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Reactivity of the Strongest Oxidizing Species in Aqueous Solutions: The Short-Lived Radical Cation $\text{H}_2\text{O}^{\bullet+}$

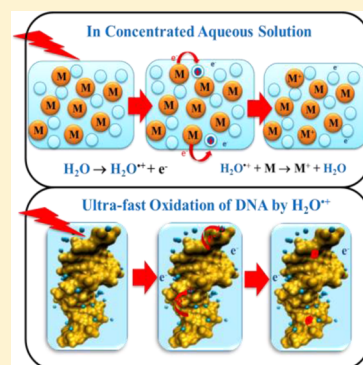
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S Supporting Information

ABSTRACT: The radical cation $\text{H}_2\text{O}^{\bullet+}$ formed under irradiation of liquid water undergoes an ultrafast proton transfer reaction and consequently exhibits an extremely short lifetime. The proton transfer yields an oxidizing OH^\bullet radical whose reactivity has been extensively studied. By contrast, $\text{H}_2\text{O}^{\bullet+}$ reactivity with molecules other than water has not been established experimentally and was subject to controversy. The direct oxidation by $\text{H}_2\text{O}^{\bullet+}$ can take place in various situations. In highly concentrated solutions, the radical cation $\text{H}_2\text{O}^{\bullet+}$ may also be involved in ultrafast electron transfer reactions. We have applied picosecond pulse radiolysis conducted at the electron accelerator ELYSE on solutions with various H_2SO_4 concentrations to determine the scavenging yield of $\text{H}_2\text{O}^{\bullet+}$. The yield of $\text{H}_2\text{O}^{\bullet+}$ at a few tens of femtoseconds is estimated to be around $5.3 \times 10^{-7} \text{ mol J}^{-1}$, and its reactivity is quantitatively determined. Moreover, a simple estimation of the reduction potential of this short-lived radical cation shows that it is the most powerful oxidizing species.

SECTION: Kinetics and Dynamics



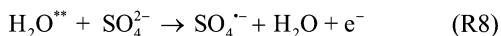
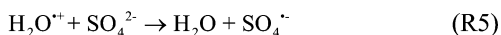
One electron oxidation is an important class of chemical reactions in solution. Examples are the corrosion that is the alteration of a material by an oxidant, or the oxidative stress in biological cells.^{1–3} Among the common oxidizing species, some (such as O_2 , O_3 , H_2O_2), are relatively stable, whereas radical species such as OH^\bullet , HO_2^\bullet , $\text{CO}_3^{\bullet-}$, NO_3^\bullet and $\text{SO}_4^{\bullet-}$ are highly reactive. These radicals play an important role, especially in the respiratory metabolism, where their reactivity has been extensively studied.^{4,5} Serious diseases are triggered by these radicals, and they also act as intermediates in many chemical reactions. Some of these radicals can also be used to treat certain diseases, such as in cancer radiotherapy, or applied in water treatment.

The lifetime of these species ranges from nano- to milliseconds, and is highly dependent on the environment. Electron accelerators are used to generate the radical species, and the time-resolved detection of their optical properties is used to observe their reactions. The OH^\bullet radicals, which are very efficient oxidizing species, are formed during the ionization of water.⁶ They react with many electron-rich or H-rich molecules, and the rate constants of these reactions have been reported.⁷

However, when the water molecule is ionized (R1) (by energetic photons or charged particles), the primary species formed is the radical cation $\text{H}_2\text{O}^{\bullet+}$ that subsequently undergoes proton transfer, yielding H_3O^+ and OH^\bullet radical (R2).

Recently, it was shown that this radical cation can be also produced by core ionization of water through the formation of a dicationic $[\text{H}_2\text{O}^{\bullet+} \cdots \text{H}_2\text{O}^{\bullet+}]$ complex.⁸ However, the radical cation $\text{H}_2\text{O}^{\bullet+}$ is replaced very quickly, within a few tens of femtoseconds, via a proton transfer reaction involving a

Scheme 1. Primary Reactions Involved in Pulse Radiolysis of Highly Concentrated Sulfuric Acid Solutions^a



^aR1, R4, and R7 are due to the direct effect of radiation.

neighboring water molecule (R2). There is not yet a precise lifetime measurement of this radical cation. The observation of $\text{H}_2\text{O}^{\bullet+}$ was performed in neat liquid water using an ultrafast 30 fs laser, suggesting that the radical cation $\text{H}_2\text{O}^{\bullet+}$ absorbs light in the visible spectral domain.⁹ Recently, its lifetime was estimated to be around 200 fs by polarization anisotropy measurements.¹⁰ If diffusion is necessary to encounter the species to be oxidized by electron transfer, reaction R2 is the dominant path for the

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decay of $\text{H}_2\text{O}^{\bullet+}$. Therefore, the only possible reaction for $\text{H}_2\text{O}^{\bullet+}$ radical cation with a molecule other than H_2O is a “static reaction”. That is to say, to react, the radical cation must be at contact with the target molecule as soon as it formed. In this case, diffusion is not necessary, and $\text{H}_2\text{O}^{\bullet+}$ can oxidize the solute molecule in its immediate vicinity before it undergoes reaction R2.

In solutions containing high concentration of NaCl, NaBr, or HNO_3 , it was difficult to reach the clear conclusion about the possible reaction of $\text{H}_2\text{O}^{\bullet+}$ with Cl^- , Br^- , and NO_3^- , as OH^\bullet radicals may also contribute to the oxidation of these anions.^{11–13} However, it was suggested that the ultrafast proton transfer reaction (R2) of the radical cation $\text{H}_2\text{O}^{\bullet+}$ could compete with the electron transfer reaction (R3).^{14,15}

The objective of the present study is to establish the occurrence of electron transfer to $\text{H}_2\text{O}^{\bullet+}$ in competition with the OH^\bullet formation and the subsequent reactions. To this end, concentrated sulfuric acid solutions were chosen because (i) it is possible to study almost neat H_2SO_4 (98%) in order to directly obtain the radiolytic yield of the oxidation via the direct effect of radiation, (ii) sulfuric acid is itself a strong acid that is insensitive to proton transfer, (iii) the molar absorption coefficient of the secondary radical $\text{SO}_4^{\bullet-}$ is well established, (iv) contrary to Na^+ cation, the counterions H^+ are not involved in the direct effect production of such radicals and the electron transfer reactions, and (v) in contrast to the halides and HNO_3 , H_2SO_4 does not react with the OH^\bullet radical in the picosecond time scale even at high concentration. In addition, pulse radiolysis on the picosecond scale on ELYSE facility¹⁶ allows to obtain the radical yields on a short time when the binary reactions in radiolytic spurs are still negligible. For these reasons, H_2SO_4 serves as the perfect model system to study reactivity of $\text{H}_2\text{O}^{\bullet+}$. In the past, this system has been subject of several studies, but the mechanism involving $\text{H}_2\text{O}^{\bullet+}$ was not recognized.^{17–20} Therefore, in the present report the oxidation of sulfate anions by $\text{H}_2\text{O}^{\bullet+}$ generated by picosecond electron pulse radiolysis is examined. The experimental observable is the absorption of the secondary sulfate radical $\text{SO}_4^{\bullet-}$ probed by ultrafast broadband detection (More details on the picosecond pulse radiolysis setup are reported in the Supporting Information (SI)).

Due to the strong intermolecular-hydrogen bonding,^{21,22} islands of water clusters or other inhomogeneous water distributions are not reported in the mixtures of sulfuric acid and water, and even at high concentrations, these samples can be considered as real solutions. Therefore, for statistical reason, in concentrated solutions, each water molecule is in contact with one or more solute molecules. Under these conditions, the proton transfer reaction to H_2O becomes less likely than the reaction of electron transfer to $\text{H}_2\text{O}^{\bullet+}$. Indeed, our picosecond measurements demonstrate that $\text{H}_2\text{O}^{\bullet+}$ can oxidize SO_4^{2-} . Once $\text{H}_2\text{O}^{\bullet+}$ is formed under irradiation, it may in situ capture the electron of the neighboring anion SO_4^{2-} to form $\text{SO}_4^{\bullet-}$.²³ The similar oxidation reaction by the OH^\bullet radical would be at least 10^5 times slower.²⁴

In the case of sulfuric acid solutions, the radical $\text{SO}_4^{\bullet-}$ (or acid form of the radical HSO_4^\bullet generated in highly acidic solutions of 16 and 18 M) absorbing at 450 nm (or 460 nm) is generated (Figure 1) within the duration of the electron pulse (7 ps).^{20,20,25} We note that under the same irradiation conditions, i.e., for the same dose of radiation that is absorbed by the solution, the initial end-of-pulse yield of the $\text{SO}_4^{\bullet-}$ increases with the concentration of the sulfate up to 12 M, and

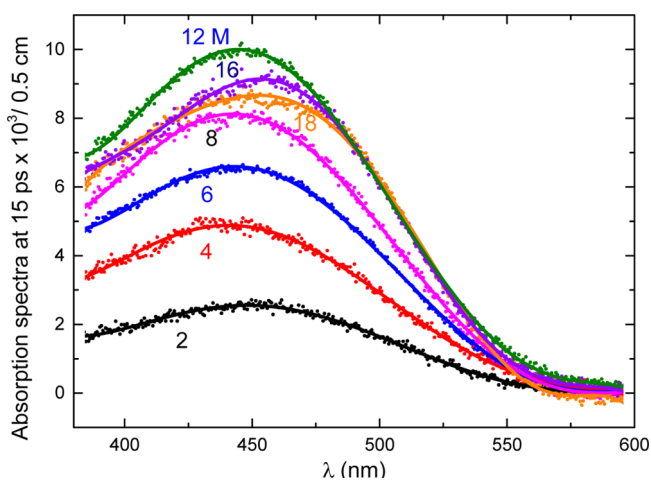


Figure 1. Transient absorption at 15 ps in sulfuric acid solutions of various concentrations, recorded with the pump–probe setup at ELYSE. The contribution from the solvated electron absorbance that is observed at concentrations lower than 6 M was subtracted.

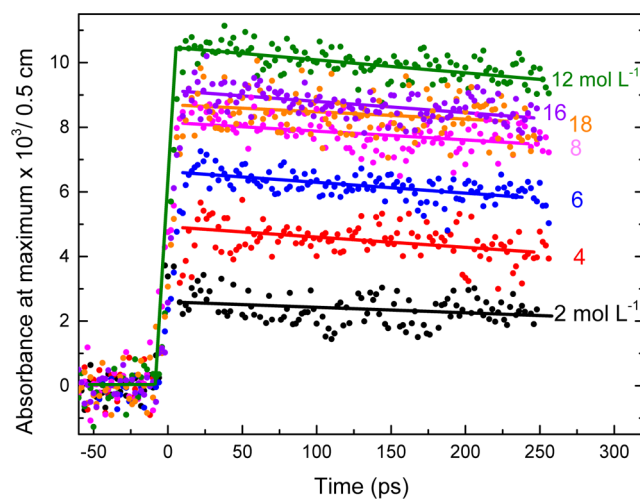


Figure 2. The formation of $\text{SO}_4^{\bullet-}$ (or HSO_4^\bullet) radical anion within the electron pulse of 7 ps at various concentrations of H_2SO_4 , as observed around 450 nm. The slow decay after the initial formation of this radical is due to the reaction of this species with H^\bullet atoms in radiolytic spurs.

then it decreases (see also Figure 2). For concentrations higher than 4 M solvated electron disappears within the pulse and the decay observed at 450 nm is only due to $\text{SO}_4^{\bullet-}$. For lower concentrations (2 and 4 M), the decay of solvated electron lasts about 150 ps. The absorption observed at longer time is only due to $\text{SO}_4^{\bullet-}$. Therefore, the contribution of solvated electron absorption known from transient absorbance around 700 nm is subtracted in both Figure 1 and 2.

Based on the contribution of the direct effect yield (G_{dir}) and solvent effect yield (G_{w}) on the formation of the secondary radical according to the following equation:

$$G_{\text{exp}}(\text{SO}_4^{\bullet-}) = f_s G_{\text{dir}} + f_w G_w$$

where f_s is the solute electron fraction and f_w is solvent electron fraction, the analysis of the initial experimental yields of $\text{SO}_4^{\bullet-}$ (Figure 3) indicates that its instantaneous formation is partly due to the direct absorption of energy by H_2SO_4 (direct effect, R4 and R7) for which the efficiency is determined from the

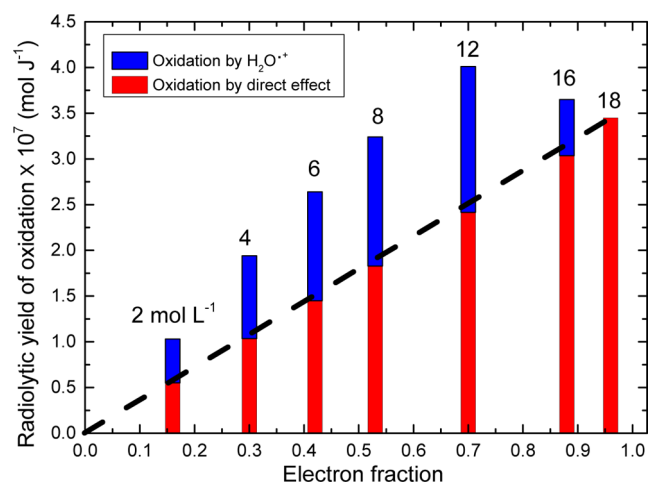


Figure 3. Radiolytic yield of SO_4^{2-} (or HSO_4^*) versus electron fraction for SO_4^{2-} in sulfuric acid solutions. Dashed line: linear contribution of the direct effect determined from neat H_2SO_4 data.

experiments on (almost) pure H_2SO_4 . Another contribution is due to the reaction R5. When sulfuric acid is almost pure (18 mol L^{-1}), water molecules are extremely rare, and the contribution of the $\text{H}_2\text{O}^{+\bullet}$ radical cation to the oxidation of the sulfate becomes negligible.

The formation of the secondary radical through an excited state, SO_4^{2-*} , can be considered (R7) and can constitute another possibility for the direct effect. During radiation of the solutions, short-lived excited states in water are also produced. It is considered that these excited states relax to ground state or, as in neat water, generate H_2 , O^* , OH^* , and H^* atoms with a low radiolytic yield. Even if reaction R8 cannot be excluded, in this work it is assumed that chemical effect on SO_4^{2-} of these excited states is negligible. In fact, the amount of solvated electron observed at 15 ps (not reported here) for different concentration of sulfuric acid confirms our assumption.

As the redox potential of the couple $E^\circ(\text{SO}_4^{\bullet-}/\text{SO}_4^{2-}) = 2.5 \text{ V}_{\text{NHE}}$ relative to normal hydrogen electrode is very high,²⁶ the oxidation of SO_4^{2-} is thermodynamically prohibitive, and it requires a uniquely strong oxidant.

From (i) the concentration-dependent yield of the radical formation within the electron pulse, (ii) the competition between the proton transfer and electron transfer reactions, and (iii) the calculated contribution of the direct effect, the rate constant of the oxidation reaction of electron transfer (reaction R5) is found to be greater than 10^{13} s^{-1} . Note that the process is not controlled by the diffusion but involves species in contact.

It is important to note that the yield of scavenged $\text{H}_2\text{O}^{+\bullet}$ is increasing with the concentration of sulfuric acid (Figure 4). Especially interesting is the behavior observed at concentrations of 12 and 16 mol L^{-1} , at which the amount of water is so low that reaction R2 is almost suppressed, and where the $\text{H}_2\text{O}^{+\bullet}$ scavenging occurs within a few tens of femtoseconds. For these two solutions, the yield of scavenged $\text{H}_2\text{O}^{+\bullet}$ is found to be about $5.3 \times 10^{-7} \text{ mol J}^{-1}$, which is larger than the yield of hydrated electron at 1 ps ($4.7 \times 10^{-7} \text{ mol J}^{-1}$).²⁷ This means that reactions R2 and R5 are also in competition with geminate recombination (R6) and that the yield of ionized water in the femtosecond range is no less than $5.3 \times 10^{-7} \text{ mol J}^{-1}$, within the experimental uncertainty.

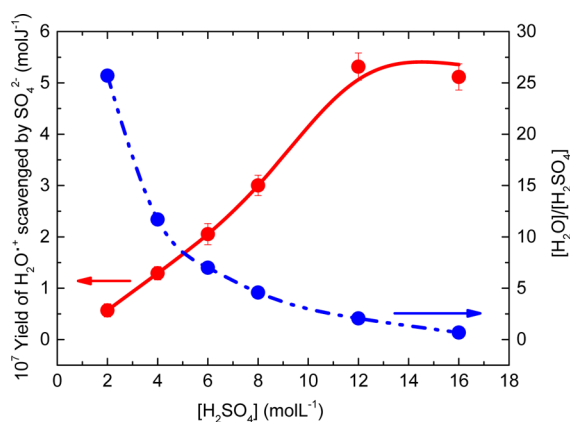


Figure 4. Yield of scavenged $\text{H}_2\text{O}^{+\bullet}$ and the ratio $[\text{H}_2\text{O}]/[\text{H}_2\text{SO}_4]$ plotted as a function of sulfuric acid concentration.

It is important to estimate the value of the redox potential of the $\text{H}_2\text{O}^{+\bullet}/\text{H}_2\text{O}$ couple in neat water. Considering that the hole $\text{H}_2\text{O}^{+\bullet}$ is constituted with a positive charge localized on one water molecule,⁹ a thermodynamical cycle based on the ionization energy of a water molecule in the gas phase (12.6 eV, known experimentally), and on the hydration energies of a water molecule (-0.27 eV) and of $\text{H}_2\text{O}^{+\bullet}$ (estimated to be -4.4 eV , slightly larger than that of H_3O^+), gives us simple estimation of the value of the redox potential of this very short-lived radical which is larger than 4 V_{NHE} . This is an extremely strong oxidant and no chemical species is an oxidant strong enough to form $\text{H}_2\text{O}^{+\bullet}$ in water: the only way to produce $\text{H}_2\text{O}^{+\bullet}$ is to ionize water with highly energetic photons, charged particles, or high voltage current. Moreover, any molecule at contact could be oxidized by this radical. Numerical simulations are necessary to calculate its reduction potential with more accuracy.

In addition to irradiation of concentrated H_2SO_4 solutions, the direct oxidation by the $\text{H}_2\text{O}^{+\bullet}$ can take place in other situations where the probabilities of its nearest neighbors being H_2O or another molecule are comparable. Some examples are given below:

- **Radiotherapy and radiobiology:** It is known that a large amount of hydrating water molecules are in direct contact with DNA. When ionizing radiation is applied, part of the radiation energy is absorbed directly by DNA and breaks in sugars, phosphates, and nucleobases units some bonds, while some is also absorbed by the water adjacent to the DNA. In that case, the generated $\text{H}_2\text{O}^{+\bullet}$ radical cations may induce a chemistry different from OH^* radicals. This possibility has not yet been underlined enough and needs to be reevaluated considering our results.^{28,29}

- **Treatment and storage of fuel in the nuclear industry:** Spent nuclear fuel is processed in highly concentrated nitric acid, and in this case, the radical cation $\text{H}_2\text{O}^{+\bullet}$ may react with nitrate ions to yield the NO_3^* radical, which is also a highly oxidizing species. Alternatively, when radioactive waste of low and medium level is coated by cement or any other porous material, the interface is extensive, and the formation of radical cation $\text{H}_2\text{O}^{+\bullet}$ and its oxidation reactions should be taken into account.

When the core of a nuclear power plant comes into contact with water, as occurred during the Fukushima incident in Japan, the amount of radiation deposited at the interface of the exposed fuel/water is important. The present work suggests

that, in this situation, metal corrosion by H_2O^{*+} may be involved.

Though often discussed in the past, the role of H_2O^{*+} in oxidation processes of irradiated systems was a subject of controversy and speculation. Here, it has been demonstrated by the picosecond pulse radiolysis of highly concentrated sulfuric acid that H_2O^{*+} may act as an extremely strong oxidant.

■ ASSOCIATED CONTENT

● Supporting Information

The picosecond pulse radiolysis setup is described in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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