THE RADIATION-CHEMICAL YIELDS OF H$_3$O$^+$ AND OH$^-$ AS DETERMINED BY NANOSECOND CONDUCTIMETRIC MEASUREMENTS†

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Abstract—The radiation-chemical yields of ionic species formed upon irradiation of water by 3.5 MeV electrons have been determined directly using dc conductivity and optical measurements. Yields (expressed in μmol J$^{-1}$) at 10 and 110 ns after the end of a 10 ns pulse are: for H$_3$O$^+$ = 0.371, 0.320; for OH$^-$ = 0.082, 0.045, and for e$_{aq}$ = 0.299 and 0.275, respectively.

INTRODUCTION

Attempts to determine the yields of H$_3$O$^+$ and OH$^-$ that are formed following low LET irradiation of water [reaction (1)] have relied on (i) scavenging the e$_{aq}$ to form a relatively stable radical anion (1-4) [reaction (2)] or its conversion to OH$^-$ by reaction with N$_2$O, (1,4) [reaction (3)] and (ii) computing the best curve to the observed change in conductivity during an electron pulse. (5) The subsequent decay of the ionic species through neutralization [reaction (4)] has then been followed by time-resolved conductivity measurements and kinetic plots are extrapolated back to the time of the pulse to estimate the initial yields of H$_3$O$^+$ and OH$^-$. 

(1) H$_2$O(γ) → e$_{aq}$, ·OH, H, H$_2$O$^+$, OH$^-$, H$_2$O$_2$, H$_2$.
(2a) e$_{aq}$ + S → S$^-$
(2b) e$_{aq}$ + N$_2$O → N$_2$ + O$^-$
(3) O$^-$ + H$_2$O → OH$^-$ + OH
(4) H$_3$O$^+$ + OH$^-$ → 2H$_2$O.

The reported radiation-chemical yields of H$_3$O$^+$ and OH$^-$ do vary, e.g. from ca. 0.29(1,4) to 0.34 μmol J$^{-1}$ (2,5) for the yields of H$_3$O$^+$ in N$_2$O- and Ar-saturated water, respectively. This variation in yields might in part arise from the perturbation of intraspur reactions by high concentrations of scavengers such as N$_2$O as well as from uncertainties in the mobilities of the radical anions of scavengers and the reactions undergone by H$^+$ atoms.

In this paper we report our simultaneous measurements of the increase in conductivity and absorption of the e$_{aq}$ following pulse radiolysis of pure water. By utilizing both a short radiation pulse and a fast electronic rise time (<5 ns, 5 ns digitizer sampling interval) we have been able to determine the yields of H$_3$O$^+$ and OH$^-$ directly, both inside the spur and that which escapes the spur. Measurements were made before any significant post-spur (>100 ns) neutralization through reaction (4) occurred in the bulk solution.

EXPERIMENTAL

The dc conductivity method used utilizes a balanced, symmetrical conductivity cell which has four conducting walls and two optical faces. The cell constant 0.186 ± 0.004 cm$^{-1}$ was determined by the reduction of tetranitromethane. Details of the hybrid balun transformer, which rejects electron pulse interference, the compensated virtual-earth wideband amplifier used to overcome the low-frequency limitations of the transformer together with the optical detection system have been published. (8) The electron pulse source was the Gray Laboratory’s 4 MV Van de Graaff accelerator which produces pulses down to 1.5 ns duration at up to 5A. All irradiations were carried out at 21°C. Dosimetry was carried out using aerated KSCN solution assuming the (SCN)$^-_2$ radical produced has a radiation-chemical yield of 0.29 μmol J$^{-1}$ with a molar absorptivity ε of 758 m$^2$ mol$^{-1}$ at 472 nm. (9) Water was purified (σ = 0.06 μS cm$^{-1}$) by a Milli-Q system (Millipore Inc.) and purged free of oxygen with N$_2$ gas. Simultaneous recordings of changes in optical absorption and conductivity were recorded on a Tektronix 7612D digitizer interfaced to a PDP 11/34 computer. The consequence of averaging transients acquired by the digitizer (5 ns sample in-
Fig. 1. Typical transients obtained in N2-purged water: (A) conductance transient obtained with positive polarizing voltage, (B) conductance transient (inverted) obtained with negative polarizing voltage, (C) resultant average of A and B, representing solution conductance change, (D) optical absorption transient at 715 nm, (2 cm path length), (E) electron pulse.

Results and Discussion

The increase in conductivity $\sigma$ is a consequence of the formation of charged species during the pulse

\begin{equation}
\sigma = ([e_{aq}]_c \cdot \lambda_{e_{aq}}) + ([H_3O^+]_c + \lambda_{H_2O^+}) + ([OH^-]_d \cdot \lambda_{OH^-}),
\end{equation}

where the subscripts $c$ and $d$ refer to the concentrations of $e_{aq}$ and $OH^-$ respectively, in mol cm$^{-3}$ and $\sigma$ and $\lambda$ are expressed in S cm$^{-1}$ and S cm$^2$ mol$^{-1}$, respectively.

The conductivity arising from the $[e_{aq}]_c$ and its counterion $[H_3O^+]_c$, $\sigma^*$ (in S cm$^{-1}$) can be calculated from optical measurements of the $[e_{aq}]_c$ absorption at 715 nm where $\varepsilon = 1840$ m$^2$ mol$^{-1}$

\begin{equation}
\sigma^* = ([e_{aq}]_c \cdot \lambda_{e_{aq}}) + ([H_3O^+]_c \cdot \lambda_{H_2O^+}).
\end{equation}

The difference $\sigma - \sigma^*$ between this and the measured conductivity must arise from $[H_3O^+]_d$ and $[OH^-]_d$.

\begin{equation}
\sigma - \sigma^* = ([H_3O^+]_d \cdot \lambda_{H_2O^+}) + ([OH^-]_d \cdot \lambda_{OH^-}),
\end{equation}

and hence the total $[H_3O^+]_c + d$ and $[OH^-]_d$ produced by the pulse can be found.

The data obtained from six measurements of conductivity for each polarity together with optical measurement data (in $H_2O + N_2$) are presented in Table 1.

Using these data in eqns (5)-(7) together with the literature values$^{[1,12]}$ of $\lambda_{H_2O^+} = 331$, $\lambda_{OH^-} = 188$, and $\lambda_{e_{aq}} = 202$ S cm$^2$ mol$^{-1}$ (corrected to 21°C by $\Delta \lambda = 1.6\%$ per °C) gave the yields presented in Table 2.

The reduced conductivity in $N_2O$-saturated solution measured at 10 and 110 ns after a 10 ns pulse cannot be fully accounted for by the low mobility of the $O^-$ species (compared with that of $OH^-$) as its half-life is only 7 ns.$^{[13]}$ The measurements indicate that reaction (4), as well as reaction (8), occurs in the spurs and that charge recombination is enhanced via reaction (4) in $N_2O$-saturated solution.

\begin{equation}
e_{aq} + H_3O^+ \rightarrow H^+ + H_2O.
\end{equation}

Table 1. Optical absorbance† and conductivity values

<table>
<thead>
<tr>
<th>System</th>
<th>$10^3$ Absorbance (cm$^{-1}$ Gy$^{-1}$)</th>
<th>Conductivity (µS cm$^{-1}$ Gy$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($t(20)$ ns)</td>
<td>($t(20) + 100$ ns)</td>
</tr>
<tr>
<td>$H_2O + N_2$</td>
<td>5.59 ± 0.14</td>
<td>5.01 ± 0.15</td>
</tr>
<tr>
<td>$H_2O + N_2O$</td>
<td>0.115 ± 0.004</td>
<td>0.102 ± 0.003</td>
</tr>
</tbody>
</table>

† At 715 nm.
 Radiation-chemical yields of H$_3$O$^+$ and OH$^-$

**Table 2. Radiation-chemical yields of e$^-q$, H$_3$O$^+$, and OH$^-$ in water (pH 7) following pulse radiolysis with 3.5 MeV electrons**

<table>
<thead>
<tr>
<th>Time</th>
<th>Yield/µmol J$^{-1}$</th>
<th>e$^-q$</th>
<th>H$_3$O$^+$</th>
<th>OH$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(20)</td>
<td>0.299 ± 0.011</td>
<td>0.371 ± 0.014</td>
<td>0.082 ± 0.006</td>
<td></td>
</tr>
<tr>
<td>(20) + 100</td>
<td>0.275 ± 0.09</td>
<td>0.320 ± 0.012</td>
<td>0.045 ± 0.004</td>
<td></td>
</tr>
</tbody>
</table>

† 1 µmol J$^{-1}$ = $G$ (molecules 100 eV$^{-1}$) = 9.65.

The yield of H$_3$O$^+$ that escapes the spur is similar to other reported values$^{(2,4,5)}$ whereas the yield of OH$^-$ is lower. The yield of H$_3$O$^+$ at the shortest time measured (10 ns after a 10 ns pulse) is greater than all previous reported values.

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**REFERENCES**