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THE RADIATION-CHEMICAL YIELDS OF H_3O^+ 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_3O^+ = 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_3O^+ 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_2O,(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_3O^+ and OH^-.

(1) $H_2O \rightsquigarrow e_{aq}^-, \cdot OH, H\cdot, H_3O^+, OH^-, H_2O_2, H_2,$
(2) $e_{aq}^- + S \rightarrow S^{\cdot -},$
(3a) $e_{aq}^- + N_2O \rightarrow N_2 + O^-,$
(3b) $O^- + H_2O \rightarrow OH^- + OH,$
(4) $H_3O^+ + OH^- \rightarrow 2H_2O.$

The reported radiation–chemical yields of H_3O^+ 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_3O^+ in N_2O- 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_2O as well as from uncertainties in the mobilities of the radical anions of scavengers and the reactions undergone by $H^{\cdot}$ 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_3O^+ 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(6) 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.(7) 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 $(SCN)_2^{\cdot -}$ 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-

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† Dedicated to Professor Schulte-Frohlinde on the occasion of his sixtieth birthday.

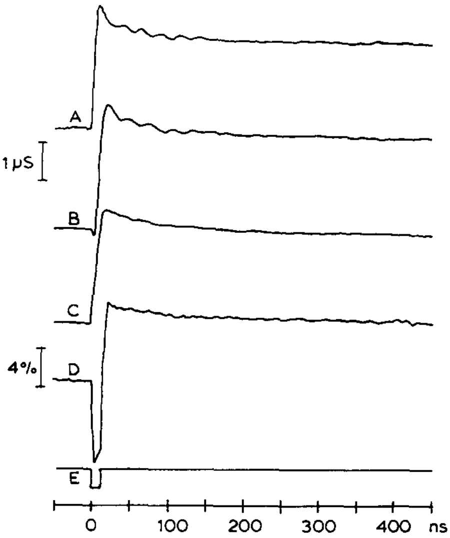

Fig. 1. Typical transients obtained in N_2-purged water: (A) conductance transient obtained with positive polarizing voltage, (B) conductance transient (inverted) obtained with negative polarizing voltage, (C) resultant average of A and B, representing solution conductance change, (D) optical absorption transient at 715 nm, (2 cm path length), (E) electron pulse.

terval) was that reliable data could only be obtained 10 ns after the pulse even though the time resolution of both detection systems was better than 5 ns. Typical signals obtained upon pulse radiolysis (3.4 Gy in 10 ns) are shown in Fig. 1. Any remaining interference which the balanced conductivity detection system does not reject is almost completely eliminated by storing two transients at opposing polarities of polarizing voltage and subtracting them. In this way the signal magnitude is enhanced and the electron pulse artifacts rejected.

RESULTS AND DISCUSSION

The increase in conductivity σ is a consequence of the formation of charged species during the pulse [reaction (1)] and can be expressed as

$$(5) \quad \sigma = ([e_{aq}^-]_c \cdot \lambda_{e_{aq}^-}) + ([H_3O^+]_{c+d} \cdot \lambda_{H_3O^+}) + ([OH^-]_d \cdot \lambda_{OH^-}),$$

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

The conductivity arising from the $[e_{aq}^-]_c$ and its counterion $[H_3O^+]_c$, σ^* (in S cm^{-1}) can be calculated from optical measurements of the $[e_{aq}^-]_c$ absorption at 715 nm where $\varepsilon = 1840\ m^2\ mol^{-1}$.(10)

$$(6) \quad \sigma^* = ([e_{aq}^-]_c \cdot \lambda_{e_{aq}^-}) + ([H_3O^+]_c \cdot \lambda_{H_3O^+}).$$

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

$$\sigma - \sigma^* = ([H_3O^+]_d \cdot \lambda_{H_3O^+}) + ([OH^-]_d \cdot \lambda_{OH^-}), \quad (7)$$

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(11,12) of $\lambda_{H_3O^+} = 331$, $\lambda_{OH^-} = 188$, 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.

$$(8) \quad e_{aq}^- + H_3O^+ \rightarrow H^{\cdot} + H_2O.$$

TABLE 1. OPTICAL ABSORBANCE† AND CONDUCTIVITY VALUES

	10^3 Absorbance (cm^{-1} Gy^{-1})		Conductivity (µS cm^{-1} Gy^{-1})	
System	t(20) ns	t(20) + 100 ns	t(20) ns	t(20) + 100 ns
$H_2O + N_2$	5.59 ± 0.14	5.01 ± 0.15	0.132 ± 0.004	0.120 ± 0.004
$H_2O + N_2O$			0.115 ± 0.004	0.102 ± 0.003

† At 715 nm.

TABLE 2. RADIATION–CHEMICAL YIELDS OF e^-_{aq}, H_3O^+, AND OH^- IN WATER (pH 7) FOLLOWING PULSE RADIOLYSIS WITH 3.5 MeV ELECTRONS

Time	Yield†/μmol J^{-1}		
(ns)	e^-_{aq}	H_3O^+	OH^-
(20)	0.299 ± 0.011	0.371 ± 0.014	0.082 ± 0.006
(20) + 100	0.275 ± 0.09	0.320 ± 0.012	0.045 ± 0.004

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

The yield of H_3O^+ that escapes the spur is similar to other reported values(2,4,5) whereas the yield of OH^- is lower. The yield of H_3O^+ at the shortest time measured (10 ns after a 10 ns pulse) is greater than all previous reported values.

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