ESCAPE RATE OF MUONIUM FROM MICELLES — AS DETERMINED BY COMPETITION KINETICS

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A competition was established for the reaction of muonium atoms (Mu) between nitrate ions in water and benzene or styrene solubilized in micelles. The nitrate was 3.3 times more efficient at inhibiting muonated free radical formation with benzene than with styrene as the radical-producing solute. Kinetic analysis of this system indicates that Mu emerges from micelles, on average, at least three times during its short (ns) lifetime, these being medium sized micelles carrying on average 3 benzene molecules. So Mu is certainly not trapped, nor even localized. Its escape rate is estimated to be $\sim 9 \times 10^8$ s$^{-1}$, which is commensurate with an ordinary diffusion time. The results were obtained by determining the yield of muonated free radicals formed within the micelles using muon-level-crossing-resonance spectroscopy.

1. Introduction

In previous studies on muonium reactions with organic solutes in water it was found that the addition of micelles often considerably enhanced the rate of reaction [1]. It is known that the organic solutes are solubilized and trapped within the micelle's hydrocarbon phase for times much longer than a muon lifetime, so the muonium atom (Mu) formed in the bulk aqueous phase has to penetrate into the micelle in order to react with the organic solutes located there. There would be a simple explanation for the observed enhancements if Mu were also ‘localized’ in the micelle. This would result in ‘mutual confinement’ and hence concentration-enhancements; but only if confinement applied to both reactants, even though Mu reactions occur by pseudo-1st order kinetics.

A critical question concerning micelle-induced enhancements thus becomes: Is Mu also ‘localized’ at micelles? In an experimental test of this

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question a few years ago [2], we showed that addition of unoccupied micelles to an aqueous solution of NO$_3^-$ ions slowed down the observed rate of decay of Mu but only enough to correspond to a mean residence time for Mu in the micelles of 2 (±1) ns. Two nanoseconds is about the period for random diffusion by Mu through a medium having the high viscosity and size of micelles. Our conclusion was that Mu is not 'localized', and therefore that other explanations had to be sought for the observed enhancements.

The only question with those test experiments [2] is whether an 'occupied' micelle creates a different (longer) mean residence time for Mu than do 'unoccupied' micelles — perhaps by providing a structural dislocation which 'traps' Mu. To test this we have now set up a reaction competition in which Mu reacts with nitrate ions in the aqueous phase versus benzene and styrene localized in micelles. This paper reports the results of that competition.

2. Experimental

In the present study muonium atoms produced in water reacted either with NO$_3^-$ ions present at 10 to 100 mM in the water or with benzene or styrene contained in 2.5 mM concentrations of micelles. The latter reactions produced muonated free radicals which were detected by the muon level crossing resonance technique, which has been fully described previously [3]. Measurements were made here with a small modulation field of 5.7 mT. The usual $\chi^2$-minimization fit to the data gave amplitudes and widths of the resonance peaks. Mu adds to benzene to give the muonated cyclohexadienyl radical with a single strong resonance at 2.08 T. With styrene, Mu gives several radicals due to addition at side chain or ortho, meta and para ring sites [4], but here we trace only the radical formed by Mu-addition to the end C whose resonance occurs at 0.905 T.

All solutions were made from freshly purified water and were deoxygenated by bubbling with N$_2$ just prior to being pumped under N$_2$ into the irradiation cell. Sodium dodecyl sulphate (SDDS) was the surfactant used to produce anionic micelles at 2.5 mM concentration. Benzene or styrene was added at 7.5 mM to give 3.0 organic solutes per micelle on average. Unfortunately, the Poisson distributions obtained with such small numbers introduce considerable statistical errors — only ~23% of the micelles actually contain the average value of 3 solute molecules and ~7% are unoccupied, but this 3-fold ratio is the preferred compromise based on prior experience [1]. In the present studies the same micelle solution of benzene or styrene was used throughout, just with different concentrations of NaNO$_3$.