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## ARTICLE

## Deciphering the reaction between a hydrated electron and hydronium ion at elevated temperatures

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

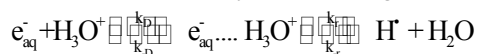
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Jun. Ma,<sup>a</sup> Shinichi Yamashita,<sup>b</sup> Yusa Muroya,<sup>c</sup> Yosuke Katsumura,<sup>b,d</sup> and Mehran Mostafavi<sup>a\*</sup>

The formation of a H<sup>•</sup> atom in liquid water from the reaction of the hydrated electron with hydronium cation is a very challenging subject in chemical processes. Here picosecond pulse radiolysis measurements are performed at elevated temperatures, up to 350 °C, of acidic H<sub>2</sub>O and D<sub>2</sub>O solutions (up to 0.1 mol L<sup>-1</sup> HClO<sub>4</sub>) with the aim of investigating several issues related to this reaction. First, the red shift of the solvated electron absorption band in D<sub>2</sub>O with increasing temperature is found to be affected by the presence of D<sub>3</sub>O<sup>+</sup> in solution. The modified absorption spectra demonstrate the formation of a transient pair between D<sub>3</sub>O<sup>+</sup> and solvated electron at elevated temperature (200-250°C) when the concentration of D<sub>3</sub>O<sup>+</sup> is higher than 0.05 mol L<sup>-1</sup>. For higher temperatures at 300 and 350 °C when the rate constant is almost diffusion controlled, the pair is no longer observable. Second, the presolvated electron in D<sub>2</sub>O is not scavenged up to 250 °C in solution containing 0.1 mol L<sup>-1</sup> D<sub>3</sub>O<sup>+</sup>. Third, the decays at picosecond range obtained under different conditions show that the rate constants are strongly affected by the temperature and by ionic strength. The model with equation of  $\log(k/k_0) = 2A(I)^{0.5}/1 + b(I)^{0.5}$  gives a good fit of the experimental results by taking into account the variation of ionic strength, *I* and, in particular, by considering the temperature dependence of the constant *A*.

### Introduction

The reaction between a hydrated electron and a hydronium cation H<sub>3</sub>O<sup>+</sup> (or D<sub>3</sub>O<sup>+</sup>) in water to form a hydrogen radical atom is the most elementary chemical processes in liquid. From a practical point of view, as the H<sup>•</sup> atom is one the precursors of H<sub>2</sub> formation, information on the mechanism and the rate constant of H<sup>•</sup> formation is a key issue for the chemistry occurring in nuclear power reactors and nuclear fuel treatments. This reaction has been the subject of several studies using the pulse radiolysis method since the first observation of the hydrated electron in 1962 by Hart and Boag.<sup>1</sup> It is well accepted that, during this reaction, due to the rearrangement of solvent molecules around both electron and H<sub>3</sub>O<sup>+</sup>, the reaction rate of this process at room temperature is not controlled by diffusion. The reaction can be modelled by the following mechanism:



At elevated temperatures, the rate constants were only measured in diluted acidic solutions with nanosecond pulse radiolysis setups. The activation energy for this reaction was determined to be around 15 kJ/mol.<sup>2,3,4,5</sup> Numerical simulations

were also performed to unravel the reaction pathway in liquid water as a proton hopping to a distorted electron that is not diffusion controlled.<sup>6-8</sup> It is generally known that the presence of non-reactive metal cations in the vicinity of the hydrated electron shifts the absorption spectrum to a lower wavelength, corresponding to a deeper stabilization of s-like ground state of solvated electron.<sup>9,10</sup> The presence of an encounter pair between hydrated electron and hydronium cation was indicated by kinetics measurements. Very recently, the signature on the formation of this intermediate, denoted  $e_{aq}^- \cdots H_3O^+$ , has been shown by measuring the transient visible absorption in highly concentrated acid solutions (from 0.2 to 6 mol L<sup>-1</sup>).<sup>11</sup> At ambient temperature, a blue shift of the absorption band of solvated electron, compared to that in neat water, was observed only in solutions containing more than 0.2 mol L<sup>-1</sup> H<sub>3</sub>O<sup>+</sup>. By comparing with the effect of non-reactive metal cation, this shift was attributed to the formation of the pair between hydrated electron and the H<sub>3</sub>O<sup>+</sup>. In diluted solution, such a shift cannot be observed because of the short lifetime of the pair compared to the diffusion reaction and its low abundance. Additionally, *ab initio* simulation of electronic and vibrational

spectra of the hydrated  $\text{H}_3\text{O}$  radical exhibit striking similarities with the spectral signatures of the hydrated electron which might also be a reason that it is not likely to observe the pair complex in dilute acidic solutions.<sup>12</sup> In contrast, the absorption band of a hydrated electron both in light water and heavy water undergoes a strong red shift as the temperature raises.<sup>13,14</sup> Molecular simulations by using a cavity model suggested that the change of the absorption band with temperature is related to lower water density and the increase of the cavity size of hydrated electron.<sup>15</sup> More recent models discarding the cavity model and describing the hydrated electron such as multimer ( $\text{H}_3\text{O}(\text{H}_2\text{O})_n$ ) or as an “inverse plum pudding” can also well describe the hydrated electron properties.<sup>16,17</sup>

As CANDU reactors in Canada and pressurized heavy-water reactors (PHWR) in India take  $\text{D}_2\text{O}$  as a moderator and coolant, the radiolysis of  $\text{D}_2\text{O}$  is an important subject. For a given temperature, the absorption band of hydrated electron in  $\text{H}_2\text{O}$  is only slightly different (several nm) from that in  $\text{D}_2\text{O}$  and the spectral shape is similar. Temperature dependence of the rate constants of  $e_{\text{hyd}}^-$  with  $\text{D}_3\text{O}^+$  was previously studied and compared with those in dilute acidic  $\text{H}_2\text{O}$ .<sup>18</sup> An Arrhenius plot of rate constants for isotope effect showed that this reaction in  $\text{D}_2\text{O}$  is slower than that in  $\text{H}_2\text{O}$  due to the lower diffusion coefficient value of  $e_{\text{hyd}}^-$  and  $\text{D}^+$  in  $\text{D}_2\text{O}$ . It is also known that the formation of hydrogen atom undergoes a proton transfer instead of an electron transfer.

Here picosecond pulse radiolysis of the perchloric acid aqueous solutions is studied at elevated temperatures. Concerning the reaction between hydrated electron and hydronium cation in acidic solution (with pH ranging from 3 to 1) several points are examined: (i) the efficiency of presolvated electron or precursor of hydrated electron scavenging at high temperature by the hydronium cation, (ii) whether the encounter pair could be observed at elevated temperature based on the spectral changes of the hydrated electron and (iii) the evaluation of the temperature-dependent rate constant of this reaction in concentrated acid aqueous solutions.

Knowledge of the absorption band of a hydrated electron as the main radiation-induced species is essential for determining the rate constant and radical yield at elevated temperatures. For example, it was reported that, for estimation of presolvated scavenging by  $\text{H}_3\text{O}^+$  at room temperature, knowledge of the maximum of the absorption band is a must.<sup>11</sup> It is expected that this maximum depends on both the concentration of hydronium and the temperature. In addition, the value of the radiolytic yield depends on the value of the molar absorption coefficient of the solvated electron. As the hydronium cation can be in contact with a hydrated electron before reacting, it is essential to determine how the red shift of the absorption band of hydrated electron at elevated temperatures is affected by the presence of cation (mainly  $\text{D}_3\text{O}^+$ ). Moreover, due to the time resolution limitation, up to now only very diluted acidic solutions ( $< 10^{-3} \text{ mol L}^{-1}$ ) were studied at high temperature.<sup>3,4,5,6</sup> The lifetime of hydrated electron at high temperatures is short

and, due to the high reactivity of hydrated electron with hydronium cation ( $k > 2.3 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ ), only picosecond pulse radiolysis measurements allow us to observe the kinetics and the absorption band of a hydrated electron in perchloric acidic aqueous (pH 3 to 1) solutions at elevated temperatures.

## Experimental

The transient absorption pulse-probe setup is based on the laser-electron intrinsic synchronization resulting from the laser triggered photocathode. More details about the well-established picosecond pulse radiolysis setups could be found elsewhere.<sup>19,20</sup> Typically, it is composed of a synchronization system and a measurement system. In the combination of the 22-MeV S-band Linac accelerator (under 10-20 Hz operation) and a femtosecond laser consisting of a Er-doped fiber oscillator (Menlo Systems, C-Fiber 780, under 119 MHz operation), a Ti:Sapphire pre-amplifier (Coherent Inc., Libra-HE, under 1 kHz) and a pulse picker operated with the same frequency of the Linac, they are used as a pulse (for irradiation sample) and a probe (for analysing light absorption), respectively, where the Ti:sapphire laser can provide 782 nm, 100 fs (FWHM), 4.5 mJ/shot pulses. Being the laser is split into two beams, one is used for analysing light and the another is, after the conversion into a 261-nm pulse with 8 ps (FWHM) duration through a third harmonic generator, used for the injection pulse in order to derive the electron beam from the laser photocathode Radiofrequency-gun which is installed at 22-MeV Linac accelerator at Nuclear Professional School of the University of Tokyo (NPS). The electron beam is accelerated at two sections, energy up to 4 MeV through a 1.6 cell accelerating cavity at the photocathode, and finally up to 22 MeV in an accelerating tube. Then, the electron pulse has a duration of 7 ps (FWHM), a charge of more than 2 nC, a normalized emittance of around  $20 \pi \text{ mm mrad}$  (rms), and an energy spread of around 1%.

Here we used the option of the supercontinuum generated in Sapphire as probe light to acquire entire visible transient spectra independently of the shot-to-shot fluctuations and possible long-term drifts of the electron source operated at 14.19 Hz.

The experiments were carried out using a picosecond pulse radiolysis system, based on a pulse-and-probe method associated with an HTHP-OFC (High Temperature High pressure-Optical Flow Cell) at (NPS). Pressure was consistently kept at 25 MPa for all conditions. Since  $\text{H}_2\text{O}$  has absorption around 1100 nm at elevated temperatures, deuterated water  $\text{D}_2\text{O}$  is mainly used for the optical spectrum measurements. However, most of the rate constant measurements are systematically conducted in light water as a solvent. To protect the setup from the corrosion, the highest acid concentration used in this work was limited to  $0.1 \text{ mol L}^{-1}$ . There are two special cases that need to be mentioned here, one is Figure 5 showing the kinetics of  $0.1 \text{ mol L}^{-1} \text{ D}_3\text{O}^+$  instead of  $\text{H}_3\text{O}^+$ . The purpose of this study focused on the reactivity of presolvated

electron other than hydrated electron in terms of a decrease of initial absorbance at 30 ps. The other one is that the absorption spectrums at 300 °C and 350 °C are obtained in H<sub>3</sub>O<sup>+</sup>.

In this pulse-probe scheme, the transient species, namely, hydrated electron are generated by an ionizing electron pulse, while the transient absorption is detected by a femtosecond laser pulse. Detailed characteristics and performances of the accelerator and of the synchronization system have been described elsewhere.<sup>19,20</sup> An HTHP-OFC is placed in front of the exit window of the accelerator, and coupled to the pulse-probe setup. The signal in pure water corresponds to the absorption of the hydrated electron and is used for dosimetry on the basis of  $G_{e^-} = 4.25 \times 10^{-7} \text{ mol J}^{-1}$  at 10 ps.<sup>21</sup> The radiation dose is 22-25 Gy per electron pulse.

Four shots are averaged to obtain the signals. Thanks in part to the use of the double-pulse method, the S/N ratio is higher than 10. The high absorption and good signal quality allow us to measure the decay kinetics of the hydrated electron at elevated temperatures, even if the signal decreases dramatically with lowering the density of water in high temperature conditions. The overall time resolution (rise of signal of solvated electron, from 10 to 90%) is about 40 ps, coming from (a) the pulse width of the electron beam, (b) the pulse width of the analysing light, and (c) the difference between the path lengths of the laser and electron beam while passing through the sample perpendicularly.

## Results and discussion

The absorption spectra of the solvated electron in acidic solutions is not far different from that in deuterated water. Since H<sub>2</sub>O has a light absorption near IR, D<sub>2</sub>O is used as a solvent to lower this absorption for measurements in HClO<sub>4</sub> solutions. Figure 1 shows one example of studied solutions for the absorption band measured in 0.1 mol L<sup>-1</sup> D<sub>3</sub>O<sup>+</sup> solutions at different temperatures. The absorption band is red shifted by increasing the temperature as already reported in neat D<sub>2</sub>O.<sup>13,14</sup> However, the change of the absorption band of the acidic D<sub>2</sub>O solution is slightly different than that of neat D<sub>2</sub>O for the temperature above 150 °C.

At 25 °C, the measurements show the same absorption band as in neat D<sub>2</sub>O, as already reported in the literature. In neat D<sub>2</sub>O, the absorption band measured at picosecond range and at different temperature can be well fitted by the equation given by Bartels *et al.* (Gaussian fit for the spectra part when  $E < E_{max}$ , and Lorentz fit when  $E > E_{max}$ ) for hydrated electron in D<sub>2</sub>O at nanosecond range.<sup>13</sup> As mentioned above, an effect of acid on the absorption band can be detected at room temperature only at high concentration (more than 0.2 mol L<sup>-1</sup>). At 150 °C, a shift of the absorption band is detected but this shift is not obvious and can be within our spectral resolution.

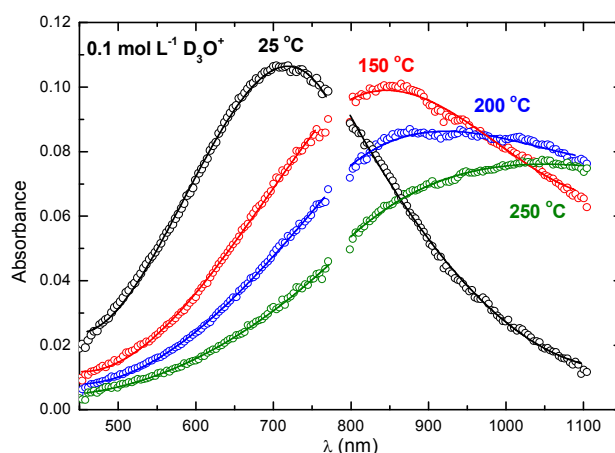


Fig. 1. Temperature-dependent absorption spectra of hydrated electron in the presence of 0.1 mol L<sup>-1</sup> acid perchloric in D<sub>2</sub>O solution measured just after the pulse. The solid lines are only eyes guide.

But at 200 °C, the equation given by Bartels *et al.* for the shape of the absorption band of the hydrated electron in neat D<sub>2</sub>O cannot fit our data in acidic conditions. The absorption band at 200 °C in neat D<sub>2</sub>O with a maximum at 1.30 eV is found at 1.36 eV when 0.1 mol L<sup>-1</sup> HClO<sub>4</sub> is present in D<sub>2</sub>O solution (Figure 2). The shift is at this temperature clearly larger than the error measurement on these broad absorption bands. The intensity of the absorption band measured in the range of 1.1 - 2.8 eV decreases rapidly with time while keeping the same shape. Additionally, the kinetics show that, for this solution at 200 °C, the lifetime of hydrated electron is very short, around 100 ps. For the same absorbed dose per pulse, the maximum of the absorption band in neat D<sub>2</sub>O is located at 950 nm but it is shifted to 900 nm for solution containing 0.1 mol L<sup>-1</sup> D<sub>3</sub>O<sup>+</sup>. The shift can also be verified by the kinetics observed at 900 and 950 nm (Figure 3 inset). In neat D<sub>2</sub>O at 200 °C, the absorbance from kinetics at 950 nm is higher than that at 900 nm while the relation gets inverted in the presence of 0.1 mol L<sup>-1</sup> D<sub>3</sub>O<sup>+</sup>.

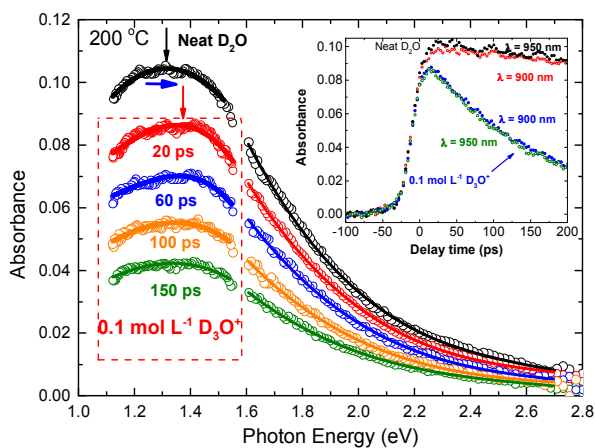


Fig. 2. Absorption spectra of hydrated electron in neat heavy water and in 0.1 mol L<sup>-1</sup> perchloric acid D<sub>2</sub>O solution at 200 °C. Inset: Kinetics observed at the wavelength of 900 nm and 950

nm in neat and acidic heavy water. The times are given after the time zero.

At 250 °C, the maximum is located at 1.17, and 1.24 eV in neat D<sub>2</sub>O and in solutions containing 0.1 mol L<sup>-1</sup> D<sub>3</sub>O<sup>+</sup>, respectively. The value of the maximum of the absorption band of hydrated electron in neat D<sub>2</sub>O and in acidic solutions at 0.1 mol L<sup>-1</sup> are presented in Figure 3. It is clear that change in the absorption band depends on the temperature and also on the concentration of hydronium cation. From room temperature up to 150 °C, within the spectral errors, there is almost no change in the absorption band in the presence of 0.1 mol L<sup>-1</sup> D<sub>3</sub>O<sup>+</sup>. But at higher temperatures (200-250 °C), the formation of complex of “ion pair” is more favored and the blue shift effect is more obvious. The equilibrium constant for the formation of this transient encounter complex was also previously estimated by Shiraishi *et al.* and the value is increasing with the temperature.<sup>3</sup> It is worth noting that in the presence of 0.1 mol L<sup>-1</sup> Li<sup>+</sup> in water at high temperatures, the shift of the absorption band of hydrated electron was not observed whereas the absorption band shifts only slightly at 1 mol L<sup>-1</sup>.<sup>22</sup> These previous results indicate that at the low ion concentration (0.1 mol L<sup>-1</sup> and lower), the spectral shift cannot be due to the ionic strength. That supports also our observations at 200 and 250 °C in the presence of 0.1 mol L<sup>-1</sup> D<sub>3</sub>O<sup>+</sup> are due to the formation of the reactive pair between D<sub>3</sub>O<sup>+</sup> and hydrated electron.

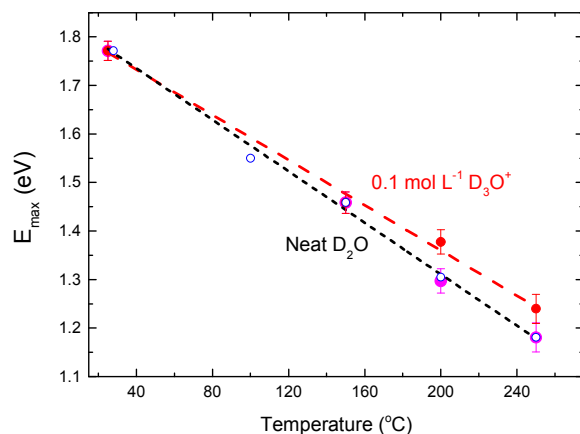


Fig. 3. Energetic position of the maximum of the hydrated electron absorption band plotted at different temperature in 0.1 mol L<sup>-1</sup> acidic aqueous solutions after the electron pulse (red). For comparison, previous results of Bartel *et al.*<sup>13</sup> (pink solid point) and Wu *et al.*<sup>14</sup> (blue open point) in neat D<sub>2</sub>O are also given. The dashed lines are eyes guide.

Due to the ultrafast decay of solvated electron, within our time resolution (30 ps), measurements at 300 °C and 350 °C were not possible for the concentration above 0.05 mol L<sup>-1</sup>. As shown in Fig.1, at these temperatures, the maximum of the absorption band is beyond our observation window. Nevertheless, the shape of the absorption band of hydrated electron between 800 and 1100 nm is almost the same in neat water at 300 and 350°C than those measured for the same temperature but in the presence of low amount of H<sub>3</sub>O<sup>+</sup> (Figure

4). In these cases, no shift of the absorption band compared to neat water is observed. This observation could be also in agreement with the finding that, at these temperatures, the activation barrier of H<sup>+</sup> atom formation disappears and the high rate constant of the reaction is almost controlled by diffusion. The absence of the spectral shift can also be explained by the fact that, for these temperatures, the proton tunnelling process can be also an important factor for the high rate constant and the absence of the pair observation. In that case the lifetime of the pair is negligible even if it is formed very quickly by fast diffusion.

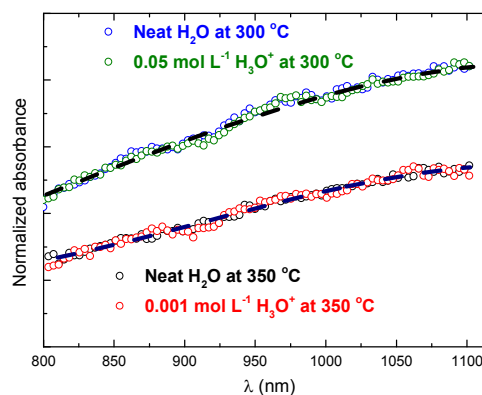


Fig. 4. Normalized absorption spectra performed at 300 °C and 350 °C in neat light water and in the presence of 0.05 mol L<sup>-1</sup> and 0.001 mol L<sup>-1</sup>, respectively. The dash line is best fit of the spectral data showing that the spectrum are almost identical between H<sub>2</sub>O and 0.001-0.05 mol L<sup>-1</sup> H<sub>3</sub>O<sup>+</sup> when the temperature is above 300 °C.

The decays of hydrated electron are observed at different concentrations and different temperatures at the maximum of the absorption band. The kinetics of hydrated electrons in a solution containing 0.1 mol L<sup>-1</sup> D<sub>3</sub>O<sup>+</sup> show that higher temperature accelerates the decays but the presolvated electron is not scavenged at this concentration even at 250 °C. At 300 °C, the decay observed is only limited for 0.05 mol L<sup>-1</sup> H<sub>3</sub>O<sup>+</sup> as the maximum of studied concentration. The decay at 300 °C also does not present any scavenging of presolvated electron. It is worth noting that the  $C_{37}$ , which is defined as the molar value of the electron scavengers to decrease the 1/e of precursor of hydrated electron of H<sub>3</sub>O<sup>+</sup> at room temperature, is 3.5 mol L<sup>-1</sup>. At such a high temperature, we could expect that the presolvated electrons react very rapidly with H<sub>3</sub>O<sup>+</sup> before becoming solvated. However, the small decrease of the initial absorbance after the pulse at high temperature is due only to the fast reaction within the electron pulse (Figure 5). Therefore, it can be considered that at 250 °C,  $C_{37}$  for presolvated electron scavenging is larger than 0.1 mol L<sup>-1</sup>. Although a femtosecond pulse is more suitable to be used to clarify the reactivity of a presolvated electron in an acidic medium, it seems at least that this scavenging reaction of presolvated electrons is not very temperature dependent.

As expected, increasing the concentration of  $\text{H}_3\text{O}^+$  at 200 °C results in faster decay (Figure 6 inset). However, the effect of the concentration on the decay is much smaller than that deduced from the previous experiments performed in diluted acid media<sup>23</sup>. The pseudo-first order rate constants are reported for 200 and 300 °C (Figure 6). The rate constants are lower than those reported in the literature without taking into account the ionic strength (dashed lines in Figure 6).

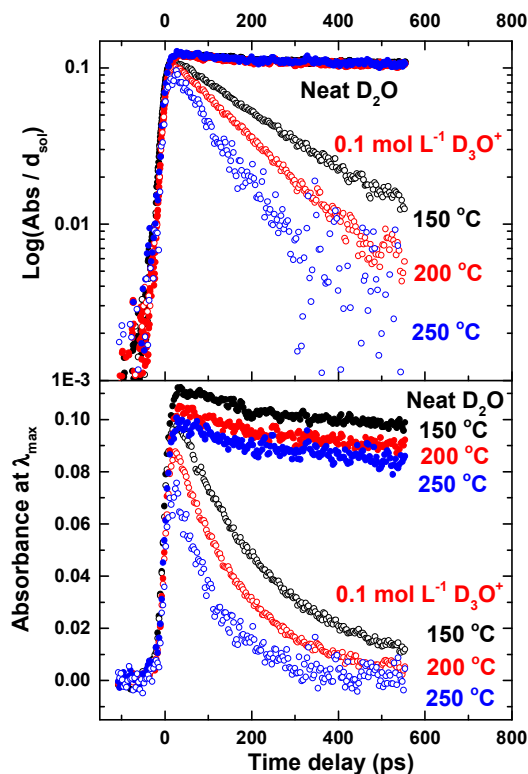


Fig. 5. Decay of solvated electron, observed at maximum of the absorption band at different temperature in neat  $\text{D}_2\text{O}$  (solid circle) and in  $0.1 \text{ mol L}^{-1}$  acid  $\text{D}_2\text{O}$  solution (open circle) (bottom). Decay in  $\text{D}_2\text{O}$  and acidic  $\text{D}_2\text{O}$  solution at 150, 200 and 250 °C in logarithmic scale and by correcting the density effect (top).

It is worth noting that the  $\text{HClO}_4$  molecule is completely dissociated up to 350 °C<sup>24</sup>. That can be explained by the fact that, in our conditions, the ionic strength is higher than when a much lower concentration of acid is used for the rate constant determination by nanosecond pulse radiolysis. The classical Brønsted-Bjerrum model can be considered to take into account the ionic strength effect. The Brønsted-Bjerrum equation is valid in the range of concentrations studied in this work. The following equation on the rate constant is:

$$\log_{10}\left(\frac{k}{k_0}\right) = \frac{2Az_Az_B\sqrt{I}}{1+\sqrt{I}} \quad (1)$$

$A$  is a constant with the value of 0.51 at room temperature.  $I$  is the ionic strength. The effect of  $I$  is not so important on the rate constant in the range of concentrations studied in this work. In fact, in the Brønsted equation, the rate constant is affected not

only by the concentration of the solutes (through  $\sqrt{I}$ ) but also by the temperature. The experimental  $k_{obs}$  values are not linear versus the concentration and the difference cannot be explained only by the variation of  $\sqrt{I}$  with acid concentration. In fact, for a given concentration, the value of  $A$  depends strongly on the temperature. The equation given for  $A$  is:

$$A = \frac{\sqrt{2}F^2e}{8\pi(\varepsilon(T)RT)^{3/2}} \quad (2)$$

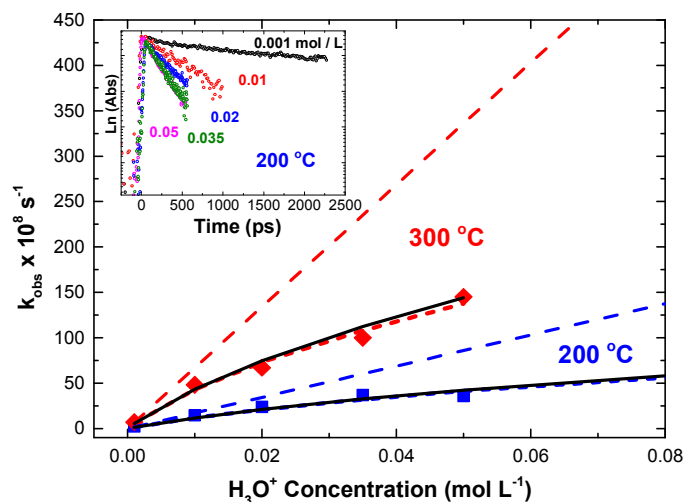


Fig. 6. Pseudo-first order rate constant versus  $\text{H}_3\text{O}^+$  concentration reported at 200 and 300 °C. For comparison, previous results given by Bartels et al.<sup>18</sup> (dashed lines at 300 and 200 °C). The dotted lines present the results by using the equation (1) and (2). Inset: the decay of solvated electron at 200 °C at different concentration of  $\text{H}_3\text{O}^+$ . Black solid line is curve from the modified equation (3) by considering the parameter “ $B$ ”.

$F$  and  $R$  are Faraday and universal gas constants, respectively.  $\varepsilon(T)$  is the temperature dependent of the dielectric constant of water. The value of the dielectric constant of water decreases from 78 to around 25 when the temperature is increased from 25 to 300 °C, respectively. By increasing the temperature  $\varepsilon(T)T$  is decreasing as the  $\varepsilon(T)$  decreases much faster. Consequently, the value of  $A$  in equation (2) increases with temperature<sup>25</sup>. We also used the modified equation of Debye - Hückel by taking into account the distance of closest approach of the ions ( $a$ ) and temperature dependent of the factor  $B$ .

$$\log_{10}\left(\frac{k}{k_0}\right) = \frac{2Az_Az_B\sqrt{I}}{1+aB\sqrt{I}} \quad (3)$$

$B$  is proportional to  $\sqrt{\varepsilon(T)T}$ . At room temperature the value of  $aB$  equals to 1 according to the so-called “limiting law” of Debye-Hückel and increase up to 1.12 and 1.29 at 200 and 300 °C, respectively by considering the changes of factor  $B$  with temperature. By taking into account the temperature change of  $B$  in equation (3), the modified curves (black solid line) are obtained (Fig.6). The temperature dependent parameter “ $B$ ” does not have much pronounced effect on the rate constant

value from Brønsted-Bjerrum equation in the conditions (at 200, 300 °C, 0.001-0.05 mol L<sup>-1</sup>) that we studied.

Therefore, compared to diluted solutions at the same temperature, increasing the concentration of acid in solution (the effect of ionic strength), decreases considerably the rate constant of reaction between solvated electron and hydronium. As reported in Figure 6, for a given concentration (a given value of *I*) for instance for 0.05 mol L<sup>-1</sup>, the effect is more pronounced at 300 °C than at 200 °C. By taking the effect of ionic strength via equations 1 and 2, the calculated values are very close to the experimental ones.

## Conclusions

The shift of the absorption band is important for all radiolytic yield determinations based on observation of hydrated electrons. Our results show that the red shift of the absorption band in neat water observed for hydrated electrons at high temperature is affected by the presence of hydronium cations. This observation confirms the formation of a pair between a hydrated electron and a hydronium cation before the reducing reaction. It is important to note that the pairing effect on the absorption band is less important than the density effect. The latter imposes a shift of the absorption band to the red, even if it is less important than in the neat water. Such a blue shift can be observed at room temperature but only at a very high concentration of acid solution. In addition, in our condition of concentration, this pair is not observed at 300 °C and higher temperatures. In fact with the decrease of the dielectric constant of water at these temperatures, the Columbic attraction becomes very strong favouring the pair formation. But in the meantime the rate constant of H<sup>+</sup> atom formation is very high and even a proton tunnelling process could occur avoiding the observation of the pair at temperature higher than 250 °C. The observation of the pair is correlated with temperature-dependent variation of the rate constant, which increases rapidly from 250 °C and become almost diffusion controlled at 350 °C.

The decay kinetics are dependent on H<sub>3</sub>O<sup>+</sup> concentration, showing that this reaction remains a proton transfer reaction even at elevated temperatures. Moreover, the rate constant is highly affected by the ionic strength of the solution at elevated temperatures. According to our knowledge, up to now the classic Brønsted-Bjerrum equation has not yet been successfully applied to such an elementary reaction involving radicals at elevated temperatures. The decrease in the rate constant of the hydrated electron decay observed with increasing concentration of acidic solutions can be generalized with other charged species involved in the mechanism at elevated temperatures. In fact, knowledge of the rate constants at extreme conditions (high temperature and ionic strength) is required for the best fits in the simulations codes usually used in radiation chemistry.

## Notes and references

<sup>a</sup> Laboratoire de Chimie Physique/ELYSE, Université Paris-Sud 11, UMR 8000, Bât. 349, Orsay, France.

<sup>b</sup> Nuclear Professional School, School of Engineering, The University of Tokyo, 2-22 Shirakata-shirane, Tokai-mura, Naka-gun, Ibaraki 319-1188, Japan.

<sup>c</sup> The Institute of Scientific and Industrial Research (ISIR) Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

<sup>d</sup> Japan Radioisotope Association (JRIA), Honkomagome 2-28-45, Bunkyo-ku, Tokyo 113-8941, Japan.

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