

第 60 回放射線化学討論会  
水分解ラジカルカチオンの超高速反応

京都大学  
パリ南大学

馬 駿\*, 関 修平  
Mehran Mostafavi

Liquid water is the key compound for our existence on this planet and it is involved in nearly all biological and chemical processes. The role of contemporary physics and chemistry of liquid water exposed to ionizing radiation (photon, fast electron, X-rays, heavy ions, etc.) is significant in such diverse fields as photon science, radiotherapy, nuclear reactors, radiation chemistry and nuclear waste management etc.<sup>1-3)</sup> Since the discovery of X-rays and natural radioactive phenomena, the chemistry derived from water radiolysis has been studied intensively over the last one hundred years. The interaction of highly energetic photons or charged particles with water initially result in the ejection of a quasi-free electron from the valence shell in general, leaving behind a positively charged radical cation ( $\text{H}_2\text{O}^{\bullet+}$ ) on the timescale of attoseconds ( $10^{-18}$  s) or subfemtosecond. In addition to their recombination, both of these two charged species subsequently follow their own pathway of chemical reactivity. The hot electron relaxes into solvent molecules and gets trapped as a hydrated electron ( $e_{\text{hyd}}^-$ ) whilst  $\text{H}_2\text{O}^{\bullet+}$  rapidly forms oxidizing  $\bullet\text{OH}$  radical via proton transfer.

The chemical framework in which water radiolysis involving  $\bullet\text{OH}$  and  $e_{\text{hyd}}^-$  occur is now well understood experimentally as well as theoretically. The  $\bullet\text{OH}$  radical has been thought to be mainly responsible for much of the radiation-induced oxidation that occurs in dilute aqueous solutions and biological system. However, the ultrafast chemistry of

its precursor, water holes ( $\text{H}_2\text{O}^{\bullet+}$ ) immediately following ionization of liquid water, is still a puzzling and very challenging subject in radical chemistry induced by ionizing radiation (Fig. 1). Until now, real-time observation of this species  $\text{H}_2\text{O}^{\bullet+}$  is still lacking because of the limitation of the time resolution in currently available high energy pulse techniques to typical picosecond time scales. The situations where  $\text{H}_2\text{O}^{\bullet+}$  undergoes ultrafast one-electron oxidation in competition with proton transfer have an important practical influences upon nuclear waste storage, nuclear fuel processing and radiotherapy, and remain to be clarified in order to better assess the safety concerns such as the component corrosion and hydrogen emission.

On the other hand, the accumulative time-resolved studies of  $e_{\text{hyd}}^-$  at femtosecond scale ( $10^{-15}$  s) have clearly demonstrated the existence of precursor states of  $e_{\text{hyd}}^-$  even if there are some debates on the solvation model. Prehydrated electrons ( $e_{\text{pre}}^-$ ) are electron species that at least exist in two different states lying at higher energy localizations sites than  $e_{\text{hyd}}^-$ . Thus, it is rationalized that in some of the aqueous systems the precursors of  $e_{\text{hyd}}^-$  may trigger the reductive reactions that completely differ from those by  $e_{\text{hyd}}^-$ . For instance, in highly acidic condition, the scavenging of  $e_{\text{pre}}^-$  by  $\text{H}_3\text{O}^+$  giving rise to  $\text{H}^\bullet$  radicals is much faster than the reaction of  $e_{\text{hyd}}^-$ ; they are also suggested to rapidly dissociate the DNA subunits via dissociative electron transfer rather than the formation relatively stable radical anions.

In the past years, the ultrafast electron transfer of  $\text{H}_2\text{O}^{\bullet+}$  has been investigated in highly concentrated solutions using picosecond pulse radiolysis technique. By observing the formation of secondary radicals such as  $\text{NO}_3^\bullet$ ,  $\text{SO}_4^{\bullet-}$ ,  $\text{X}_2^{\bullet-}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) or  $\text{H}_2\text{PO}_4^\bullet$  at picosecond scale,<sup>4-6)</sup> the radiolytic yield of  $\text{H}_2\text{O}^{\bullet+}$  participating in

Ultrafast Chemistry of Radical Ions Following Ionization of Liquid Water

Jun MA\* and Shu SEKI (Kyoto University), Mehran MOSTAFAVI (Univeristé de Paris-sud),

〒615-8510 京都府京都市西京区京都大学桂 A クラスター A4 棟

TEL: 075-383-2573, E-mail: ma.jun.26m@st.kyoto-u.ac.jp

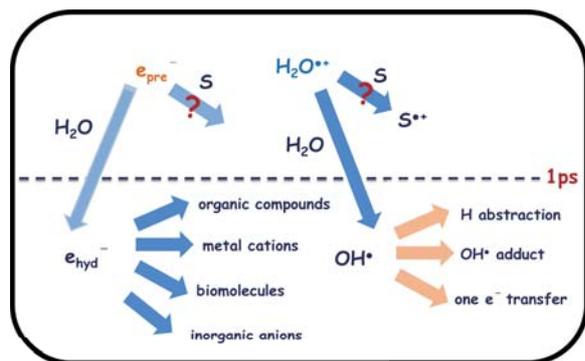


Figure 1. The reactivity of water radical cation ( $\text{H}_2\text{O}^{\bullet+}$ ) and prehydrated electrons ( $\text{e}_{\text{pre}}^-$ ) are not yet fully explored in radiation chemistry and their reaction patterns much differ from those induced by  $\bullet\text{OH}$  radicals and  $\text{e}_{\text{hyd}}^-$ .

the reaction as a function of concentration is obtained and isotopic effects have been comparatively studied. Our results imply the chemical situations where the reactivity of  $\text{H}_2\text{O}^{\bullet+}$  or  $\text{H}_2\text{O}^{\bullet+}$  plays a more important role in competition with proton transfer to generate  $\bullet\text{OH}$  or  $\bullet\text{OD}$  radicals. In addition, the reactivity of prehydrated electron with hydronium ions and DNA bases has been studied by observing the changes of initial yield of hydrated electron<sup>7,8</sup>. In contrast to previous reports, it shows the direct evidence of prehydrated electron reacting with hydronium ions when the transient absorption spectra of  $\text{e}_{\text{hyd}}^-$  was taken into account. Prehydrated electron reacting with silver cyanide complex,  $\text{Ag}(\text{CN})_2^-$  gives rise a transient product  $\text{Ag}_0\text{CN}^-$  rather than  $\text{Ag}(\text{CN})_2^{\bullet-}$ , but when reacting with DNA bases, the reaction only yields the stable radical anions ( $\text{DNA}^{\bullet-}$ ).

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