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Abundant Production of Reactive Water Radical Cations under Ambient Conditions

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Abstract

Water radical cations, the crucial intermediates in many aqueous reactions and biochemical processes, are difficult to be experimentally investigated due to its short lifetime and low abundance. Herein, a homemade device based on energy-tunable discharge was employed to deposit suitable amounts of energy to atmospheric pressure pure water vapor for abundant production of water radical cations, which were stabilized as $(H_2O)_n^+$ (n=2-5) with the maximal abundance ($\geq 8.3 \times 10^6$ cps) for $(H_2O)_2^+$ as characterized by mass spectrometry (MS).

The abundance of water radical cations was optimized by adjusting the experimental parameters such as discharge voltage (2.5 kV), temperature of the MS inlet (140 °C), carrier gas flow (20 mL/min) and the distance between the discharge tip and the MS inlet (12 mm). The ambient formation of water radical cations was further confirmed by the high reactivity of the as-prepared water radical cations, which instantly reacted with benzene, ethyl acetate and dimethyl disulfide, showing rich chemistry with the ionic and radical characters. Moreover, the computations confirm that the O-O single-electron bound dimer (B) as well as the hydronium hydroxyl radical complex (A) accounts for the unusual chemistry of the water radical cations, providing a facile approach to access the high reactivity of water radical cations under the ambient condition.

Keywords

water; radical cation; mass spectrometry; O-O single-electron bound dimer of water radical cation; hydronium hydroxyl dimer of water radical cation
**Introduction**

The study of systems comprising small numbers of water molecules is a topic of immense interest. As well documented, the functional biomolecules, such as DNA,\(^1\)\(^-\)\(^2\) RNA,\(^3\)\(^-\)\(^5\) and proteins,\(^6\)\(^-\)\(^10\) are affected by the water molecules surrounding them. Besides neutral small clusters,\(^7\)\(^-\)\(^11\) the protonated forms\(^12\)\(^-\)\(^14\) starting with the hydronium ion, have marked periodicity in properties while the bonding in hydrated electrons (solvated water radical anions) has been studied using detailed spectroscopy and computation.\(^15\)\(^-\)\(^18\) By contrast, few reports on the spectroscopy or computational studies\(^19\)\(^-\)\(^24\) of the chemistry of the water radical cation and its solvated forms exist. The inconvenience of generating water radical cations with small numbers of waters of solvation is responsible for this situation. To date, water radical cations have been created by exposing water vapor to vacuum-UV photoionization,\(^22\)\(^,\)\(^25\)\(^,\)\(^26\) electron-impact ionization,\(^24\)\(^,\)\(^27\)\(^,\)\(^28\) dinitrogen chemical ionization,\(^29\)\(^-\)\(^32\) femtosecond multiphoton ionization,\(^33\) photoionization in a supersonic jet expansion\(^34\) or soft X-ray radiation.\(^35\)\(^,\)\(^36\)

In general, methods of water radical cation formation reported previously have the following features: i) water radical cation or the clusters \((\text{H}_2\text{O})_n^+\) \((n\leq10)\) were observed in extremely low yield;\(^22\)\(^,\)\(^37\) ii) high vacuum \((10^{-5}\text{-}10^{-8}\text{ Torr})\)\(^18\)\(^,\)\(^19\)\(^,\)\(^22\)\(^,\)\(^23\)\(^,\)\(^28\) or low temperature \((<20\text{ K})\)\(^24\)\(^,\)\(^36\) were required to suppress their dissociation. However, when collisions with water vapor are allowed, the products are invariably the hydronium ion and its solvated clusters. These features have severely limited the access to chemistry of water radical cations, particularly the \((\text{H}_2\text{O})_n^+\) \((n=1\sim3)\) species, which are believed to have fundamental significance in life science,
physics, chemistry, biomedicine and interstellar chemistry since they are the key self-solvated water radical cations.

Herein, a homemade device based on energy-tunable discharge was employed to generate water radical cations \((n=2-5)\) instead of high vacuum or low temperature with substantial amounts of mono-solvated water radical cation \((\text{H}_2\text{O})_2^{+•}\) as the main product. The ionic products were conveniently characterized by tandem mass spectrometry experiments with additional information from isotopic labelling, computation and high-resolution MS measurements. Furthermore, the ambient formation of water radical cations was experimentally confirmed by the high reactivity of the as-prepared water radical cations, which instantly reacted with ethyl acetate, dimethyl disulfide and benzene, showing rich ionic and radical character of the O-O single-electron bound dimer \((B)\), as well as the hydronium hydroxyl radical complex \((A)\). Therefore, the approach provides adequate water radical cations, which benefit the advanced studies and applications of water clusters.

Results and Discussion

Production and Characterization of water radical cations

In the experiment, pure water evaporated freely and the vapor was carried by an inert gas \((e.g., \text{N}_2, \text{He}, \text{etc.})\) to intersect the ambient ionic plume generated by the energy-tunable corona discharge (Figure 1a). Under the optimized conditions, the water radical cation signal \(\text{H}_2\text{O}^{+•} (m/z\ 18)\) and its solvated counterparts \((\text{H}_2\text{O})_n^{+•} (n =\)
2, 3; m/z 36, 54) were abundantly detected (Figure 1b) in the mass spectrum, with the dimer of m/z 36 being the base peak (> 8.3E10 cps). The assignments for the signals at m/z 36 (Figure S1a) and m/z 54 (Figure S1b) were also validated by the characteristic ionic fragments observed using tandem mass spectrometry and high-resolution mass measurements (Figure S2). The mass spectral pattern shown in Figure 1b provided experimental data showing that the small water radical cation clusters (H₂O⁺• and (H₂O)₂⁺•) were favourably formed rather than the large ones ((H₂O)_n⁺•, n≥3). Extra reference experiments demonstrated that the production of water radical cations was not ratiocinated from the inert gases, because no dependence of the signals (m/z 18, 36, and 54) on the gas (Ar, Ne, or He) which was used to transport the water vapor was observed (Figure S3). The signal at m/z 55 was confirmed as (H₂O)_3H⁺ by collision induced dissociation (CID) data (Figure S4) and high-resolution MS measurements (Figure S5). Additionally, the formation of water radical cations was verified by using deuterated water to observe the water radical cations of (D₂O)₂⁺• (m/z 40) and (D₂O)_3⁺• (m/z 60) (inset of Figure 1b) in high abundance. Traces of D₂O⁺• ions (m/z 20) were also observable when the mass spectrum was expanded 100 times (inset of Figure 1b). The presence of adventitious water was also detectable from the isotopic composition of the monomer, dimer and trimer clusters. These results indicates that water radical cations were produced by energy-tunable discharge with relatively low energy.

Note that the hydronium ions were preferably produced and the water radical cations were hardly detected if the corona discharge energy was not systematically optimized. However, abundant water radical cations were
reproducibly obtained under the optimized experimental conditions. Figure 1c shows the MS signal intensities for m/z 36 and m/z 37 ions as a function of discharge voltage. With increase of the discharge voltage, the abundance of (H\textsubscript{2}O\textsubscript{2})\textsuperscript{+} (m/z 36) changed slightly while the abundance of (H\textsubscript{2}O\textsubscript{2})H\textsuperscript{+} (m/z 37) showed a steady increase. Thus, the intensity ratios between (H\textsubscript{2}O\textsubscript{2})\textsuperscript{+} and (H\textsubscript{2}O\textsubscript{2})H\textsuperscript{+} decreased dramatically with the increasing discharge voltage (Figure 1c), suggesting that the water radical cations were only produced with a narrow range of suitable discharge voltage, by which a strong electric field was created to facilitate electron stripping from neutral water molecules. However the radical cations were favorably dissociated into hydronium ions in the solvated form once excessive energy (i.e., high voltage ≥ 2.5 kV) was deposited to the water radical cations.

Similarly, other factors such as the temperature of the capillary, carrier gas flow rate, the distance between the discharge tip and the ion entrance, etc. affect the total energy input onto the water radical cations. Figure 1d shows the MS signal intensities for m/z 36, m/z 37, m/z 54 and m/z 55 ions as a function of the temperature of the capillary used for ion transfer. With the temperature increasing, the abundance of (H\textsubscript{2}O\textsubscript{2})\textsuperscript{+} (m/z 36) increased due to better dissolution/detection and then decreased markedly at around 140 °C mainly because of the accelerated dissociation. Meanwhile, the ions of m/z 54 showed similar temperature feature as the m/z 36 ions, but the breakdown temperature was about 100 °C, which was much lower than that of the m/z 36 ions, probably because the three waters cluster would be more easily broken than the dimers under high temperature (≥100 °C).

By contrast, the absolute abundance of (H\textsubscript{2}O\textsubscript{2})H\textsuperscript{+} (m/z 37) and (H\textsubscript{2}O\textsubscript{3})H\textsuperscript{+} (m/z 55) shows little temperature effects,
probably the hydronium ions were much more stable than the radical cation clusters. These data suggest for better performance of the m/z 36 ions the capillary temperature should be maintained at about 140 °C. The overall effects of carrier gas flow (Figure S6) and the distance between the discharge tip and the MS inlet (Figure S7) on the production of water radical cations are detailed in supporting information. Briefly, the gas flow rate brought no differential tendency on the ions of either m/z 36 or m/z 37, probably because the effect was mainly caused by the collisions in the gaseous flow. The distance effect (Figure S7) was reciprocally similar to the contribution of the discharge voltage (Figure 1c), probably because the distance also correlated with energy. However, different discharge voltages and different distances caused remarkable changes in the mass spectra (Figure S8). Taking both the abundance of (H₂O)₂⁺⁺ and the abundance ratio of (H₂O)₂⁺⁺/(H₂O)₂H⁺ into account, a discharge voltage of 2.5 kV, distance of 12 mm, ion transfer temperature of 140 °C, and carrier gas flow of 20 mL/min represent the optimized conditions, providing a facile method for abundant production of water radical cations requiring neither high vacuum²⁸⁻³¹ nor low temperature.²⁶

**Chemical reactions of water radical cations**

Theoretically, water radical cations should bring unique chemistry through reaction with substances which might not react with water. Therefore, the possibility of water radical cations to react with chemical reagents and biofunctional groups were explored using benzene, ethyl acetate, and dimethyl disulfides as the mode compounds. (H₂O)₂⁺⁺ was chosen as the main reactant as it has the highest abundance.
Reactions of water radical cations and benzene

Benzene was introduced as vapor into the ion trap where the \((\text{H}_2\text{O})_2^{++}\) ions \((m/z \ 36)\) were mass-selectively isolated. Upon CID, the ions of the reactant, benzene radical cations and phenol radical cations \((m/z \ 94)\) were detected in the spectrum (Figure 2a). \(\text{H}_2\text{O}^{++} \ (m/z \ 18)\) might be the by-product of self-dissociation of \((\text{H}_2\text{O})_2^{++} \ (m/z \ 36)\) in the ion trap reaction with benzene. The ions of \(m/z \ 94\) produced characteristic fragments of \(m/z \ 66\) and \(m/z \ 65\) (Figure 2b) by the loss of neutral CO \((28 \text{ Da})\) and \([\text{HCO}]^{+} \ (29 \text{ Da})\), respectively. Furthermore, fragments of \(m/z \ 65\) (tentatively the cyclopentadiene ion), \(m/z \ 51\) (cyclobutadiene ion), \(m/z \ 40\) (cyclopropene radical cation) were obtained by CID of ions of \(m/z \ 66\) (inset of Figure 2b). The characteristic \(m/z \ 66\) fragment of the phenol radical cation, \(\text{C}_6\text{H}_5\text{OH}^{++} \ (m/z \ 94),^{39,40}\) produce an ion of \(m/z \ 40\) (cyclopropene radical cation), through the elimination of acetylene \((26 \text{ Da})\). These results strongly suggest that the ion of \(m/z \ 94\) (the exact value at \(m/z \ 94.0414\)) is the the phenol radical cation \(\text{C}_6\text{H}_5\text{OH}^{++}\), which was validated by the exact \(m/z\) matching experiments with high mass accuracy \((1.0 \text{ ppm})\) (Figure S9a). The observation of phenol radical cation \((m/z \ 94)\) indicated that \((\text{H}_2\text{O})_2^{++}\) shows character of OH radical. Thus the phenol radical cation was produced as below:

\[
\text{C}_6\text{H}_6 + (\text{H}_2\text{O})_2^{++} \rightarrow \text{C}_6\text{H}_5\text{OH}^{++} + \text{H}_2\text{O} + \text{H}_2
\]

(1)

through which the hydrogen gas was also detected and showed proportional respondence on the reactants and ion current (Figure S10). Furthermore, the phenol cations were solflanded for characterization by infrared
absorption (Figure S11) and LC (Figure S12), which validated the production of phenol and hydrogen through equation 1.

When the reactant was isotope-labeled as $\text{H}_2^{18}\text{O}^+$, the ionic product has ion of $m/z$ 96 (Figure 2c). Upon CID, the characteristic fragments of $m/z$ 66 and $m/z$ 65 were recorded (Figure 2d), with the loss of $\text{C}^{18}\text{O}$ (30 Da), $[\text{HC}^{18}\text{O}]^+$ (31 Da), respectively. More convincingly, the fragment ions of $m/z$ 66 themselves fragmented further to give the ionic species of $m/z$ 65, 51, 40 as recorded in the MS$^3$ spectrum (inset of Figure 2d), showing the identical fragmentation pattern observed for the major fragment ($m/z$ 66, Figure 2b) of $\text{C}_6\text{H}_5^{16}\text{OH}^+$ ($m/z$ 96). The exact $m/z$ value measured with high mass resolution for the ionic complex was 96.0456 (Figure S9b), which exactly matched the expected $\text{C}_6\text{H}_5^{18}\text{OH}^+$ complex (theoretical value of $m/z$ 96.0456). Once deuterated benzene was used, ions of $m/z$ 99 (Figure S9c), which generated daughter ions of $m/z$ 71 (Figure S9d), were found at $m/z$ 99.0726 (Figure S9e), which ideally matched the expected $\text{C}_6\text{D}_5\text{OH}^+$ complex (theoretically valued at $m/z$ 99.0727). These results suggested that, the whole OH group of $\text{C}_6\text{H}_5\text{OH}^+$ may be derived from the water radical cation. Traditionally, synthesis of phenol requires harsh conditions through multi-step reactions, which brings less “green chemistry” and tedious treatment for by-products separation. In contrast, this work might lead to an alternative choice for phenol production with easy operation and maximal green chemistry.

*Reaction between water radical cations and ethyl acetate*
Lipids are important compounds in chemistry and biological objects, in which water radical cations likely coexist. Therefore, reactions between the water radical cation and ethyl acetate (EA, 88 Da) were conducted, yielding the proton transfer product (EA+H)⁺ as well as a major product ion of m/z 106 (Figure S13a). The exact mass for m/z 106 was 106.0624 (theoretical m/z 106.0624, Figure S14), suggesting the formation of a radical cation complex (EA+H₂O)⁺. This was confirmed by CID (30% CE) of the mass-selected product ions (m/z 106), which generated a major peak at m/z 88 (Figure S13b) by the loss of H₂O (18 Da). In figure S13c, the abundance of ions of m/z 36 (H₂O)⁺ decreased while that of ions of m/z 106 increased after the EA was introduced into the reaction. Therefore, it was proposed that (H₂O)₂⁺ (m/z 36) reacted with EA to produce a radical cation complex (EA+H₂O)⁺ (m/z 106). However, no covalent bond cleavage in either EA or water was observed during the reaction or CID process of the (EA+H₂O)⁺, suggesting that EA was highly stable upon the attack of water radical cations, probably due to its unique molecular structure.

**Reaction between water radical cations and dimethyl disulfides**

Disulfide bonds play key roles in biochemistry. To evaluate its vulnerability, the disulfide bond of dimethyl disulfide (CH₃SSCH₃, M₁), a mode disulfide bond believed less active than those in typical biochemicals, reacted with (H₂O)₂⁺ (m/z 36) to generate the proton transfer product (M₁+H)⁺ and disulfide-water radical complex (M₁+H₂O)⁺ (m/z 112) (Figure 3a). The detection of the (M₁+H₂O)⁺ complex was confirmed by the exact mass measurements (Figure S15a) with the mass accuracy 0.9 ppm. In figure S15b, it is observed that the signal of
m/z 36 decreased dramatically after introducing dimethyl disulfide, indicating that the ($\text{H}_2\text{O}$)$_2$$^+$ ($m/z$ 36) reacted with dimethyl disulfide. Upon CID (30% CE), the ions of $m/z$ 112 created predominant product ions of $m/z$ 66 and $m/z$ 65 in the MS/MS spectrum (Figure 3b), which were formed by the loss of CH$_2$S (46 Da) and CH$_3$S$^*$ (47 Da), respectively, indicating that the disulfide bond in the complex ($m/z$ 112) was activated upon binding to ($\text{H}_2\text{O}$)$_2$$^+$. Extra experimental data revealed two facts: (i) the nucleophilic and radical character of ($\text{H}_2\text{O}$)$_2$$^+$ both likely contribute to S-S cleavage and (ii) the abundance ratio between the ionic fragments of $m/z$ 66 and $m/z$ 65 was unity, due to the equal elimination of CH$_2$S (46 Da) and CH$_3$S$^*$ (47 Da) during the CID process. The fragment ions of $m/z$ 66 and $m/z$ 65 in turn generated products of $m/z$ 48 (Figure S16a) and $m/z$ 47 (Figure S16b), both by the loss of H$_2$O (23% CE). Therefore the precursor ions were ascribed to [CH$_3$SH$_2$OH$_2$]$^+$ and [CH$_3$SOH$_2$]$^+$, respectively. Consequently, the overall results of the reactions between dimethyl disulfide and ($\text{H}_2\text{O}$)$_2$$^+$, as well as the CID process were summarized as follows:

$$2\text{H}_2\text{CSSCH}_3+2(\text{H}_2\text{O})_2^+ \rightarrow [\text{CH}_3\text{SOH}_2]^++\text{CH}_3\text{S}^*+[\text{CH}_3\text{SHO}_2]^++\text{H}_2\text{S} \quad (2)$$

The reaction between ($\text{H}_2\text{O}$)$_2$$^+$ and dimethyl disulfide was also confirmed by D$_2$O isotope labeling experiments (Figure S17 and S18). In general, the experimental data confirm the above reactions and the cleavage of disulfide bond under the relatively mild conditions, indicating that the disulfide bonds in biomolecules might be likely attacked by water radical cations to cause unexplored biochemistry process.
Calculations and Possible Mechanism

The reactional data not only confirm the production of the highly reactive water radical cations, but also bring
the motivation to probe the structural fundament for the reaction. Therefore, theoretical calculation of the
(H2O)2•+ structure was performed at the UCCSD(T)/AUG-cc-pVTZ//UMP2/AUG-cc-pVDZ level. Our results
demonstrated that there are two forms of water radical cations (Table S1), labeled as structure A and structure
B. Structure A containing the hydrogen atom bound is of more stable structure, which has bond lengths and
angles consistent with a hydronium ion hydrogen-bonded to a hydroxyl radical, with most of the charge on the
hydronium ion. The structure B is a true symmetrical dimer with a single-electron O-O bond (two electrons in
a sigma bonding orbital and one in an antibonding orbital), in which the charge is equally shared by the two
oxygen atoms. According to our calculations (Table S1), the bond between atom 2 (O) and atom 5 (H) in structure
A is 1.469 Å, which is the longest so the energy of this bond is lowest. Thoeretically such a bond is easy to
break, as observed in the CID experiments (Figure 2b). Similarly, the longest bond in structure B is located
between the two oxygen atom (2.039 Å), which is the one easiest to cleavage as shown in Figure 3b. Our
calculations (Table S2) also show that the fragmentation of both A and B isomers is endoergic. For instance, the
proton-bound isomer (A) is dissociated into H3O+ and •OH by 94 kJ/mol, and the O-O bonded isomer (B) is
dissociated into H2O•+ and H2O by 165 kJ/mol (Table S3). Meanwhile, as shown in Table S1, the atom 2 (O) in
isomer A has the lowest charge (-0.346), which easily attack the benzene ring to form the intermediate, yielding
the phenol cations, H\textsubscript{2} and H\textsubscript{2}O (detailed in SI, see Figure S19 and S20). Based on these results, benzene was oxidized mainly by isomer A, which provides the hydroxyl radicals as confirmed by the data shown in Figure 2c (the isotop labelling experiment). The bond angle of H-O-H in isomer B is lower than that in isomer A, probably because the lone pair in isomer B creates strong repulsion to hydrogen-oxygen bonds. Such a structure allows the O-O group simultaneously attack the disulfide bond in dimethyl disulfide (detailed in SI, see Figures S21-22), generating the characteristic fragments as observed in the CID experiments (Figure 3b). Therefore, the data suggest that the O-O single-electron bound dimer (B) mainly accounts for the unusual chemistry such as the reaction with disulfide bond of the water radical cations.

**Conclusion**

In summary, water radical cations (H\textsubscript{2}O\textsuperscript{n+} (n=2-5) were abundantly produced under ambient conditions using an homemade device based on energy-tunable discharge. The energy deposited on pure water vapor was changed by adjusting experimental parameters such as discharge voltage (2.5 kV), temperature of the MS inlet (140 \degree C), carrier gas flow (20 mL/min) and the distance between the discharge tip and the MS inlet. The results suggest that only suitable energy can produce abundant water radical cations. Due to the high reactivity of the as-prepared water radical cations, the formation of water radical cations was further confirmed by reacting with several substrates (benzene, ethyl acetate and dimethyl disulfide). Computations and experiments confirm the existence of two forms of the dimer, a hydronium hydroxyl radical complex (A) and an O-O single-electron bound dimer.
(B), which bring interesting chemistry unexplored previously. This study provides a convenient method to 
prepare adequate highly reactive water radical cations for advanced chemistry studies.

Supporting Information

Supporting Information is available and includes experimental sections, Figures S1-S22, and Table S1-S3.

Conflict of Interest

There is no conflict of interest to report.

Acknowledgments

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References


**Figures**
Figure 1. Ambient Production of abundant water radical cations. a) Schematic diagram of the energy-tunable discharge for generation of water radical cations; b) Typical mass spectrum of water radical cations produced under optimized conditions using N₂ as the carrier gas, inset: typical mass spectrum of deuterated water radical cations produced under the optimized conditions; c) Peak intensities detected at either $m/z$ 36 or $m/z$ 37 and their ratios ($I_{36}/I_{37}$) as the function of discharge voltage; d) MS signal intensities for ions $m/z$ 36, $m/z$ 37, $m/z$ 54, and $m/z$ 55 as the function of ions transfer temperature.

Figure 2. Mass spectrometric characterization of reaction between (H₂O)₂⁺ and benzene. a) Typical mass spectrum collected with benzene present showing C₆H₅OH⁺ formation in the ion trap; b) Collision-induced dissociation spectra of C₆H₅OH⁺, $m/z$ 94→ products, inset: $m/z$ 94→66→ products; c) Typical mass spectrum
with benzene and H$_2^{18}$O showing C$_6$H$_5^{18}$OH$^{* *}$ formation; d) Collison-induced dissociation spectra of C$_6$H$_5^{18}$OH$^{* *}$,

$$m/z \quad 96 \rightarrow \quad \text{products, \ inset: } \quad m/z \quad 96 \rightarrow 66 \rightarrow \quad \text{products.}$$

a) Typical mass spectrum recorded with dimethyl disulfide showing [M$_1$+H$_2$O]$^{* *}$ formation; b) CID of [M$_1$+H$_2$O]$^{* *}$, m/z 112 → product ions.

Figure 3. Mass spectrometric characterization of reaction between (H$_2$O)$_2$$^{* *}$ and dimethyl disulfide (M$_1$).