Notes on the Muonium Data Base

This site attempts to collate all relevant published kinetic data on the reactions of the muonium atom (Mu) with solutes in solution. The data are presented in Tables A to F. Access to these Tables is achieved by placing the cursor over "TABLES" then selecting and clicking a particular Table. Table A records reactions of Mu with inorganic solutes in water; Table B, organic solutes in water; Table C, solutes in water which react too slowly with Mu to measure; Table D, solute reactions with Mu in solvents other than water; Table E, the record of early attempts to measure k_M before the direct Mu-decay method was perfected (ref. 3 above).[These muonium rate constants were determined in early 70-ies by two independent groups using indirect model-fitting procedures (12,13) which resulted in rate constants markedly different from current data.] The final Table F, summarises the fractional yields of muonium (P_M) and diamagnetic muons (P_D) in various solvents.. There are also solutes for which reactions of muonium have been studied in aqueous micelles. These "micelle" data are added to the individual files of each solute in Tables A and B.

For each solute, these tables give the reported Mu rate constant, k_M. When the analogous k_H value is available (corresponding to the rate of the reaction of the H-atom with that solute) then their ratio is given as the kinetic-isotope-effect (KIE). KIE is represented here as lighter-over-heavier, k_M/k_H, and it is the mass ratio of 0.11 of Mu to H which makes this ratio of particular use in chemistry.

Furthermore, this considerable mass ratio has revealed a number of reactions in which Mu and H undergo alternative reaction paths (such as addition versus abstraction, or addition at different o-, m-, and p- positions). Sometimes these different reaction mechanisms have different specific KIE's that lead to an overall "observed" k_M/k_H which is a compromise of these two opposite KIE's (see ref 9 above). But the tables here give only the empirical KIE's as deduced directly from the observed overall k's without any breakdown into the competing reaction paths.

Most k_M values were obtained from measurements of the enhanced rate of decay of Mu atoms by the presence of a solute at various concentrations as seen in muon-spin-rotation studies (µSR). One of the fitting parameters in a µSR experiment is a pseudo first order decay constant λ, which, when plotted against the solute concentration, gives the absolute bimolecular rate constant (k_M) as its slope. Random errors on the values of k_M typically vary from about 10 to 25%. When combined with both random and systematic error-bars on k_H, KIE values are invariably no better than ±30%. But, as KIE values range from <0.01 to >100, these 30% errors are fully acceptable.

Data presented in these tables refer to room temperature studies (293-298K) unless otherwise specified. The temperature span is given when an activation energy was

determined for a specific solute. This compilation is aimed at presenting data on reactions of muonioum and hydrogen atoms at ambient temperatures and normal pressure. In view of continuous interest in chemistry and radiation chemistry of supercritical water (SCW), however, some rate constants obtained for muonium reacting in aqueous solutions at very high temperatures and pressures have been included. For some systems activation volumes have been calculated and the relevant data are presented.

For aqueous solutions the pH was not adjusted (and therefore close to 7) unless indicated and deliberately changed to enhance a particular ionic state of a solute. Mu has a pK_a of about 11, so any pH-dependence of its reactions at pH $<<11$ can be attributed to the ionic state of the solute rather than to that of Mu.

Muonium, even more so than H, can undergo a remarkable variety of reactions (see ref 8 above) which is what makes its role in chemistry so significant. It can undergo the following reaction types: "reduce" a solute (Mu→μ+); act as a "Brönsted acid" (Mu → e_s^-); "abstract" an H atom (Mu→MuH); "substitute" for another atom in a molecule (Mu + CCl_4 → $MuCCl_3$); "add" to a double or triple bond to form a Mu-radical (Mu + CN^- →MuC=N$^-$); "combine" with a free radical to form a covalent bond (Mu + NO → MuNO); or, and this is a process uniquely detectable for Mu (by muon spin rotation), undergo an "electron spin exchange" interaction which converts "triplet Mu" (observable) to "singlet Mu" (unobservable) Mu^T + Ni^{2+} → Mu^S + Ni^{2+}.

One of these seven reaction types is often suggested in the Tables, but the mechanism is only inferred from general reaction principles because detection of a Mu-reaction product almost never occurs (due to the muon's 2.2 microsecond lifetime). The exception here is when a transient Mu-radical is formed. Many such Mu-radicals have now been observed and identified by a combination of high-field μSR and LCR (the Level Crossing Resonance technique, also reported with ALC as its acronym). Occasionally the formation rate of a Mu-radical observed by LCR has been used to deduce a value for k_M for the corresponding addition reaction.