the ratio of the hyperfine frequency ω_r in $C_6H_6Mu\cdot$ to the hyperfine frequency ω_0 in muonium is taken to be

$$\frac{\omega_r}{\omega_0} = \frac{47.71\,\mu_\mu/\mu_p}{1588} = 0.095\,. \tag{8}$$

This value was used to obtain the best fit to the data (solid lines in Fig. 4) corresponding to the best values for the fitted parameters, as listed in Tables I and II; a trial-and-error search for the best empirical value for ω_r/ω_0 gave a minimum χ^2 for $\omega_r/\omega_0 \approx 0.03^{+0.04}_{-0.02}$.

Although it was not possible to dissolve enough iodine in benzene to achieve full "repolarization," we were able to study the dependence of P_{res} upon $[I_2]$ in C_6H_6 over a large enough region to determine that the results were consistent with those observed for Br_2 in C_6H_6. These results are also listed in Tables I and II.

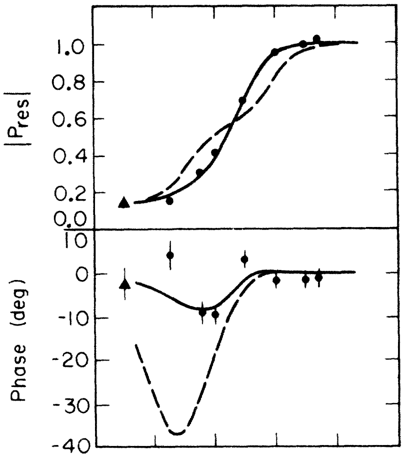

FIG. 4. Residual muon polarization in benzene as a function of the concentration of dissolved bromine. Uncertainties of $|P_{res}|$ data are less than the dimensions of the points. Dashed curve: best fit without radicals; solid curve: best fit with radicals.

C. Mu chemistry in aqueous solutions

In spite of its rather large hot fraction ($h \sim \frac{1}{2}$), water has proved to be a nearly optimal solvent for muonium chemistry. Most important, our results show that H_2O is, more or less inert with respect to thermal chemical reactions with Mu—that is, any reaction of Mu + H_2O has a rate constant $< 10^7$ liter/mole sec. Thus all significant thermal reactions of muonium are with the reagent. This situation would be expected to favor many examples of the proper muonium mechanism, but instead we have found a number of more complicated mechanisms, all involving radicals.

1. Hydrogen peroxide

Perhaps the most elegant system we have studied is Mu with H_2O_2 in H_2O. The experimental dependence $P_{\text{res}}([H_2O_2])$ at a field of 100 G is shown in Fig. 5 along with the best fits to the data. Again, the dashed curve is the best fit with the proper muonium mechanism, and the solid curve is the best fit with the general mechanism, including radicals. Clearly radicals are present. In this case we assume that the muonium reacts with hydrogen peroxide to form a diamagnetic compound containing the muon, presumably according to

$$\mathrm{Mu} + \mathrm{H_2O_2} \xrightarrow{(k_{mxd})} \mathrm{HO}\cdot + \mathrm{MuHO}\,, \tag{9}$$

and (competitively) to form a muonic radical, presumably according to

$$\mathrm{Mu} + \mathrm{H_2O_2} \xrightarrow{(k_{mxr})} \mathrm{MuO}\cdot + \mathrm{H_2O}\,, \tag{10}$$

and that the radical MuO· subsequently reacts with H_2O_2 to leave the muon in a final diamagnetic environment:

$$\mathrm{MuO}\cdot + \mathrm{H_2O_2} \xrightarrow{(k_{rxd})} D' \text{ (unidentified)}\,. \tag{11}$$

These assumptions are consistent with most interpretations of H-atom reactions with H_2O_2, as described later. Nevertheless, it is possible that the radical species has been misidentified. If, for instance, the predominant radical species were $MuO_2\cdot$ rather than MuO·, the value assumed for ω_r would be incorrect, possibly introducing errors of as much as an order of magnitude in the rate constants, as discussed previously. However, regardless of possible ambiguities in the identification of chemical species, the conclusion that the presence of radicals is essential to the over-all depolarization mechanism is inescapable.

The effective hyperfine field at the unpaired electron due to the proton in the hydroxyl radical HO· is known[19] to be 41.3 G (isotropic average), which would imply $\omega_r/\omega_0 = 0.0825$ for MuO· [recall Eq. (8)]. This value was used to obtain the results listed in Tables I and II. The empirical value giving a minimum χ^2 was $\omega_r/\omega_0 = 0.175 \pm 0.1$, consistent with the predicted value.

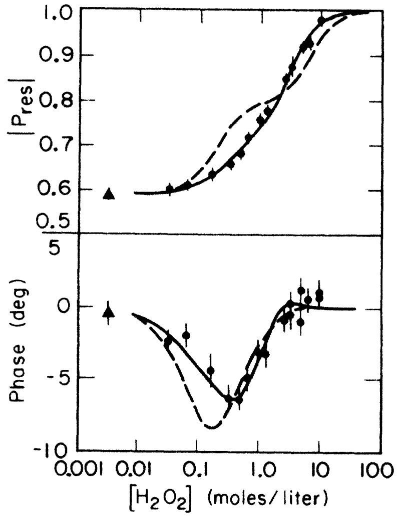

FIG. 5. Residual muon polarization in water as a function of the concentration of dissolved hydrogen peroxide. Dashed curve: best fit without radicals; solid curve: best fit with radicals.

2. Strong acids

Preliminary results show a great deal of variety in the reactions of muonium with various acids. In HCl, as noted earlier by Swanson,[20] there seems to be no "repolarizing" effect at any concentration. The muon precession in 10*M* HCl is virtually indistinguishable from that in pure water. Therefore, no combination of reactions between, Mu, H^+, and Cl^- leads to a diamagnetic compound containing the muon in times shorter than about 10 nsec. Similar results in concentrated $MnCl_2$ solutions indicate that these conclusions are relatively independent of pH.

However, addition of nitric acid to water causes marked "repolarization," with a maximal asymmetry reached at about 10*M*. Experimental results for $P_{\text{res}}([HNO_3])$ at 100 G are shown in Fig. 6. We assume that HNO_3 dissociates sufficiently that the Mu reacts predominantly with the anion, NO_3^-. Again, the proper muonium mechanism (dashed curve) is a poor fit, but an excellent fit (solid curve) can be obtained if we assume the following reactions are significant: First, the usual direct reaction leading to a diamagnetic compound:

$$\mathrm{Mu} + \mathrm{NO_3^-} \xrightarrow{(k_{mxd})} D \text{ (unidentified)}\,; \tag{12}$$

in addition, the competitive reaction leading to a muonic radical:

$$\mathrm{Mu} + \mathrm{NO}_3^- \xrightarrow{(k_{mxr})} R \text{ (unidentified)}, \qquad (13)$$

followed by the final reaction of the radical to place the muon in a diamagnetic environment:

$$\mathrm{R} + \mathrm{NO}_3^- \xrightarrow{(k_{rxd})} D' \text{ (unidentified)}. \qquad (14)$$

Here we have not attempted to identify any of the product species but only the types of processes taking place; all the fitted results listed in Table II, including ω_r/ω_0, are obtained by minimizing χ^2. Results for $P_{\mathrm{res}}([\mathrm{HNO}_3])$ at a field of 4500 G are consistent with these, but are much less sensitive to the presence of radicals.

Similar results are seen for solutions of HClO_4 in water at 4400 G. However, we have not yet undertaken a study of HClO_4 at low field, where the results are sensitive to radical formation, so the existing data are interpreted only in terms of the proper muonium mechanism. Such interpretation predicts a rate constant $k(\mathrm{Mu} + \mathrm{HClO}_4) \approx 10^9$ liter/mole sec.

3. *Ferric salts*

The quenching effect of ferric ions on μ^+ depolarization has been reported earlier. Results for $\mathrm{Fe(NO_3)_3}$ at 11 kG were first interpreted strictly in terms of a strong relaxation of the muonium electron by Fe^{3+} ions, assuming the rate ν_m of that relaxation to be proportional to Fe^{3+} concentration.[17] Although this mechanism may be present, the model considered in Ref. 7 included this additional assumption that the mean chemical lifetime of muonium was independent of reagent concentration, which is clearly incorrect. Results for FeCl_3 and $\mathrm{Fe(ClO_4)_3}$ at 4500 G were treated as evidence for the proper muonium mechanism,[13] with the assumption that the only important reaction was

$$\mathrm{Mu} + \mathrm{Fe}^{3+} \xrightarrow{(k_{mxd})} \mu^+ + \mathrm{Fe}^{2+}, \qquad (15)$$

where either the free muon itself or the product of its subsequent reaction with anions in the solution constitutes a diamagnetic environment for the muon. In light of the lack of reaction of muonium with HCl, we might expect the system Mu + FeCl_3 in $\mathrm{H_2O}$ to provide a good example of the proper muonium mechanism. Results at 4500 G are consistent with this assumption, but low-field measurements must be made to test for the presence of radicals in the depolarizing mechanism.

Results for $\mathrm{Fe(NO_3)_3}$ and $\mathrm{Fe(ClO_4)_3}$ at high field should not be interpreted strictly in terms of the proper muonium mechanism. The conclusive evidence for radical formation in nitric acid suggests that muonium might form radicals in $\mathrm{Fe(NO_3)_3}$ solutions as well; again, low-field data may resolve this question. For $\mathrm{Fe(ClO_4)_3}$ there is no doubt that radical formation is involved. Figure 7 shows the experimental dependence $P_{\mathrm{res}}[\mathrm{Fe(ClO_4)_3}]$ at 100 G. The best fit without radicals (dashed curve) is very poor; only by assuming that muonium reacts with dissolved $\mathrm{Fe(ClO_4)_3}$ to

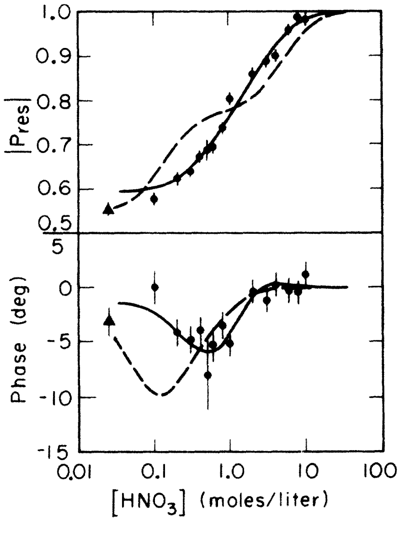

FIG. 6. Residual muon polarization in water as a function of the concentration of dissolved nitric acid. Dashed curve; best fit without radicals; solid curve: best fit with radicals.

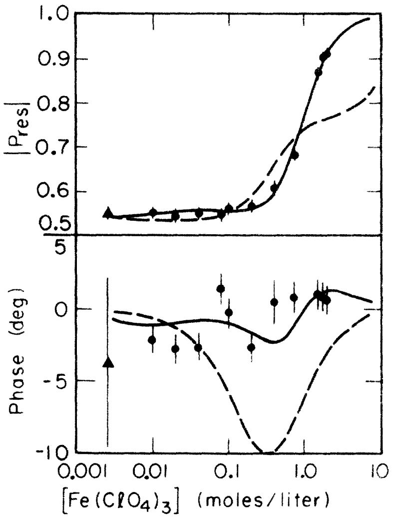

FIG. 7. Residual muon polarization in water as a function of the concentration of dissolved ferric perchlorate. Dashed curve: best fit without radicals; solid curve: best fit with radicals.

form a muonic radical can we obtain an acceptable fit (solid curve). The situation here is formally the same as in reactions (12)–(14) for NO_3^-, with the additional process (15) for Fe^{3+}. Again, we do not attempt to identify chemical species. The results listed in Tables I and II are obtained by minimizing χ^2. The existence of muonic radicals in $Fe(ClO_4)_3$ solutions leads us to expect that radical formation will be found to play an important role in $HClO_4$ as well; low-field measurements should confirm this.

It should be mentioned here again that the muonium "spin-flip" frequency, ν_m, may not be negligible in solutions of paramagnetic ions. Although the absence of any significant "repolarization" in concentrated Mn^{2+} solutions[13] demonstrates that the repolarizing effect of other paramagnetic reagents are due mainly to the types of chemical mechanisms described above, some concentration-dependent muonium relaxation (as postulated in Ref. 17) could serve to partially quench the phase variations and generally mimic the effects of radicals shown in Fig. 7. Consequently, estimates of the contribution of radicals to the depolarization mechanism in paramagnetic solutions are to be regarded as tentative, pending further clarifying experiments.

D. Conclusions regarding the model

Several of the above results are particularly important in resolving certain controversies about the theory. First, the results for I_2 in CH_3OH at 102 G firmly establish that the residual polarization in pure methanol is due solely to hot-atom chemistry. If, as claimed by Babaev *et al.*,[15] $P_{res}(CH_3OH)$ were nonzero due to thermal classical reaction of the type

$$\mathrm{Mu} + CH_3OH \xrightarrow{(k_{msd})} D \text{ (unidentified)}, \qquad (16)$$

muonium atoms would never remain uncombined long enough to precess, and there could be no phase dip. In fact, such reactions must be totally unimportant to the mechanism in order to explain the return of the phase to zero as $[I_2] \to 0$. Therefore, we can confidently state that $k_{16} < 10^7$ liter/mole sec and that the fraction of muonium reacting epithermally with methanol at room temperature is $h(CH_3OH) = 0.53 \pm 0.01$. Similarly, the results for benzene indicate $h(C_6H_6) = 0.13 \pm 0.01$, but are not as conclusive regarding $k_{msd}(C_6H_6)$, due to the small phase dip. However, since the asymmetry in pure benzene is so small, we can still be sure that $k_{msd}(C_6H_6) < 10^8$ liter/mole sec.

The incomplete depolarization in water is also exclusively due to hot atom chemistry, as is especially clear from the curves of P_{res} versus hydrogen peroxide concentration in water. This is somewhat surprising in light of the marked drop in $P_{res}(H_2O)$ as water freezes, which was earlier interpreted in terms of thermal chemistry.[23] Further theoretical and experimental studies of the temperature dependence of the hot fraction may provide valuable information about the dynamics of that process.[24] Our best value for $h(H_2O)$ is 0.55 ± 0.03; the anomalously high value (0.59 ± 0.01) of $h(H_2O)$ obtained in the fit of the H_2O_2 results is probably a reflection of the low value for A_0 in the same instance, which in turn could be due to the low density of concentrated H_2O_2 solutions compared to other concentrated aqueous solutions. A higher-density target gives a slightly increased A_0; such variations of A_0 with density are not allowed for in the fits. This introduces a systematic error of ~5% in the numerical results for A_0 and h, but does not significantly distort the other results.

The second general conclusion to be drawn from these results is that formation of fast-reacting radicals plays a central role in many (if not most) examples of μ^+ depolarization in liquids. If the radicals formed by reactions of Mu were relatively stable, or if radicals were rarely formed at all (proper muonium mechanism), the model formulated by Ivanter and Smilga in Ref. 9 would be completely adequate for analysis of muonium chemistry. It is clear, however, that the more general case derived in Ref. 4 is necessary for most practical applications; the new formalism also has the advantage of being rather easy to modify by adding new processes not yet included.

These sensitive distinctions between mechanisms would be impossible without the new technique of measuring variations of the initial phase of P_{res}, effectively doubling the amount of useful information available in comparing theory with experiment. Since longitudinal-field measurements lack this extra information, transverse-field data are clearly advantageous for such applications.

The most important consequence of these advances in theory and experimental technique is the promise of their application to the quantitative study of muonium hot-atom chemistry and fast thermal chemical reactions of muonium and muonic radicals. The results we obtain in various solutions are typical of the sort of chemical information available from this technique. Their interpretation in light of the analogy between muonium and atomic hydrogen is the subject of Sec. V.

V. COMPARISON WITH H-ATOM CHEMISTRY

Absolute rates of reaction in solution are difficult to estimate reliably from first principles, due to the complexity of the processes involved. It is possible, however, to make some qualitative predictions of how rates will depend upon the mass of one reactant when all other physical parameters are held constant. Such pure isotope effects can be expected in reactions of Mu and H atoms, which have the same size and ionization potential (within 1%)[1] but different masses: $m_{\mathrm{Mu}}/m_{\mathrm{H}}=0.1131$.

A naive argument based on gas-phase kinetics predicts[2,13] that the rate constants will depend upon the mass m of Mu or H only through the mean thermal velocity $\bar{v}\propto 1/\sqrt{m}$, which determines the rate at which the light, mobile Mu or H atoms collide with the heavier, nearly stationary reagent molecules. This picture predicts the "kinetic ratio"

$$\frac{k\,(\mathrm{Mu}+X)}{k(\mathrm{H}+X)}=\left(\frac{m_{\mathrm{H}}}{m_{\mathrm{Mu}}}\right)^{1/2}\approx 3\,.$$

Unfortunately, such a treatment is only appropriate for gases, where the mean free path is many molecular radii and the concept of a " collision rate" is well defined. In liquids, each reagent molecule is continually surrounded by a "cage" of solvent molecules which severely restrict its thermal motion.[25] The reactants must diffuse through this crowded environment to find each other, and when they do approach they are apt to stay in each other's presence for some time. The probability of reaction in such a prolonged "encounter" is often close to unity. Such reactions are called "diffusion controlled" (DC), since the rate of reaction depends only upon how fast the reactants diffuse through the solvent to meet each other. Since diffusion in liquids proceeds primarily by "squeezing" and "tumbling," such rates are largely determined by the geometrical properties of solvent and reactant molecules, and the mass dependence is generally weaker than in gases. In some cases DC rates may be independent of the mass of the reactants, all other parameters being held constant.

A rough estimate of the diffusion controlled rate for reactions of Mu atoms in water or methanol is $k_{\mathrm{DC}}(\mathrm{Mu})\approx 10^{11}$ liter/mole sec. Most of our measured rate constants for Mu are near this limiting value. Rate constants less than k_{DC} usually reflect an "activation energy" E_a required to form the activated complex $\mathrm{HX}^{\ddagger}$ (the double dagger is a standard way of indicating an activated complex) in the reaction $\mathrm{H}+X\rightarrow \mathrm{HX}^{\ddagger}\rightarrow$ products.[26] The rate constant then acquires an exponential temperature dependence via the Boltzmann distribution: $k\propto e^{-E_a/k_BT}$. The quantity E_a may depend upon factors such as the vibrational frequencies of bonds formed in the activated complex, which may in turn depend upon the mass of the light atom. Even in the case of diffusion-controlled reactions, the diffusion process itself requires an activation energy[26,27] which may depend upon mass. In addition, quantum mechanical tunneling, which may be important for many reactions of H,[28] can be expected to be quite significant for muonium. Such "dynamic" isotope effects can cause dramatic differences between $k(\mathrm{Mu}+X)$ and $k(\mathrm{H}+X)$.

Table III shows a comparison between Mu and H rate constants for the most unambiguous reactions we have studied.

TABLE III. Comparison of over-all rate constants of H and Mu with various reagents. Rate constants are in units of liter/mole sec. Source of values for H is Anbar and Neta (Ref. 29) except where otherwise specified.

	Hydrogen		Muonium		
Reagent	Solvent	k_{H}	Solvent	k_{Mu}	$k_{\mathrm{Mu}}/k_{\mathrm{H}}$ (approx.)
CH_3OH	H_2O	$(1.6\pm 0.1)\times 10^{6}$	CH_3OH	$<10^{7}$	...
C_6H_6	H_2O	$(7\pm 3)\times 10^{8}$ [a]	C_6H_6	$(8^{+5}_{-3})\times 10^{8}$	1
H_2O	H_2O	*Nil*	H_2O	$<10^{7}$	...
I_2	H_2O	4×10^{10}	CH_3OH	$(13.3\pm 1)\times 10^{10}$	3
			C_6H_6	$(5.7\pm 1)\times 10^{10}$	1
Br_2	H_2O	$(12\pm 6)\times 10^{10}$ [b]	C_6H_6	$(9.4\pm 0.3)\times 10^{10}$	1
H_2O_2	H_2O	$(9\pm 5)\times 10^{7}$ [c]	H_2O	$(1.09\pm 0.15)\times 10^{10}$	100
NO_3^-	H_2O	$(9\pm 5)\times 10^{6}$ [d]	H_2O	$(13\pm 6)\times 10^{10}$	10^4
ClO_4^-	H_2O	*Nil*	H_2O	$\sim 4\times 10^{10}$	?

[a] Sauer and Ward (Ref. 20) and Michael and Hart (Ref. 21).

[b] Farhataziz (Ref. 30).

[c] Sweet and Thomas (Ref. 31).

[d] Navon and Stein (Ref. 32).

A. Rates near the diffusion-controlled limit

We extract a rate constant $k_4 = (1.33 \pm 0.1) \times 10^{11}$ liter/mole sec for reaction (4) of Mu with I_2 in CH_3OH. This is near the DC limit for muonium in methanol. The corresponding H atom rate has been measured in aqueous solution[29] to be 4×10^{10} liter/mole sec, in qualitative agreement with our résult. The rate constant $(5.7 \pm 1) \times 10^{10}$ liter/mole sec for $Mu + I_2$ in C_6H_6 indicates that diffusion of Mu through benzene is about one-half as fast as through methanol, if reaction (4) is truly diffusion-controlled. Such an assumption is supported by the fact that the rate constant $k_5 = (9.4 \pm 0.3) \times 10^{10}$ liter/mole sec for reaction of Mu with Br_2 in C_6H_6 is nearly the same as with I_2. This value agrees well with the measured[30] rate $(12 \pm 6) \times 10^{10}$ liter/mole sec for $H + Br_2$ in water.

B. Reactions with solvents

The rate constant for $H + CH_3OH$ in aqueous solution is[29] $(1.6 \pm 0.1) \times 10^6$ liter/mole sec. While this result cannot rigorously be compared with our rate in pure CH_3OH, where diffusion is irrelevant, it does qualitatively corroborate our value $k_{16} < 10^7$ liter/mole sec for $Mu + CH_3OH$. The reaction rate of thermalized H atoms with benzene to form cyclohexadienyl [analogous to reaction (6)] was measured by pulsed radiolysis in aqueous solution[20,21] to be about $(7 \pm 3) \times 10^8$ liter/mole sec, whereas we measured $k_6 = (8^{+5}_{-3}) \times 10^8$ liter/mole sec in the pure solvent. Again, these two rates in different solvents cannot legitimately be compared in an absolute sense; nevertheless, the fact that they agree constitutes some justification for the assumption that the radical is formed by thermal, rather than "hot atom," reactions. In water, our results are consistent with $k(Mu + H_2O) < 10^7$ liter/mole sec. We are not aware of any evidence for fast reactions of H with H_2O.

C. Reactions of muonium in aqueous solution

1. Hydrogen peroxide

The basic reaction of H with hydrogen peroxide is thought to be[31]

$$H + H_2O_2 \rightarrow HO\cdot + H_2O\,. \tag{17}$$

The rate constant for this reaction has been measured[31] over a range of pH to be $k_{17} = (9 \pm 5) \times 10^7$ liter/mole sec. The reaction is presumed to involve a cleavage of the O-O single bond, but from the above equation it is impossible to tell whether the original H atom emerges in the H_2O as in reaction (9) ("OH abstraction") or in the $HO\cdot$ as in reaction (10) ("O abstraction"). Our results indicate k_{10} nearly 4 times higher than k_9. One would expect $k_9 + k_{10}$ to be the Mu rate analogous to k_{17}; we find $k_9 + k_{10} = (1.09 \pm 0.15) \times 10^{10}$ liter/mole sec, roughly a factor of 100 higher than the corresponding H atom rate. Such a large anomaly is probably attributable to dynamic isotope effects. Even a gross error in our assumed value of ω_r (caused, for instance, by misidentification of the radical) would not explain such a discrepancy between the two rate constants.

2. Strong acids

Since HCl, HNO_3, and $HClO_4$ are all highly dissociated in aqueous solutions, their reactions with Mu can be considered primarily in terms of the ionic species H^+, Cl^-, NO_3^-, and ClO_4^-. As mentioned earlier, HCl solutions up to $10M$ do not repolarize the muon; we must conclude that no combination of reactions with H^+ and/or Cl^- leads to a stable diamagnetic environment for the muon in times less than about 10^{-8} sec.

In nitric acid, on the other hand, we measure a net reaction rate $k(Mu + NO_3^-) = k_{12} + k_{13} = (1.3 \pm 0.6) \times 10^{11}$ liter/mole sec, an essentially diffusion-controlled rate. This result is a factor of 10^4 higher than the measured[32] H-atom rate constant $k(H + NO_3^-) = (9 \pm 5) \times 10^6$ liter/mole sec. Assuming that we have measured the rates of the same reactions, such a dramatic isotopic effect probably reflects a tunneling process.[28] As in the case of H_2O_2, such a large discrepancy cannot be explained simply by postulating an error in ω_r.

As a test of pH dependence, we ran one solution of concentrated $NaNO_3$ and found complete repolarization, as for concentrated HNO_3. While a full curve of $P_{res}([NaNO_3])$ is necessary to clarify the details of the chemical processes involved, this single measurement is sufficient to indicate that Mu reacts with NO_3^- at approximately the same rate, independent of the presence of H^+. Also, highly reactive species such as NO_2, O_2, and NO_2^- should not have been present in significant concentrations in the freshly prepared $NaNO_3$ solution.

We have also studied muon repolarization by $HClO_4$ in high magnetic field. A fast reaction is suggested, $k(Mu + ClO_4 \rightarrow D) \approx 10^9$ liter/mole sec, for the complete process leaving the muons in diamagnetic compounds. Until studies are made in low field, the details of the process are uncertain. However, we can predict that radical formation is important on the basis of results at 100 G with $Fe(ClO_4)_3$, which show a rate constant $k_{mxr} = (3.8 \pm 0.8) \times 10^{10}$ liter/mole sec. Here Fe^{3+} is unlikely to react with Mu to produce a radical, so we expect that this rate represents

k_{18} for the reaction

$$\mathrm{Mu} + \mathrm{ClO_4}^- \xrightarrow{(k_{mxr})} (\text{muonium-containing radical}) . \tag{18}$$

Since reactions of H atoms with $\mathrm{ClO_4}^-$ are regarded as virtually nil,[29] we again have a dramatic disagreement between Mu and H rates.

3. *Ferric salts*

The data for $\mathrm{Fe(ClO_4)_3}$ at 100 G provide us with detailed information about the rates and qualitative features of several reactions, but the large number of species involved complicates the extraction of rates of specific reactions of Mu with $\mathrm{Fe^{3+}}$ and/or $\mathrm{ClO_4^-}$ to produce both diamagnetic and paramagnetic products. In strong fields, even less detail is available[4] from the data, and in the case of $\mathrm{Fe(NO_3)_3}$ we can only conclude that a fast reaction does take place.

The situation with $\mathrm{FeCl_3}$ solutions should be much simpler, since Mu does not appear to react significantly with $\mathrm{Cl^-}$. Interpreting the high-field data on $\mathrm{Mu} + \mathrm{FeCl_3}$ strictly in terms of reaction (15), we obtain a rate constant $k_{15} = (2.1 \pm 0.2) \times 10^{10}$ liter/mole sec. The H atom rate constant for the direct oxidation-reduction reaction analogous to (15) has been measured[29] to be $(9 \pm 1) \times 10^7$ liter/mole sec in moderately acidic solutions such as ours. Taken at face value, our rate is 200 times that for hydrogen. However, it is unlikely that the process involved is as simple as reaction (15). Ferric ions are known[33] to form complexes in solution, in particular $\mathrm{FeCl^{2+}}$ and $\mathrm{FeCl_2}^+$, whose rate constants for reaction with H atoms are respectively 4.5 and 9.0×10^9 liter/mole sec (see Ref. 29). It is possible that we actually observed reactions of Mu with one or both of these species.

D. Reactions of radicals

The μ^+ depolarization technique also allows measurement of rate constants for reactions of various radicals incorporating muonium. This capability is a direct result of the expansion of the theory[4] to incorporate reactive radicals. In comparing these rate constants with the corresponding rates for analogous radicals in which the muon is replaced by a proton, the difference in masses of Mu and H should affect only the "dynamics" of the processes. Even MuO$\cdot$, the lightest muonic radical envisoned, should diffuse through liquids at the same rate as HO$\cdot$, its protonic analog. Comparisons of reaction rates of muonic and protonic versions of these radicals should therefore admit of straightforward interpretation in terms of the dynamics of the activated complex.

The most serious difficulty with this interpretation is the uncertainty as to which radical is actually being produced. In the cases of $\mathrm{HNO_3}$ and $\mathrm{Fe(ClO_4)_3}$ solutions, for instance, we do not attempt to identify the radical species. The fitted value for ω_r/ω_0, while imprecise, does provide a hint as to likely candidates, suggesting MuO$\cdot$ in the case of $\mathrm{HNO_3}$ and some species with a weaker hyperfine coupling in the case of $\mathrm{Fe(ClO_4)_3}$. However, this cannot be regarded as conclusive evidence, and the products of reactions (13) and (18) must be regarded as unknown. It would be possible to determine the hyperfine coupling in the radicals to higher precision by using a longitudinal-field technique, but this has not yet been undertaken.

In some cases it is possible to deduce the identity of the radical, if there is only one species of "reagent" and the products of its reaction with H are well known. In hydrogen peroxide solutions, for instance, it seems most probable that reactions (9) and (10) should dominate,[31] making MuO$\cdot$ the most likely radical species. Our value for the rate constant for reaction of MuO$\cdot$ with $\mathrm{H_2O_2}$ is $k_{11} = (1.4 \pm 0.2) \times 10^9$ liter/mole sec. The corresponding rate for $\mathrm{HO\cdot} + \mathrm{H_2O_2}$ is[29] about $(3 \pm 2) \times 10^7$ liter/mole sec, a factor of 50 slower. Unless we have misidentified the radical, this difference is almost certainly due to dynamic isotope effects in the $(\mathrm{MuO} + \mathrm{H_2O_2})^\ddagger$ complex.

The addition of H to benzene to form cyclohexadienyl is also a well-established reaction,[22] a fact which lends credence to the assumption that $\mathrm{C_6H_6Mu\cdot}$ is the radical involved in reactions (6) and (7). We are unaware of any measurement of the reaction rates for $\mathrm{C_6H_7\cdot}$ with $\mathrm{Br_2}$ or $\mathrm{I_2}$; our measurements of $k(\mathrm{C_6H_6Mu\cdot} + \mathrm{Br_2}) = (3.6 \pm 1.0) \times 10^9$ liter/mole sec and $k(\mathrm{C_6H_6Mu\cdot} + \mathrm{I_2}) = (2 \pm 1) \times 10^9$ liter/mole sec may represent the only information available on these reactions. In view of the large size of the $\mathrm{C_6H_6Mu\cdot}$ molecule and the similarity of the rates with $\mathrm{Br_2}$ and $\mathrm{I_2}$, the reaction is probably diffusion controlled in liquids.

E. Prospects for muonium chemistry

In summary, there are evidently a number of startling exceptions to the naive expectation[2,13] that Mu and H should react at similar rates in analogous processes. The present results, far from settling the issue, call for further investigations, both experimental and theoretical. Although experimentally difficult, attempts should be made to measure radical hyperfine frequencies directly. Moreover, interpretation of the experimental data could be refined by taking into account hitherto neglected components of the μ^+ depolarization process. The accuracy of H atom measurements may also need critical examination. It should be clear from our results, however, that such comparisons of Mu and H atom chemistry are feasible, and that one may expect to encounter large differences in rates. The interpretation and final understanding of these differences, presumably in terms of dynamic isotope effects, may be of great significance to the chemical physics community.

ACKNOWLEDGMENTS

We are indebted to J. Vale and the crew of the 184-in. cyclotron for cooperation and assistance in running the experiment. We are also grateful to Dr. D. C. Walker of the University of British Columbia Chemistry Department, Dr. M. Anbar of Stanford Research Institute, and several members of the Berkeley Chemistry Department for helpful discussions regarding the chemical interpretations of our results. One of the authors (F. N. G.) would like to thank SIN and Dr. J. P. Blaser of the Swiss Institute of Technology in Zurich for making it possible for him to participate in μ^+ depolarization research at LBL.

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

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