

Authors' Preface

"Curiouser and curiouser" said Alice in amazement at the White Rabbit's words and then hastily poured him another cup of tea so that he should not stop this remarkable tale. Wiping his whiskers and paws very carefully the rabbit repeated grandly,

"Yes, quite an exciting discovery, in my opinion one whose impact still has to be fully explored. And the machines they used, you cannot imagine how complicated they were.."

"Yes, yes", stamped Alice a little impatiently, "but what did they discover?"

"Why, the muonium atom of course".

"The what?"

Breathing heavily the White Rabbit rose to his full height.

"The muonium atom."

"What is that? It sounds a very curious thing to get excited about."

"Ah - how can I describe it - a species older than homo-sapiens, a transient atom birthed by an electron alighting on a short-lived positive muon, formed with unique negative handedness, first in the new periodic table of atoms, never still in its watery trap, and so quick to react with everything,"

"Gobbledygook!" interrupted Alice.

The White Rabbit stood up, gave her a quelling look and returned to the laboratory bench. As he worked, he muttered, "What did she want me to say? That it is the A_M parameter in the MuSR fitting equation $N_t = N_0 [I + A_D \cos(\omega t + c) + A_M \cos(\omega' t + c') + B]$."

Alice, overhearing him as she cleared away the cups and saucers, admitted to herself, "Well, that is much clearer and a lot more descriptive ..."



Introduction

The muonium atom (chemical symbol Mu) is composed of a positive muon as nucleus with a 1s ground-state electron. As an atom it should reside in the first box of the Periodic Table, because its Bohr radius and ionization energy are within 0.5% those of H, D and T. Furthermore, Mu's mass is only one ninth the mass of H, and its muon nucleus lives for a mere 2.2 microseconds, so Mu can be regarded as a super-light and radioactive isotope of hydrogen. Its comparison with H is ideal for studying kinetic isotope effects.

The first observation of Mu and studies of its chemical reactivity were in the gas phase (1). These were followed a few years later by deductions of its reactions in liquids (2) and then of direct observation of Mu in water and initial studies of its principal reactions (3). In this presentation we will discuss only reactions of Mu in solution --- and almost all are with solutes in water. Most of these data are at room temperature, but those with variable temperature have produced activation energies and pre-exponential factors (4). There already exists an enormous wealth of information on H-atom reactions in water with which to compare these Mu reactions (5, 6).

Whereas H is not easy to produce in water nor to observe its reactions directly on a short timescale, Mu can be directly observed in any solution at any temperature and any pH --- given (!!) a source of muons and advanced nuclear physics counting techniques. Mu is observed through its natural radioactivity decay; but this decay also has unique spin characteristics which allow much more reactivity information to be obtained. The muon's formation and decay processes violate the parity-invariance principle, which results in the muons being initially spin polarized then decaying asymmetrically. Various muon spin polarization techniques are based on these unique characteristics and have been developed to enable one to determine the chemical association of the muon at its moment of decay. Additionally, one can evaluate the actual yield and rate of disappearance of these states. One of the states directly observable is the free Mu atom. So its rate of disappearance in the presence of an added solute can be converted to a chemical rate constant --- in much the same way that pulse radiolysis, coupled with spectrophotometry or time-dependent ESR, can directly 'observe' H, OH and solvated electrons as they react with solutes (5,7).

The primary technique involved in rate constant measurements of Mu is that of muon spin rotation (MuSR, here). The actual method of analysis involves a fitting procedure in which one of the variables is an exponential decay of the Mu component of the overall muon signal. The decay constant is interpreted as the pseudo first-order rate constant for all chemical reactions which convert 'triplet' Mu to 'singlet' Mu, or from the free atomic state to a diamagnetic species or to a free radical (8). Given the presence of a reactive ingredient at a known concentration, this pseudo 1st order rate constant can be converted to a real second order rate constant (k_M).

In the following Tables these values of k_M are given for the reaction of Mu with the specified solute -- - in water at room temperature (293-298K), unless otherwise indicated. A few reactions have been studied at other temperatures and in other solvents, as signified in the Tables.

The Tables report the observed kinetic isotope effect (KIE) of Mu versus H, given as lighter-over-heavier isotope, k_M/k_H . Several different types of KIE's emerge as a result of studies of Mu vs. H. The following categories have been delineated (9):

- (a) Reactions in which KIE is >1: Due to the lighter isotope diffusing more rapidly than the heavier isotope.

(b) Reactions in which H reacts faster than Mu: Because the reaction rate is controlled by the activation barrier --- and this is higher for Mu than H. [This is contrary to the first-inclinations of many chemists, who are ingrained with the common premise that the lighter isotope will react faster. But the reactions of Mu and H involved here are reactions of free atoms, so the potential energies of the reactants are essentially equal and it is only the relative energies of the activated complexes that count. So the higher zero-point energy of the Mu complex gives it a higher activation barrier and hence a smaller rate constant than its H analogue.]

(c) Sometimes there are two reaction paths available to the two isotopes in their reactions towards a particular solute. For instance, in reaction with acetone, Mu and H can either abstract an H to form HMu or H₂, or they can add across the C=O double bond to form a muonated or hydrogenated free radical. When the KIE's for individual paths are of the opposite sense (>1 for one path and <1 for the other) then the overall reaction observed can lead to different paths being preferred by Mu compared to H, resulting in different reaction products. The KIE determined from the observation of rates of loss of Mu and H atoms is thus a composite value. In the case of acetone, Mu evidently adds faster than it abstracts, while H undergoes the converse, and the overall observed KIE happens to be >1.

(d) Because of their small masses, quantum mechanical effects are particularly significant for Mu and H, especially Mu. Thus, for reaction types with narrow activation barriers, quantum tunneling undoubtedly plays a role and Mu should win handsomely. On the other hand, as in (b) above, the zero-point energy quantum mechanical effect should invariably favour H.

Perhaps 95% of the Mu rate constants have been determined by observing the loss of 'triplet' muonium atoms in the presence of a solute, as noted above, utilizing Mu's spin rotation/precession frequency in external transverse magnetic fields (MuSR). This process 'observes' Mu as it reacts. Thus, in the absence of a notation to the contrary in the following Tables, the k_M reported will have been determined by MuSR. Occasionally, however, k_M has been evaluated by other techniques. These are also based on the spin polarization of the muon and its characteristic asymmetric decay, but they follow Mu indirectly and often have to make assumptions about the reaction mechanism. One of these involves measuring the forward-to-backward spin distribution in longitudinal magnetic fields in the presence of various concentrations of solute at various magnetic fields. We will refer to this as mSR in the Tables to follow. Its values can be used to identify those processes which can be described as purely electron-spin-exchange interactions in nature. Such longitudinal field studies subdivide the values of k_M obtained by MuSR into spin-exchange and other reaction types (abstraction, addition, reduction, combination, etc) when the reactant is paramagnetic. Another technique which has been used is evaluating the lifetime of Mu from its linewidth (10). And finally, a value of k_M can sometimes be deduced from measurements of the yield of muonated free radicals when these are reaction products due to the presence of various concentrations of an unsaturated solute. Both high transverse field muon spin rotation (called RSR here) and muon level-crossing-resonance (LCR or ALCR) techniques have been used in this regard (11).

The following Tables follow the format of the widely acclaimed Critical Review of Hydrated Electrons, H Atoms and OH Radicals by Buxton, Greenstock, Helman and Ross (5). These data were preceded by earlier reviews and together they give full measure to the extent and value of such compositories. We hope this compilation will prove useful to all researchers who are interested in hydrogen atom reactions or kinetic isotope effects.

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