Primary Radical Yields in Pulse Irradiated Alkaline Aqueous Solution

The relative primary radical yields of hydrated electrons, H atoms and OH radicals have been determined by measuring the amount of hydrated electron formed following a single 4-μsec pulse of X-rays.

Renewed interest in measuring free radical and molecular product yields of ionizing radiations in alkaline solutions has resulted from the discovery of the hydrated electron, $e_{aq}^-$. Recent papers have established that in addition to primary $e_{aq}^-$ yield, $g(e_{aq}^-)$, there is a primary H-atom yield, $g(H)$, in neutral and alkaline solutions. However, beyond a pH of 12, particularly conflicting results are obtained. The problem of measuring primary radical yields in alkaline solutions above pH 12 is aggravated by the incidence of chain reactions; by the ionization of the hydroxyl radical and of hydrogen peroxide; and by carbonate ion, a common impurity and hydroxyl radical scavenger.

To resolve the question of free radical yields beyond pH 12, the pH dependence of $g(e_{aq}^-)$ was determined by direct observation of $e_{aq}^-$ developed by a pulse of X-rays. The optical density of an irradiated solution was measured at 7000Å under carefully controlled conditions.

In neutral solution, the amount of hydrated electron produced corresponds to $G(e_{aq}^-)$, and at high pH values an additional amount is formed corresponding to $G(H)$ by the reaction H + OH$^-$ = H$_2$O + $e_{aq}^-$. In the presence of dissolved hydrogen, the OH radical in yield $G(OH)$ is also converted to hydrated electrons by reaction with hydrogen. The high optical absorption of the hydrated electron at 7000Å is used as a measure of its concentration. A pH range from 7 to 14.5 is covered.

Above pH 12, the total radical yield, $G(e_{aq}^-) + G(H) + G(OH)$, is constant as is the total reducing yield, $G(e_{aq}^-) + G(H)$. These relative yields are placed on an absolute basis by measuring the manganese ion yield in a formate-permanganate solution.

$G(e_{aq}^-)$ is 2.7 in neutral and 3.1 in strong alkaline solutions. The primary radical yields $g(e_{aq}^-)$, $g(H)$, and $g(OH)$, computed from diffusion theory, are 3.04, 0.53 and 2.81, respectively, at pH 13 and $g(e_{aq}^-)$ equals 2.65 at pH 7. There was essentially no difference in the sum $G(e_{aq}^-) + G(H) + G(OH)$ in the pH range from 12 to 14.

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Patent status:
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