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, εaq. Recent papers have established that in addition to primary εaq yield, g(εaq), 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 radicals beyond pH 12, the pH dependence of g(εaq) was determined by direct observation of εaq developed by a pulse of X-rays. The optical density of an irradiated solution was measured at 7000 Å under carefully controlled conditions.

In neutral solution, the amount of hydrated electron produced corresponds to G(εaq), and at high pH values an additional amount is formed corresponding to G(H) by the reaction H + OH⁻ = H₂O + εaq. 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 7000 Å 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(εaq) + G(H) + G(OH), is constant as is the total reducing yield, G(εaq) + G(H). These relative yields are placed on an absolute basis by measuring the manganese ion yield in a formate-permanganate solution.

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

Notes:
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:
Inquiries concerning rights for commercial use of this innovation may be made to:
Mr. George H. Lee, Chief
Chicago Patent Group
U.S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois 60439

Category 02