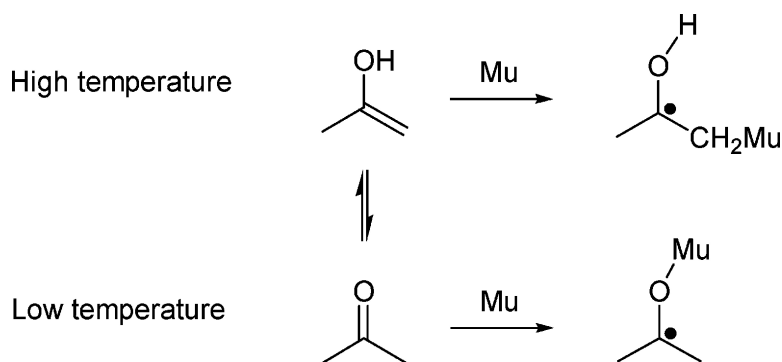Communication

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Enolization of Acetone in Superheated Water Detected via Radical Formation

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Current interest in organic reactions in superheated water is motivated by a surprising diversity of applications: geochemical production of petroleum, biology in hydrothermal vents, corrosion in steam generators, destruction of hazardous waste, and the development of environmentally benign chemical processes.[1,2]

There is relatively little information on the kinetics and mechanisms of chemical reactions under hydrothermal conditions, and most studies have relied on end-product analysis and modeling to infer multistep reaction sequences. Ideally, reaction intermediates should be studied in real time in situ. In practice, most techniques are limited by the technical demands of the harsh environment − a corrosive solvent under high pressure at high temperature (hydrothermal chemistry is important up to and through the critical point of water, at 374 °C, 220 bar). The study of free radicals is particularly difficult under such conditions. One approach is to use pulse radiolysis with optical spectroscopy.[3−5] A remarkable new development is the use of direct sampling mass spectrometry to identify radicals and other reaction intermediates.[6]

Our own work employs μSR, a magnetic resonance technique that uses the muon as a spin probe.[7] Because a positive muon can act as the nucleus of a hydrogen-like atom, muonium (Mu), it can be used to study H atom reactions and free radicals incorporating H. In recent years, we have demonstrated the ability to detect muonium in water over a wide range of conditions, from standard to supercritical,[8] to determine rate constants for its reactions[9] and to detect muoniated free radicals.[10] The work described here involves radicals formed from the reaction of muonium with acetone in water.

In water at room temperature, H atoms react with acetone by both H abstraction and addition to the carbonyl oxygen.[11] Abstraction is slower for Mu atoms, so the predominant product is the 2-muoxyprop-2-yl radical $(CH_3)_2\dot{C}OMu$.[12] However, we found evidence for a different radical in aqueous solutions of acetone at high temperature, which led to the systematic study reported here.

Transverse field μSR experiments were carried out at the M9 beam line of the TRIUMF cyclotron facility in Vancouver, Canada. Oxygen-free samples of 0.08, 0.29, and 0.69 mol fraction acetone in water were investigated; experimental details of the equipment and procedures can be found elsewhere.[10] μSR spectra were recorded over a wide range of temperatures, from 58 to 390 °C. Two examples of the spectra are given in Figure 1. The existence of muoniated free radicals is evident from the characteristic pair of muon spin precession frequencies (labeled R) in each spectrum.[7] The sum of these frequencies gives the muon-electron hyperfine constant (hfc),[13] and it is obvious that two different radicals are formed at the two temperatures.

The muon hfc's are plotted in Figure 2, which shows a dramatic change at about 250 °C. Below this temperature, our results are consistent with literature data,[12c] denoted by the open symbols. The small shift between the data sets is consistent with changes in
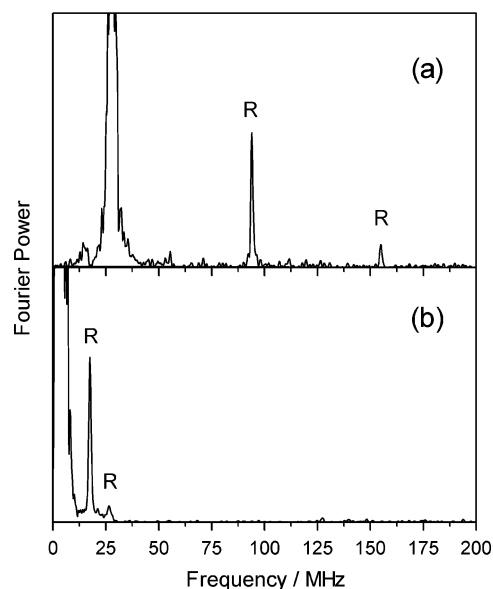

Figure 1. Muon precession signals from aqueous solutions of acetone at (a) 370 °C, 250 bar, 2 kG; (b) 170 °C, 190 bar, 320 G. In each case, the pair of peaks labeled R is characteristic of a muoniated free radical.

solvent properties for different concentrations of acetone.[12c] The positive temperature dependence has been interpreted in terms of hindered internal rotation about the C−O bond in $(CH_3)_2\dot{C}OMu$, with a minimum-energy conformation in which the O−Mu bond is very close to the nodal plane of the p orbital containing the unpaired electron.[12]

Above 250 °C, a different radical was detected; its muon hfc is about 250 MHz and falls with temperature. This is typical behavior for a β-muoniated alkyl radical,[14] and we assign the spectrum to $CH_3\dot{C}(OH)CH_2Mu$. This is the expected product from Mu addition to the enol form of acetone, as shown in Scheme 1. Unambiguous identification would require measurement of the proton hfc's, in principle obtainable by muon avoided level-crossing resonance, but we currently lack the equipment to perform such experiments on a sample in a high-pressure cell.

The existence of keto−enol tautomerism is well known, but despite the extensive literature on enols[15] there is very little data on the temperature coefficient of the equilibrium constant. Rate constants for enolization of acetone in water and the reverse process have been determined up to 54 °C; combination of the activation parameters gives $\Delta H° = 10.31 \pm 0.45$ kcal mol^{-1} for the equilibrium.[16] This leads to the prediction that pK_E falls from 8.33 at 25 °C to 4.70 at 300 °C. On the other hand, non-Arrhenius kinetics seem to be a common feature of hydrothermal systems,[9] so a large extrapolation of the equilibrium constant according to the van't Hoff equation seems hardly credible. Water itself exhibits markedly nonlinear behavior, with a maximum in K_w close to
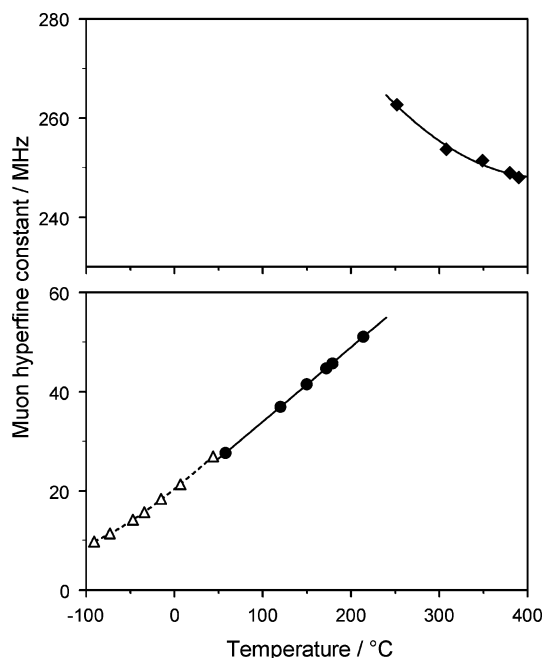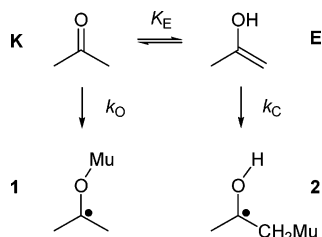
Figure 2. Muon hyperfine constants for the two radicals detected in aqueous solutions of acetone (filled symbols) at various pressures and concentrations (see Supporting Information for details), compared to literature data (open symbols) for 0.7 mol fraction acetone in water taken from ref 12c.

Scheme 1. Muonium Addition to the Keto and Enol Forms of Acetone

$300 \, ^\circ C$.[1] Thus, estimation of K_E for acetone in water at high temperature is at best qualitative, with the prediction that the enol is probably still only present at low concentration.

Given the lack of data from other sources, it is worth discussing the limits imposed by our own observations. Because the rates of enolization and ketonization are both slow[16] as compared to the microsecond time-scale of the μSR experiment, the competition between the parallel reactions of muonium (Scheme 1) results in a ratio of products given by $[\mathbf{2}]/[\mathbf{1}] = k_C[\mathbf{E}]/(k_O[\mathbf{K}])$. At room temperature, the rate constant for Mu addition to C=C is $\sim 10^2$ times greater than that for addition to C=O; hence $[\mathbf{2}]/[\mathbf{1}] \approx 10^2 K_E \ll 1$. At high temperature, the two rate constants will be approximately equal, at a limit imposed by collisions in the solvent cage.[9] Thus, the detection of radical **2** implies that $K_E \geq 1$ under these conditions. A lower limit for the enol concentration can also be estimated from the phase coherence implicit in the detection of strong radical precession signals.[7] This imposes a limit

$k_C[\mathbf{E}] \geq 10^{10} \, s^{-1}$. Because the upper limit for Mu rate constants is $10^{11} \, M^{-1} \, s^{-1}$,[9] we deduce that the enol concentration was greater than 0.1 M.

Our finding of large concentrations of enol under hydrothermal conditions is consistent with rapid and almost complete H–D exchange reported for the α positions of ketones in superheated water.[17]

Supporting Information Available: Table of muon hyperfine constants displayed in Figure 2 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Strictly speaking, the hyperfine constant is given by the difference of the precession frequencies, one of which is negative, a feature which is not apparent in the real Fourier transforms displayed in Figure 1. Also, in view of the low amplitude of the upper radical frequency, the hyperfine constants were computed from the lower frequency and the muon Larmor frequency (the large truncated peak in each spectrum).

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JA036377X