

CERN  $\mu$ SR COLLABORATIONPROPOSAL FOR A NEW SC EXPERIMENT  
"MUONS AND MUONIUM IN MOLECULAR PHYSICS"

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A new experimental code is requested under which the Collaboration would extend the scope of its application of the  $\mu$ SR technique to molecular physics and chemistry. The new code would cover fundamental aspects of the radiation chemistry of the positive muon, the formation of atomic muonium, and the nature and mechanism of the muon's association with molecules of different characteristics. The scientific background and the detailed proposal are presented. No substantial new allocation of resources to the Collaboration is sought from CERN.

The proposal fulfills the Collaboration's statement of intent registered by the PSCC at its meeting in May 1982 <sup>1</sup>(CERN/PSCC/82-83, PSCC M105).

## 1. INTRODUCTION

Experiment SC82 was begun as a simple attempt to substitute positive muons into polymer molecules, and thereby to use the  $\mu$ SR technique to study the mechanical relaxation of the different molecular groups. The experiment has since developed in several directions and has produced a wealth of information on the properties of muonic molecules, and adequately demonstrated the enormous potential of  $\mu$ SR as applied to molecular physics and chemistry <sup>2,3</sup>(CERN EP/81-166,167).

These developments were in answer to questions raised by the early experiments:

- with which chemical substances will the positive muon readily associate or "react"?
- what is the nature of the association, and the mechanism of the reaction?
- what are the properties of the muonic molecules created?

Most fruitful were our studies of muonic free radicals in organic solvents and monomers. Apart from the sheer novelty of the species created, various aspects of the results may be noted. The first arises from considering the positive muon for these purposes simply as a lightweight proton ( $m \sim 1/9m_p$ ). Properties of the molecules which are susceptible to isotope effects may then be examined critically. The mass range previously accessible to chemists through replacement of hydrogen with deuterium (or exceptionally tritium) is greatly extended. A particularly severe isotope test of our understanding of these properties becomes possible.

This is true not only of the properties of the final product (for instance isotope effects in the hyperfine interaction constants may be interpreted in terms of the conformation, the vibration or the rotation of molecular groups<sup>2,4</sup>) but also in the selectivity of the muon or muonium addition, which may be compared with that for protons or atomic hydrogen.

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A second aspect concerns chemical properties of the molecule which are unaffected by the muonic substitution. The muon can then be regarded simply as a "radio-active proton" which conveniently labels the molecule and allows its intrinsic behaviour to be observed. Thus in muonic radicals the muon is sufficiently far from the active centre of the molecule not to affect its reactivity, yet the  $\mu$ SR signal allows a direct measurement of the rate of chemical reaction<sup>3,5</sup>

Somewhere between these limits the example may also be cited of the use of  $\mu$ SR to measure the rate of internal rearrangement of a molecule<sup>6</sup>

The more fundamental questions raised by these experiments, those concerning for instance the mechanism of the radical formation, have proved more difficult to answer. There is for instance a tantalising indication from the phases of our  $\mu$ SR signals<sup>2</sup> that the radical precursor may not be atomic muonium, as is generally supposed.

Neither is all the incoming muon polarisation recovered in the radicals created - that is in the paramagnetic products. A proportion is always observed at (or very close to) the muon Larmor frequency. Since the muon - by analogy with the proton - cannot remain chemically free, this is supposed to represent products in which the muon is in diamagnetic association with the host molecules. The exact nature of the association remains unknown, although our study of how the diamagnetic fraction may be correlated with various electronic properties of the host molecules reveals how progress may be made in identifying these products<sup>3</sup>

in addition, a proportion of the polarisation is often completely unaccounted for. Sometimes attributable to a depolarisation of the muonium component by nuclear spins or magnetic impurities, this "missing fraction" remains in many cases a longstanding puzzle.

## 2. PROJECT REDEFINITION

### 2.1 SC82

Those applications of  $\mu$ SR, which, broadly speaking, may be described as muon labelling, we propose to continue under the existing code SC82. These preserve the spirit of the original proposal and include studies where the position occupied by the muon in the molecule (or crystal lattice) is readily established and the  $\mu$ SR signal is exploited to reveal the intrinsic properties of the material. (Analysis of small isotope effects in terms of the molecular dynamics need not of course be excluded by this definition). The revised title would be " $\mu$ SR IN ORGANIC AND FREE RADICAL CHEMISTRY".

This we intend to imply that  $\mu$ SR is simply used as an experimental tool in chemistry, as other tools (most analogously EPR, NMR or ENDOR for example) are already used.

### 2.2 SC??

As recorded by the PSCC at its meeting in May 1982 we consider it appropriate now to request a new experimental code, under which to extend the scope of our investigations to the more fundamental aspects. These concern the mechanism of the muonic attack on different molecules, the

question of muonium formation in different substances and its subsequent reaction with those substances, and the study of those products - particularly diamagnetic - where the nature of the muonic association with the molecules is uncertain. The new code would also cover those aspects which could be described as radiation chemistry or "hot-atom" chemistry - in many cases it is still not clear to what extent the residual kinetic energy of the implanted muon plays some role - and those which appear to be unique to the implantation of positive muons.

Some of these questions have already been tackled, either as a necessary forerunner to investigations under SC68 and SC82 or as interesting by-products of these investigations. We consider now however that this work is:

- a) distinct from, and
- b) sufficiently advanced,

to deserve definition as a separate project. The proposal also reflects

- c) the collaboration of a new group,

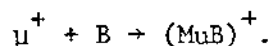
that of M C R Symons, Professor of Physical Chemistry, University of Leicester, for the purposes of this work. The title of the new experiment would be

"MUONS AND MUONIUM IN MOLECULAR PHYSICS".

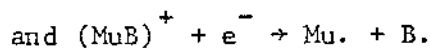
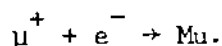
### 3. DETAILED PROPOSAL

#### 3.1 The diamagnetic fraction.

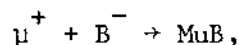
##### 3.1.1 To establish the occurrence of an acid-base reaction of the type



Such an association is indicated by our correlation of the diamagnetic amplitudes with basicity.<sup>2</sup> It would be in competition, however, with the potential sources of muonium

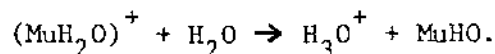
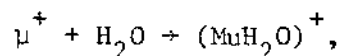


We propose to study this competition using an anionic base in high concentration

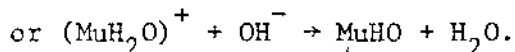
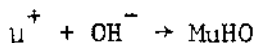


or by using suitably rapid muon or electron scavengers.

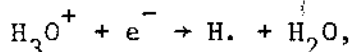
Aqueous systems, or other protic solvents exhibiting rapid proton exchange, should be particularly interesting:



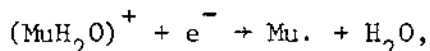
These reactions should "protect" the muon since the reaction of MuHO with electrons is expected to be relatively slow. Addition of alkali should enhance this protection:



Addition of acid, although increasing the rate of proton exchange, is likely to enhance the diamagnetic yield through a scavenging effect:



(unless the equivalent muonic reaction, which the scavenging studies are designed to suppress,



should for some reason have a higher rate).

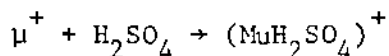
Preliminary results from our recent pH studies broadly support these contentions although suggest a somewhat more complicated behaviour. The use of more sophisticated scavengers such as  $\text{CrO}_4^{2-}$  (chromates)  $\text{NO}_3^-$  (nitrates),  $\text{SeO}_4^{2-}$  (selenates),  $\text{C}_6\text{H}_4\text{O}_2$  (p-benzoquinone) etc, possibly in alkaline solution, should allow us to test these effects more thoroughly, as well as to obtain particularly high diamagnetic yields.

### 3.1.2 To distinguish between different types of $(\text{MuB})^+$ species.

This would best be done through an examination of the chemical shifts of the  $\mu\text{SR}$  frequency - a procedure familiar in NMR spectroscopy. It would require some development of our existing apparatus and experimental techniques to obtain the necessary resolution and establish a suitable frequency (or phase) reference. We note merely that the existing spectrometer magnet is well suited to providing the higher fields which may be desirable and comment here on the chemical systems likely to exhibit the greatest shifts.

Maximum shielding (shift to high field) is shown by  $\text{H}^-$ , as in LiH, NaH etc. Hydride ions have not been detected in the liquid phase and it is not easy to see how to create  $\text{Mu}^-$  in our systems. Next best are hydrides such as  $\text{BH}_4^-$ ,  $\text{AlH}_4^-$ ; the preparation of their muonic equivalents  $\text{MuBH}_3^-$ ,  $\text{MuAlH}_3^-$  may prove possible. Then come hydrocarbons generally, and we are already familiar with the substitution of muons into organic molecules.

Assuming  $\mu^+$  cannot live long enough as a bare entity to be observed, then in the species  $\text{B}\mu^+$ , the weaker the base B, the greater the shift to low field: maximum de-shielding occurs in strong acids. For example in sulphuric acid, the following species should be formed:

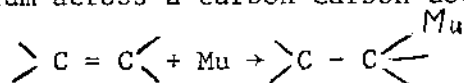


the chemical shift for  $\text{MuHSO}_4$  is expected to be large, that for  $(\text{MuH}_2\text{SO}_4)^+$  huge. These systems should have the advantage for such studies that efficient electron scavenging should enhance the diamagnetic yield.

### 3.1.2 The Paramagnetic Fraction

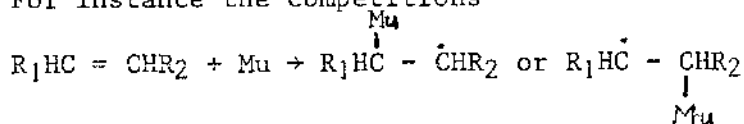
The fact that muonium can be detected in many systems is encouraging, and suggests that even very unstable hydrogen-atom adducts may also be detectable -  $\mu$ SR having a natural advantage here over the conventional magnetic resonance methods.

- i) Attention has been concentrated so far on the formal addition of muonium across a carbon-carbon double bond.

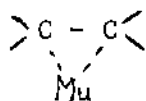


Undoubtedly more can be done on this front, using a range of different R-groups in  $R_1R_2C=CR_3R_4$ .

For instance the competitions

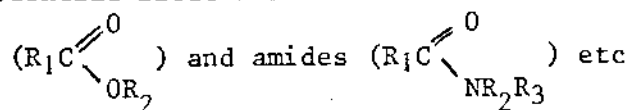


could be studied (rather as the Zürich group are presently studying isomer yields<sup>7</sup>) and the possibility of bridging could be investigated.



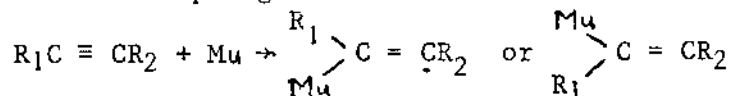
as this is the subject of some controversy.

- ii) Addition across the carbon oxygen double bond,  $R_1R_2C=O$  is a huge potential field which could be extended to esters

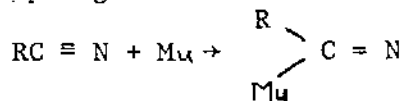


The principal interest here is that many of the potential adducts are not known in ESR work.

- iii) Addition across triple bonds has not, to our knowledge, been studied in muon chemistry, but should give rise to two isomers with very different coupling constants



(analogous to the Zürich investigation of methacrylate isomers<sup>7</sup>). Addition to  $RC \equiv N$  systems should give particularly large hyperfine couplings.



### 3.1.3 Isotope effects, and characteristics of $\mu$ SR.

In all these topics there is immense interest in the comparison of the behaviour of positive muons with that of implanted protons, and of the chemical properties of muonium with those of atomic hydrogen.

$\mu$ SR spectra are typically simpler than those obtained by conventional magnetic resonance methods, and there are no magnetic or pairwise interactions between muons to obscure the chemical interpretation of the spectra. These are two advantageous consequences of the extreme dilution of the muon probe. The timescale accessible by  $\mu$ SR measurements, determined by the muon's radioactive lifetime, may allow observation of faster processes or shorter-lived species than is possible by conventional time-domain magnetic resonance.

## 4. PROVISIONS

### 4.1 Apparatus.

The experiments would use the transverse field  $\mu$ SR spectrometer presently set up on the CJI beamline in the Proton Hall of the SC. No modification to the existing apparatus (beyond improvements already envisaged by the Collaboration) is necessary for the muonium or scavenger studies.

The RAL magnet on which this spectrometer is based is capable of generating any value of field likely to be required in the chemical shift measurements. Any upgrading of the field homogeneity, or the provision of any auxiliary equipment (such as facilities for RF irradiation, or spinning, of the sample) would be undertaken by RAL.

### 4.2 Beamtime.

An adequate provision for beamtime has already been included in the request made by the Collaboration to the PSCC in May: the 90 shifts requested for chemical studies would be allocated between SC82 and the new code by the Collaboration.

### 4.3 Personnel.

Experiments would be manned by personnel from RAL and the University of Leicester, supported by the Collaboration.

One of the authors of this proposal, A Hill, who is largely responsible for the development of the chemical applications of  $\mu$ SR at CERN, holds a CERN Fellowship until January 1983. Dr Hill expects to secure employment by a UK institution (beginning April 1983, that is, the UK financial year 1983/84), which will allow her to continue this work. We therefore request that the PSCC recommends an extension of the CERN Fellowship to cover the intervening period; and to make provision for visits for discussion with the Leicester and RAL participants.

REFERENCES

1. CERN/PSCC/82-23; PSCC M105
2. CERN EP/81-166
3. CERN EP/81-167
4. E Roduner et al (In Press)
5. E Roduner )  
                  )
6. P Burkhard)Private Communications  
                  )Zurich University Group (Prof H Fischer)
7. W St̄rub    )