USING MUONIUM TO PROBE THE KINETICS OF THE REACTION BETWEEN THE H ATOM AND OH⁻ IN SUPERHEATED WATER

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Abstract

Operation of a supercritical-water-cooled nuclear reactor requires knowledge of water chemistry over a wide range of conditions. The considerable knowledge gap for conditions above the operating temperature of current-generation CANDU reactors is the target of this study. Since the H atom is difficult to probe at the desired temperatures and pressures, muonium is used as an alternative. In the current CANDU reactors, coolant pH is controlled using LiOH. We are studying how the rate constants for the reaction of muonium with LiOH and NaOH change with temperature and pressure.

1. Introduction

Knowledge of the aqueous radiolysis-induced chemistry under supercritical conditions is vital to the understanding of the integrity of materials to be used in a supercritical-water-cooled reactors (SCWRs). Specific computer radiolysis models are being developed to gain insight into radiolysis processes and to enable chemistry control to be developed [1].

In current PWRs, it is common to use LiOH for chemistry control adjustments, in particular to adjust the pH in currently used reactors [2, 3]. Therefore it is important to investigate the kinetics of OH^- reactions with reactive intermediates produced by the radiolysis of water.

The temperature dependence of the $H + OH^-$ reaction in supercritical water was first studied by Ghandi et al. [4], using muonium (Mu) as an analogue of H, and later by Marin et al. [5] for a more limited range of conditions.

In the work described here we investigated the rates of reaction of Mu with hydroxide in heavy and light water above and below the critical point by means of muon spin spectroscopy (μSR). The motivation was to probe the reaction of H atoms with hydroxide ions:

$$H + OH^- \rightarrow e_{aq}^- + H_2O \quad (1)$$

In their pulse radiolysis study of H in aqueous solutions of KOH from 3–330°C, Marin et al. [5] reported two regions of differing activation energies: 38.2 ± 0.6 kJ/mol with pre-exponential factor $(1.27 \pm 0.27) \times 10^{14}$ $M^{-1}s^{-1}$ for 3-98°C, and 25.4 ± 0.8 kJ/mol with pre-exponential factor $(1.76 \pm 0.36) \times 10^{12}$ $M^{-1}s^{-1}$ for 100–330°C. In comparison, Ng et al. found an activation energy of 40 ± 5 kJ/mol with pre-exponential factor $(2.4 \pm 0.1) \times 10^{14}$ $M^{-1}s^{-1}$ for the equivalent reaction of Mu in the range 1-84°C [6]. Mu and H should have similar chemical reactions,

$$\mathrm{Mu} + \mathrm{OH}^{-} \rightarrow \mathrm{e}_{\mathrm{aq}}^{-} + \mathrm{HOMu} \tag{2}$$

$$\mathrm{Mu} + \mathrm{OD}^{--} \rightarrow \mathrm{e}_{\mathrm{aq}}^{-} + \mathrm{DOMu} \tag{3}$$

but the rates may be affected by kinetic isotope effects [7, 8], in particular zero-point energy shifts at the transition state, exemplified by late-barrier reactions [9] ($k_{\mathrm{Mu}}/k_{\mathrm{H}} << 1$) and quantum tunnelling exemplified by early-barrier reactions [10] ($k_{\mathrm{Mu}}/k_{\mathrm{H}} >> 1$ at low temperatures and concomitantly with much smaller activation energies for Mu reactions.

2. Experimental

Solutions of lithium and sodium hydroxide were prepared at concentrations of 0.16 mM, 0.30 mM and 1.6 mM using distilled and deionized H_2O. LiOH and NaOH were obtained from Aldrich without further purification. LiOH was 99.95% pure with 0.05% trace metals, and NaOH was ≥ 97.0% pure. Dissolved oxygen was removed from the solutions by the “pump and shake” method: a sample of solution was repeatedly pressurized with argon or nitrogen, shaken, and vacuum pumped. After five or six cycles the samples were stored in glass bulbs under ~2 bar gas to aid transfer into the evacuated target cell. When no longer needed, samples were removed from the target cell by introducing nitrogen gas to the top of the cell and pumping from the bottom. To minimize any error associated with residual sample in the system, experiments were performed in order of increasing concentration.

The target pressure cell is made of titanium alloy (Ti6Al-4V) and safety rated to sustain pressures of up to 500 bar at 500°C. The temperature was regulated with a standard PID controller that drives a commercial heating element (Watlow) wrapped non-inductively around the body of the target cell. The pressure was adjusted by means of a hand pump, relief valve, and ballast volume as described previously [4, 11] and in our other papers in this conference.

Experiments were carried out at the M9B muon beam line at the TRIUMF cyclotron facility in Vancouver, British Columbia, Canada. The muon beam momentum was typically set at about 75 MeV/c, with somewhat lower values for low density samples, the point being to select a momentum sufficient to allow muons to penetrate through the cell window, but allow them to stop in the fluid sample inside the cell.

A weak magnetic field (~5 gauss) was applied transverse to the muon spin direction and standard transverse-field μSR experiments [7, 8] performed. The resulting spectra have two components: a signal from muonium (characterized by a 1.4 MHz/G spin precession frequency), and a diamagnetic signal from muons which precess at the muon Larmor frequency (0.01355 MHz/G). The latter is due to the muonium in diamagnetic environment like MuOH and/or MuH, but it is the muonium signal which is of interest here.

The relaxation rate of the muonium signal is of particular importance since it represents chemical decay of muonium and/or spin relaxation caused by interaction of muonium with other paramagnetic atoms or molecules. The diamagnetic muon relaxation rate is invariably slow enough to be ignored in studies of muonium reactivity in liquids.

In the homogeneous kinetics regime of interest in this work muonium decays according to the simple first-order expression:

$$[\mathrm{Mu}]_t = [\mathrm{Mu}]_0 e^{-\lambda_{\mathrm{Mu}} t} \tag{4}$$

where $\lambda_{\mathrm{Mu}} = k_{\mathrm{Mu}}$ [X] is a pseudo first-order rate constant (the effective concentration of muonium atoms is too low to affect the concentration of hydroxide) and k_{Mu} is the bimolecular rate constant for the reaction of muonium with reactant X.

There is also a background relaxation, λ_0, due to reaction of Mu with the solvent, spin relaxation, and other physical and instrumental effects. To account for this, muonium decay rates were measured in the pure solvent under a variety of conditions and an empirical relationship was determined for λ_0 as a function of density. Muonium decay rates were then converted to rate constants using the following equation:

$$k_{\mathrm{Mu}} = \frac{(\lambda_{\mathrm{exp}} - \lambda_0)}{[\mathrm{X}]_0} \cdot \frac{\rho_0}{\rho(T,P)} \tag{5}$$

where λ_{exp} is the decay rate of the muonium signal for a sample solution, ρ is the sample density (which varies with temperature and pressure), and $[\mathrm{X}]_0$ and ρ_0 are the reactant concentration and sample density under standard conditions.

3. Results and discussion

Two examples of muonium signals in a 0.3 mM solution of NaOH are presented in Figure 1. As expected, the decay rate of the muonium signal (the fast oscillations) increases with temperature. At room temperature (25°C), there is negligible pressure dependence of rate constants between 10 and 250 bar.

Although the bimolecular rate constant can be determined from muonium decay rates at each thermodynamic condition by application of equation (5), it is also possible to obtain the rate constant from the slope of a plot of decay rate as a function of reactant concentration. Figure 2 shows such a plot for the reaction of muonium with OH^- in solutions of LiOH in water at room temperature.

In addition to the trivial effect of density, the concentration of hydroxide ion in solution changes slightly with temperature and pressure because the ionic product of water is temperature and pressure dependent.

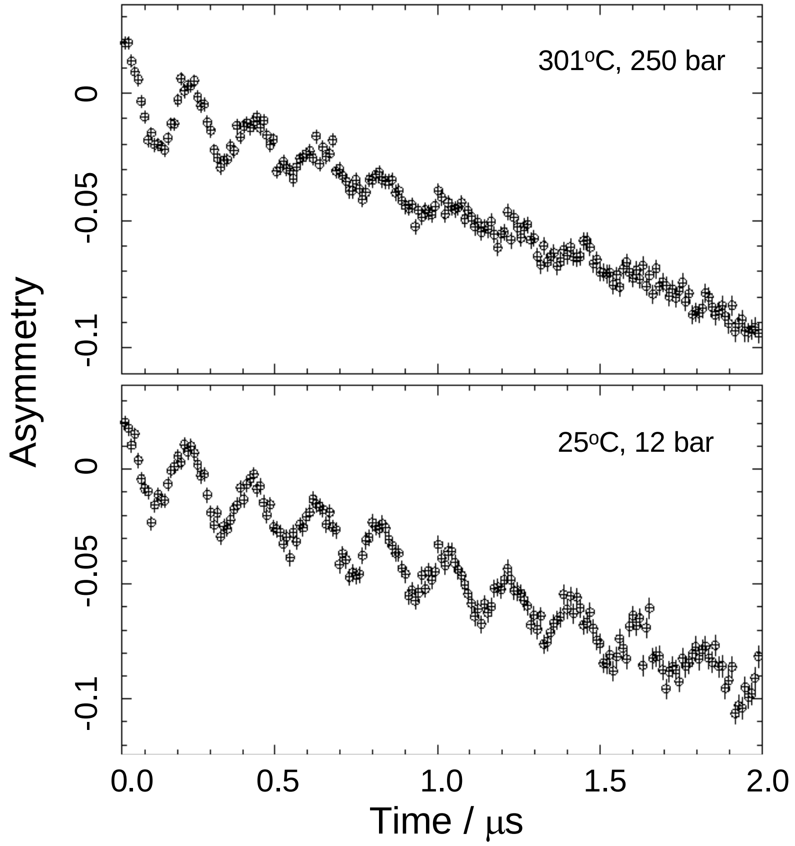

Figure 1. Examples of low transverse field μSR spectra obtained from an aqueous solution of 0.3 mM NaOH under different conditions. As expected, the decay rate of the muonium signal (the fast oscillations) increases with temperature.

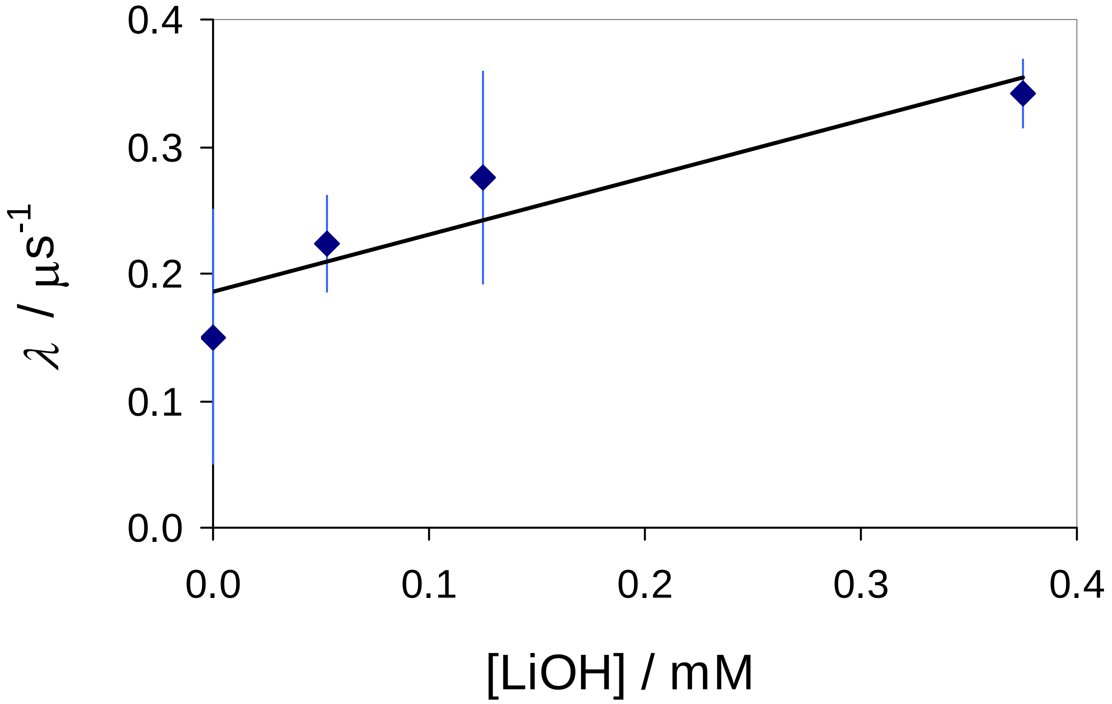

Figure 2. Muonium decay rates as a function of LiOH concentration in water at room temperature. The line is a best fit through the data.

Figure 3 shows the pK_w of water as a function of temperature at two pressures used in our studies. The values were calculated from the international formulation for the ion product of water substance issued in 1980 by the International Association for the Properties of Steam [12]. The corresponding hydroxide concentrations at 234 and 300 bar are shown in Figure 4.

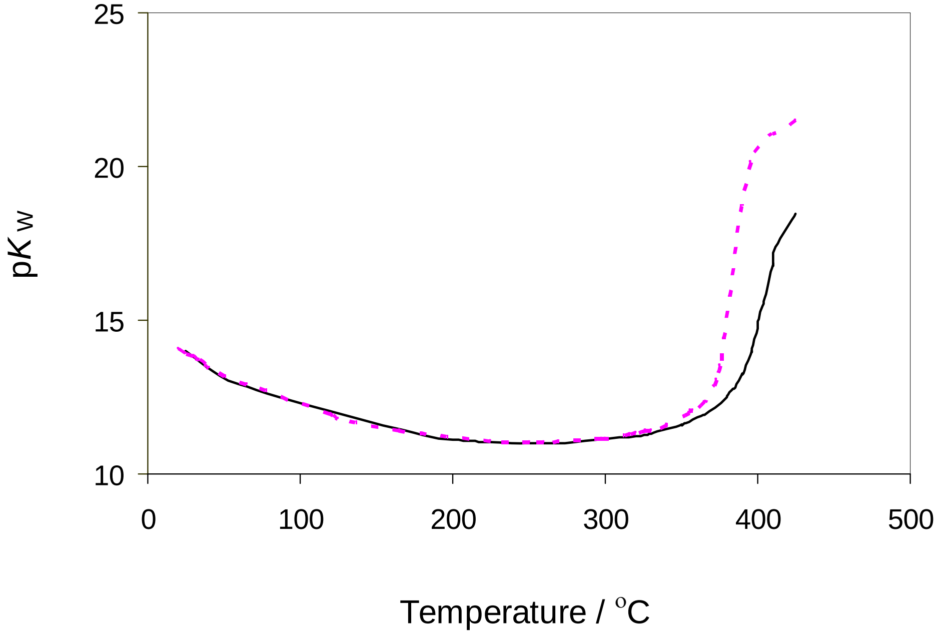

Figure 3. pK_w (= -log [K_w/(mol kg^{-1})^2]) as a function of temperature at 300 bar (solid black line) and 234 bar (dashed pink curve).

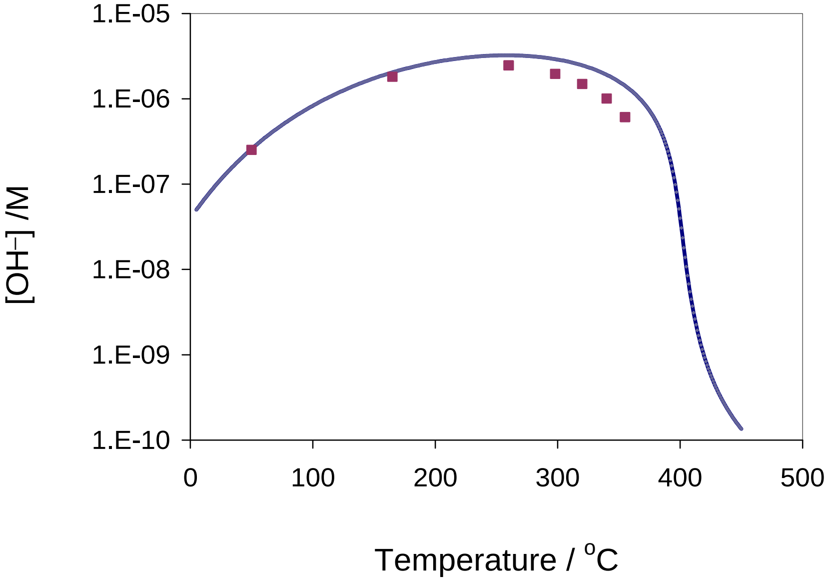

Figure 4. [OH$^-$] as a function of temperature at 300 bar (blue line) and at some temperature points at 234 bar (brown squares).

The effect of [OH$^-$] from the ionization of water (Figure 4) is small compared to the concentration range of solutions used in our studies and therefore has a minor effect on the calculation of rate constants. The maximum error caused by ignoring the [OH$^-$] from the ionization of water is estimated to be ~ 1% and occurs at temperatures between 250°C and

325°C. Larger errors arise from temperature gradients, pressure fluctuations and the background relaxation rates.

Our new results are compared in Figure 5 with our previous data on the temperature dependence of the rate constant for the reaction of muonium in NaOH solutions. The older measurements were performed with apparatus for which it was possible to have a significant temperature gradient (up to 10ºC at 350ºC) across the sample. Not only does this mean that there is a possibility of a 10ºC error in the recorded temperature, this could also result in an error in density and therefore [OH^-] concentration. The present setup uses a smaller pressure cell and measurements of temperature is made in the centre of the cell and so is much less prone to error.

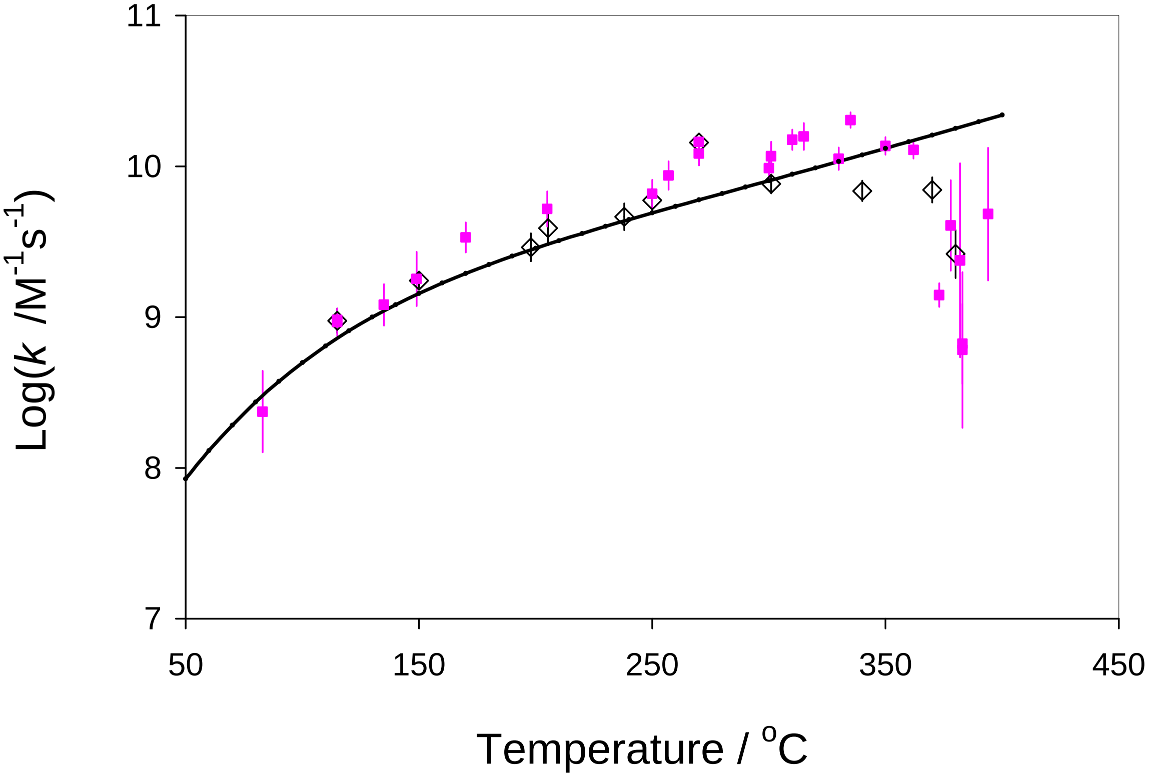

Figure 5. Second-order rate constants for the bimolecular reaction between muonium and OH^- (or NaOH) as a function of temperature at 245 (±5) bar. The pink squares show our earlier data [4] and the open black diamonds represent the 2010 data set. The curved line is from the data on H atom from Ref. 13.

In the range 70–330°C our data exhibits an activation energy of 25.8 ± 0.5 kJ/mol with a pre-exponential factor of (3.31 ± 0.07) × 10^{12} $M^{-1}s^{-1}$ [4], in good agreement with the pulse radiolysis results for reaction of H with KOH from 3–330°C [5]. Similarly, the lower temperature study of Ng *et al.* [6] gave activation parameters for the muonium reaction in agreement with H kinetics below 100°C. This shows that there is an excellent agreement between muonium and pulse radiolysis measurements. For better comparison the data for H atom from Ref. 13 is plotted in Figure 5. The experimental data on H atom is limited to 330°C. The agreement of muonium and H atom data over such a wide range of temperatures is surprising and was one of the motivations for our current study; we had expected there to be a kinetic isotope effect. Considering that practically there is no significant kinetic isotope effects we believe that the Mu data for this reaction can be used directly to estimate the rate constant for H atom at higher temperatures where the H atom data is not available.

One possibility for the apparent lack of a kinetic isotope effect is an accidental cancelling of a real isotope effect by a counter ion effect in the opposite direction (our original study [4] used NaOH but the pulse radiolysis work [5] employed KOH). We have now made preliminary measurements with LiOH but we have found no significant counter ion effects.

If we conclude that there is indeed no isotope effect in the $H + OH^-$ reaction, this could mean that the Mu-O (H-O) bond is not forming in the rate-determining step. This consideration will serve as a basis for further explorations of solvent isotope effects (H_2O vs. D_2O) and counter-ion effects).

4. Summary

New kinetics data were obtained for the reaction of muonium with NaOH in H_2O, using improved apparatus. These data were compared to previous results by our group for muonium in H_2O solutions of NaOH [4] and with the data for solutions of KOH in H_2O at lower temperatures from another group [6].

The new data are in reasonable agreement with our previous results, except for a slight discrepancy around 350ºC, which may be due to systematic errors in our earlier work. In particular, temperature was measured at the edge of the pressure cell in the early work, in contrast to the centre of the cell in the new apparatus.

A general observation for both sets of data is that the rate constants go through a broad maximum followed by a sharp fall. We have previously shown that the main reason for this behaviour is the change in the number of collisions per encounter as the solvent becomes less dense [11].

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