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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 $H + OH^- = H_2O + e^-_{aq}$. 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 manganate 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.

Notes:

1. The report, "Primary Radical Yields in Pulse Irradiated Alkaline Aqueous Solution," *Radiation Research*, **32,** No. 3, pp. 564-580 (1967) includes a detailed description of methods used and results. Additional information is available in "A Unique New Ion — The Hydrated Electron," *Argonne Reviews*, Vol. 1, No. 4, October 1964.
2. Inquiries concerning this report may be directed to:

   Office of Industrial Cooperation
   Argonne National Laboratory
   9700 South Cass Avenue
   Argonne, Illinois 60439
   Reference: B69-10167

Source: E. M. Fielden and E. J. Hart
Chemistry Division
(ARG-10322)

Patent status:

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Mr. George H. Lee, Chief
Chicago Patent Group
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Chicago Operations Office
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Argonne, Illinois 60439

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