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ON THE MECHANISM OF RADIOLYSIS IN AQUEOUS FORMIC ACID SOLUTIONS

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ON THE MECHANISM OF RADIOLYSIS IN AQUEOUS FORMIC ACID SOLUTIONS[1]

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In detailed kinetic studies of the indirect action of γ-radiation on dilute formic acid solutions, Hart[2] has shown that H and OH free radicals

(2) E. J. Hart, (a) J. Phys. Chem. 56, 594 (1952); (b) J. Am. Chem. Soc. 76, 4198 (1954); (c) ibid 76, 4312 (1954).

formed by radiation decomposition of water react with formic acid according to

$$OH + HCOOH \longrightarrow H_2O + COOH \text{ (or HCOO)} \quad (1)$$

$$H + HCOOH \longrightarrow H_2 + COOH. \quad (2)$$

Radical removal then occurs via

$$H + COOH \longrightarrow H_2 + CO_2 \quad (3)$$

$$OH + COOH \longrightarrow H_2O + CO_2, \quad (4)$$

or through the alternate to 3,4, i.e.,

$$2\ COOH \longrightarrow HCOOH + CO_2. \quad (5)$$

The γ-ray data are consistent with the conclusion that no net reduction of formic acid occurs in dilute solution at pH values below 3. However, at concentrations above .05 M, evidence for the reduction of formic acid has been obtained.[2c] On the basis of the reaction scheme, 1-5, it is seen that reduction cannot involve a competing reaction of the type

$$H + HCOOH \longrightarrow HCO + H_2O \quad (2a)$$

since both 2 and 2a have the same concentration dependency. Some other intermediate is apparently involved in reaction with the HCOOH species. It has been proposed (a) that this intermediate is the secondary electron formed in the ionization process and (b) that electron capture by formic acid ($HCOOH + e = HCO + OH^-$) competes with electron capture by water ($H_2O + e = H + OH^-$) at the higher formic acid concentration.[2c]

Results recently obtained in this Laboratory indicate, however, that an alternative mechanism may be involved. It has been shown[3] that irradiation

(3) W. M. Garrison, W. Bennett, M. Jayko, and S. Cole, presented at 128th American Chemical Society Meeting, Minneapolis, Minn., 1955. Univ. of California Radiation Lab. Report, 3208 (1955).

of dilute oxygen-free formic acid solutions with cyclotron-produced helium ions results in the formation of higher organic acids and carbonyl compounds as major products. Both glyoxal and glyoxylic acid, together with smaller amounts of oxalic, glycolic, tartronic, mesoxalic, and tartaric acids are formed at radiation doses which correspond to the removal of less than one percent of the formic acid initially present in the target solution.

Evidence that the glyoxylic acid observed in these studies is not formed through secondary processes initiated by H reduction of oxalic acid can be seen in the experimental data published several years ago by Fricke, Hart, and Smith.[4] In this earlier work it was observed that hydrogen production

(4) H. Fricke, E. J. Hart, and H. P. Smith, J. Chem. Phys. 6, 229 (1938).

in the x-ray irradiation of formic acid-oxalic acid mixtures did not decrease with increasing oxalic acid concentrations until the ratio $C_{(COOH)_2}/C_{HCOOH}$ approached a value of 1. The corresponding ratio in the cyclotron irradiated solutions was approximately 10^{-3}.

On the basis of a consideration of the γ-ray and cyclotron data, it is concluded that radiolysis of formic acid solutions under both conditions can be interpreted without the assumption of competing electron capture by the solute if it is assumed that H adds reversibly to formic acid according to

$$H + HCOOH \rightleftharpoons HC(OH)_2. \qquad (2b)$$

If reaction 1 above is fast as compared to 2, then the reduced formic acid radical $HC(OH)_2$ could combine with COOH to give glyoxylic acid or dimerize to form glyoxal[5] at the high radical concentrations obtained in cyclotron irradiations, i.e.,

$$HC(OH)_2 + COOH \longrightarrow CHOCOOH + H_2O \qquad (6)$$

$$2\ HC(OH)_2 \longrightarrow (CHO)_2 + 2\ H_2O. \qquad (7)$$

(5) W. M. Garrison, W. Bennett, S. Cole, H. R. Haymond, and B. M. Weeks, J. Am. Chem. Soc. 77, 2720 (1955).

In the γ-ray irradiations, the radical concentrations are lower, and in the more dilute formic acid solutions H would be prefentially removed via 2. The concentration effect observed by Hart is then accounted for on the assumption that reaction 8 occurs as a competing process for removal of $HC(OH)_2$

$$HC(OH)_2 + HCOOH \longrightarrow HCHO + COOH + H_2O. \qquad (8)$$

A detailed study of the proposed mechanism is now in progress in this Laboratory. Information on the properties of free radical intermediates involved in the radiolysis of other aquo-organic systems is being obtained through study of radical combination reactions induced by cyclotron irradiation.

We wish to thank the staff of the 60-inch Cyclotron at Crocker Laboratory for their continued cooperation in this work.