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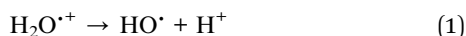
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## Comment on “Radical-mediated proton transfer enables hydroxyl radical formation in charge-delocalized water” by R. Zhao, Q. Zhang, N. Yang, L. Li, Z. Li and C. Cui, *Chem. Sci.*, 2025, 16, 11954

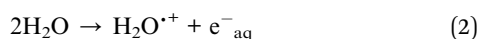
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Cui and coworkers claim that  $\text{H}_2\text{O}^{\bullet+}$  and  $\text{HO}^\bullet$  are formed spontaneously by lowering the pH to below 4. This is thermodynamically most unlikely. Thus, proton transfer does not involve  $\text{HO}^\bullet$ .

Cui and coworkers<sup>1</sup> reported recently that “proton transfer proceeds *via* a  $\cdot\text{OH}\cdots\text{H}^+\cdots\text{H}_2\text{O}$  intermediate, enabling a radical-mediated proton transfer pathway” and “that thermal energy at room temperature is sufficient to drive the formation of  $\cdot\text{OH}$  radicals in acidic solutions”.<sup>1</sup> They hypothesize that  $\text{HO}^\bullet$  originates from  $\text{H}_2\text{O}^{\bullet+}$  [dihydrodooxygen( $\cdot$ ) or oxydaniumyl], reaction (1):



The fate of the electron that was removed from  $\text{H}_2\text{O}$  is not mentioned. Possibly, Cui and coworkers assume that a hydrated electron ( $\text{e}^-_{\text{aq}}$ ) is formed, as has been suggested elsewhere,<sup>2</sup>



In any case, mass balance was not preserved. In support of their hypothesis, they claim to have detected a crown ether- $\text{H}_2\text{O}^{\bullet+}$  complex.

Science progresses by building on what has been established. For over 60 years, species like hydrated electrons, hydroxyl radicals, and other short-lived species have been studied; their thermochemical and kinetics properties are known and have been compiled (<https://kinetics.nist.gov/solution/>).<sup>3,4</sup> When one consults this body of knowledge, one must conclude that formation of  $\text{H}_2\text{O}^{\bullet+}$  and  $\text{HO}^\bullet$  as proposed is thermodynamically most unlikely. One may, of course, question this body of knowledge, but Cui and coworkers<sup>1</sup> do not do so. They acknowledge that  $\text{HO}^\bullet$  is very oxidizing, quoting the standard electrode potential ( $E^\circ$ ) at pH 14, but not the implication that  $\text{HO}^\bullet$  is energetically difficult to obtain from water. Two minor criticisms: (1) that one-electron potential should be called a reduction potential, not an oxidation potential,<sup>5</sup> and (2), it cannot be compared to the two-electron reduction potential of the  $\text{Cu}^{2+}/\text{Cu}$  couple. Below

I show that  $\text{H}_2\text{O}^{\bullet+}$  and  $\text{HO}^\bullet$  are unlikely to have been present in the solutions examined by Cui and coworkers.<sup>1</sup>

The species  $\text{H}_2\text{O}^{\bullet+}$  and  $\text{e}^-_{\text{aq}}$  are formed by ionizing radiation.<sup>6</sup>  $\text{H}_2\text{O}^{\bullet+}$  has a very short lifetime  $\tau$  of 46 fs, because reaction (1) is very fast,  $k = 2 \times 10^{13} \text{ s}^{-1}$ .<sup>7</sup> Whether  $\text{H}_2\text{O}^{\bullet+}$  can be scavenged depends on how far it can diffuse. To provide an *upper* limit on that distance, I make the assumption that  $\text{H}_2\text{O}^{\bullet+}$  has the same diffusion coefficient ( $D$ ) as  $\text{H}^+$ ,  $9.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at 25 °C.<sup>8</sup> During  $2\tau$ , after which 14% of  $\text{H}_2\text{O}^{\bullet+}$  is left, the root mean square displacement, calculated with  $(6Dt)^{1/2}$  is 72 pm, or half the radius of a water molecule. Thus, unless produced directly next to a scavenger,<sup>9</sup>  $\text{H}_2\text{O}^{\bullet+}$  decays to  $\text{HO}^\bullet$  and  $\text{H}_3\text{O}^+$ . The conclusion is clear:  $\text{H}_2\text{O}^{\bullet+}$  cannot be trapped or captured.

Little is known about the thermodynamic properties of  $\text{H}_2\text{O}^{\bullet+}$ . It has never been included in reviews of  $\text{O}_2$  and its reduced forms,<sup>4,10,11</sup> because of its short lifetime.  $E^\circ(\text{H}_2\text{O}^{\bullet+}/\text{H}_2\text{O})$  has been estimated at  $>4 \text{ V}$ ,<sup>9</sup> which makes  $\text{H}_2\text{O}^{\bullet+}$  the most oxidizing species known. Use of a thermochemical cycle that consists of the reactions (3) and (4), see Fig. 1, allows one to make a more precise estimate of  $E^\circ(\text{H}_2\text{O}^{\bullet+}/\text{H}_2\text{O})$  and of  $\Delta_r G^\circ(\text{H}_2\text{O}^{\bullet+}_{\text{aq}})$ :

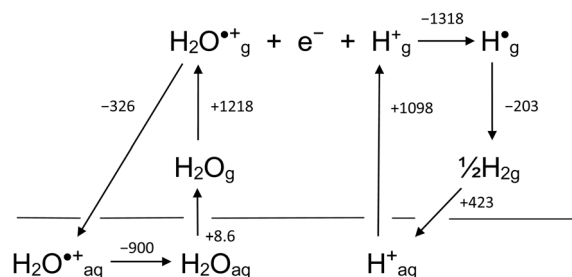
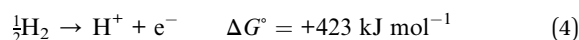


Fig. 1 Thermochemical diagram for the calculation of  $E^\circ(\text{H}_2\text{O}^{\bullet+}/\text{H}_2\text{O})$ . It shows the energetics in  $\text{kJ mol}^{-1}$  of reactions (3) and (4), which are  $-900 \text{ kJ mol}^{-1}$  and  $+423 \text{ kJ mol}^{-1}$ , respectively, as calculated from data cited in the text. The sum of the energetics of these two reactions yields  $E^\circ(\text{H}_2\text{O}^{\bullet+}/\text{H}_2\text{O}) = +4.95 \text{ V}$  *via*  $\Delta_r G^\circ = -nF\Delta E^\circ$ , in which  $n$  is 1.

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Reaction (4) is necessary because standard electrode potentials are referenced to the normal hydrogen electrode.<sup>5</sup> This approach is identical to that described by Phillips and Williams.<sup>12</sup> To provide a *lower* limit on  $E^\circ(\text{H}_2\text{O}^{\bullet+}/\text{H}_2\text{O})$ , I assume that  $\text{H}_2\text{O}^{\bullet+}$  is hydrated, that is, the solvating  $\text{H}_2\text{O}$  molecules are oriented to  $\text{H}_2\text{O}^{\bullet+}$  in an energetically most favourable way. Whether, or how fast,  $\text{H}_2\text{O}^{\bullet+}$  becomes hydrated, is a topic for another time. The standard Gibbs hydration energy of  $\text{H}_2\text{O}^{\bullet+}$  is unknown. Because the radius of  $\text{H}_2\text{O}$  is close to that of  $\text{K}^+$ , I use the standard Gibbs hydration energy of the latter,  $-326 \text{ kJ mol}^{-1}$ , for  $\text{H}_2\text{O}^{\bullet+}$ .<sup>13</sup> The ionisation potential of  $\text{H}_2\text{O}$  is 12.621 eV,<sup>3</sup> and the hydration energy of  $\text{H}_2\text{O}$  is  $-8.6 \text{ kJ mol}^{-1}$ .<sup>14</sup> For reaction (4) I use the Gibbs hydration energy of  $\text{H}^+$ ,  $-1098 \text{ kJ mol}^{-1}$ ,<sup>15</sup> the ionisation potential of  $\text{H}^+$ , 13.60 eV,<sup>3</sup> and 1/2 of the Gibbs dissociation energy of  $\text{H}_2$ ,  $+203 \text{ kJ mol}^{-1}$ .<sup>14</sup> The sum of the energetics of reactions (3) and (4) is  $-477 \text{ kJ mol}^{-1}$ , which results in  $E^\circ(\text{H}_2\text{O}^{\bullet+}/\text{H}_2\text{O}) = +4.95 \text{ V}$  and  $\Delta_f G^\circ(\text{H}_2\text{O}^{\bullet+}_{\text{aq}}) = +240 \text{ kJ mol}^{-1}$ . Both ionisation potentials are enthalpies, but as used, the two errors caused by neglect of the respective entropies are expected to cancel. Given the assumption that the Gibbs hydration energy of  $\text{H}_2\text{O}^{\bullet+}$  is close to that of  $\text{K}^+$ , I assign an error of 0.10 V to  $E^\circ(\text{H}_2\text{O}^{\bullet+}/\text{H}_2\text{O})$  and an error of  $10 \text{ kJ mol}^{-1}$  to  $\Delta_f G^\circ(\text{H}_2\text{O}^{\bullet+}_{\text{aq}})$ . Thus, reaction (1) is indeed very favourable,  $-214 \text{ kJ mol}^{-1}$ . The implication of the value of  $\Delta_{\text{rxn1}} G^\circ$  may not be immediately clear: if one imagined a solution that was 1 M in  $\text{H}^+$  and  $\text{HO}^\bullet$  each, 2.2 molecules of  $\text{H}_2\text{O}^{\bullet+}$  would be present at equilibrium in  $1 \times 10^{14}$  liter of water. This number is a *maximum*, because of the assumption that  $\text{H}_2\text{O}^{\bullet+}$  is solvated. If it is not, the solvation Gibbs energy of  $-326 \text{ kJ mol}^{-1}$  disappears from the left of Fig. 1 which results in  $E^\circ(\text{H}_2\text{O}^{\bullet+}/\text{H}_2\text{O}) \cong +8.3 \text{ V}$ , and  $\Delta_f G^\circ(\text{H}_2\text{O}^{\bullet+}_{\text{aq}}) \cong +570 \text{ kJ mol}^{-1}$ .

The absorption spectrum and properties of  $\text{e}^-_{\text{aq}}$  were described already in the early 1960s.<sup>16,17</sup>  $\Delta_f G^\circ(\text{e}^-_{\text{aq}}) = +278 \text{ kJ mol}^{-1}$ ; with  $\Delta_f G^\circ(\text{H}_2\text{O}^{\bullet+}) = +240 \text{ kJ mol}^{-1}$ , one calculates that the disproportionation reaction, reaction (2), is endergonic by  $+922 \text{ kJ mol}^{-1}$ , again, a best case scenario based on  $\text{H}_2\text{O}^{\bullet+}$  being hydrated. Thus the formation of the hydrated electron does not compensate, by far, for the one-electron oxidation of water, as was suggested by Head-Gordon and coworkers.<sup>18</sup> The statement that “pure water contains 0.3 M of fully charged water molecules”<sup>2</sup> is incorrect, as are the results of the *ab initio* calculations of Cui and coworkers<sup>1</sup> on the presence of  $\text{H}_2\text{O}^{\bullet+}$  in acidified water. In contrast, my thermochemical analysis is straightforward and yields accurate results.

I will not address in detail the evidence that, according to the authors,<sup>1</sup> supports the formation of  $\text{HO}^\bullet$  and  $\text{H}_2\text{O}^{\bullet+}$  at room temperature in acidified water, except to point out, again, that  $\text{H}_2\text{O}^{\bullet+}$  cannot be scavenged; that the reaction of  $\text{HO}^\bullet$  with benzoate<sup>19</sup> and other aromatic compounds<sup>20,21</sup> leads to hydroxylated products; decarboxylation is a very minor reaction, and that the oxidation of  $\text{I}^-$  may be due to traces of  $\text{O}_2$ . The latter reaction takes place near and below pH 4, a common observation during iodometric titrations. Deoxygenation by passing Ar

through a solution is rarely effective. To achieve full deoxygenation, use of the Schlenk technique and a glove box are essential. Other explanations for the results of the scavenging experiments of  $\text{HO}^\bullet$  must be found.

In conclusion, and contrary to the report of Cui and coworkers<sup>1</sup> and others,<sup>2,22</sup> the short lifetime of  $\text{H}_2\text{O}^{\bullet+}$  prevents it from playing a role in any reaction. The Grotthuss mechanism of proton transfer<sup>23</sup> does not involve  $\text{HO}^\bullet$ .

## Author contributions

WHK is the sole author.

## Conflicts of interest

No competing interests.

## Data availability

No experiments were carried out. All results shown were calculated from thermodynamics and kinetics data available in the literature. All sources have been referenced.

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