UCRL-9903
UC-4 Chemistry
TID-4500 (16th Ed.)

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

ON pH EFFECTS IN THE RADIOLYSIS OF AQUO-ORGANIC SYSTEMS

Warren M. Garrison, Boyd M. Weeks, and Sibyl Cole

October 1961

Printed in USA. Price 50 cents. Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D.C.

ON pH EFFECTS IN THE RADIOLYSIS OF AQUO-ORGANIC SYSTEMS

Warren M. Garrison, Boyd M. Weeks, and Sibyl Cole

Lawrence Radiation Laboratory
University of California
Berkeley, California

October 1961

ABSTRACT

In the radiolysis of air-free solutions of organic substances, $G(H_2)$ generally decreases with increasing pH. In the formic acid systems, both $G(H_2)$ and $G(CO_2)$ decrease, and $G(CO_2)$ approaches zero at pH values above 7. Oxalic acid becomes the major product in alkaline solution. Studies of the systems (I) 0.1 M $HCOONa$—.01 M $NaHC^{14}O_3$, (II) 0.1 M $HC^{14}OONa$—.01 M $NaHCO_3$ show that the oxalate does not arise through reduction of carbonate by H atoms or by solvated electrons. A mechanism for water decomposition involving the hydride ion, H^-, is given.

ON pH EFFECTS IN THE RADIOLYSIS OF AQUO-ORGANIC SYSTEMS*

Warren M. Garrison, Boyd M. Weeks, and Sibyl Cole

Lawrence Radiation Laboratory
University of California
Berkeley, California

October 1961

Recent studies of pH effects in the radiolysis of aqueous solutions have demonstrated the existence of two types of reducing species in irradiated water. The indications are that these species correspond to the solvated electron, H_2O^-, and the H atom.[1,2] Hayon and Weiss have proposed that the marked pH dependence of hydrogen yields in the radiolysis of air-free solutions of organic compounds is consistent with

$$H_2O \rightsquigarrow H_2O^+ + e \,, \qquad (1)$$

$$e + H_2O \longrightarrow H_2O^- \,, \qquad (2)$$

$$H^+ + H_2O^- \longrightarrow H + H_2O \,, \qquad (3)$$

$$H + RH \longrightarrow H_2 + R \,, \qquad (4)$$

where (3) and hence (4) become less important at the higher pH values as competing reactions lead to removal of H_2O^- through

$$2\ H_2O^- \longrightarrow H_2 + 2\ OH^- \,, \qquad (5)$$

or through capture by solute, e.g.,

$$H_2O^- + RCl \longrightarrow H_2O + Cl^- + R \,. \qquad (6)$$

Now, in the radiolysis of air-free formic acid solutions, the yield not only of hydrogen but also of carbon dioxide decreases with increasing pH, and the yield of carbon dioxide becomes essentially zero at pH 7 and above.[3] This latter phenomenon has been interpreted elsewhere[4] in terms of an effect of pH on the relative rates of the two reactions

*This work was done under the auspices of the U.S. Atomic Energy Commission.

[1] N. F. Barr and A. O. Allen, J. Chem. Phys. 63, 928 (1959) (Paper presented at the American Chemical Society Meeting, San Francisco, April 1958).

[2] E. Hayon and J. Weiss, in Proceedings of the Second International Conference on The Peaceful Uses of Atomic Energy, Geneva, 1958 (United Nations, New York, 1959), Vol. 29, 1958.

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

[4] W. M. Garrison, W. Bennett, and S. Cole, Radiation Research 9, 647 (1958).

$$2\ COOH \longrightarrow HCOOH + CO_2\ , \qquad (7)$$

$$2\ COOH \longrightarrow (COOH)_2\ . \qquad (7a)$$

Allan and Scholes, on the other hand, have recently proposed that carbon dioxide is produced under all conditions of pH (through an unspecified mechanism),[5] and that it is subsequently removed through a back reaction between carbonate and the solvated electron,

$$H_2O^- + H_2CO_3 \longrightarrow COOH + OH^- + H_2O, \qquad (8)$$

followed by (7a) or the equivalent. Although carbon dioxide in aqueous solution is known to be reduced to formic and (or) oxalic acid under various conditions of radiolysis,[5,6] there is a question as to whether or not Reaction (8) could account for the fact that the "steady-state" concentration of carbonate in alkaline formate solutions is essentially zero.[3] To obtain information on this point, we have investigated the C^{14}-labeled products formed in the γ-ray radiolysis of the systems (I) 0.1 M HCOONa – .01 M $NaHC^{14}O_3$ and (II) 0.1 M $HC^{14}OONa$ – .01 M $NaHCO_3$.

The radiometric and analytical techniques were those developed in an earlier radiation-chemical study of aqueous C^{14}-labeled formic acid solutions.[4] Both $HC^{14}OOH$ and $(C^{14}OOH)_2$ were determined because of the possibility of the step

$$HCOOH + C^{14}OOH \longrightarrow COOH + HC^{14}OOH\ .$$

At a dose of 9×10^{18} ev/ml, we obtained, with Solution (I), the values $G(HC^{14}OOH) \approx 0.14$, $G(C^{14}OOH)_2 \approx .01$. Solution (II) under the same conditions of irradiation gave $G(C^{14}OOH)_2 \approx 1.5$. It is concluded, therefore, that the reductive Reaction (8) is relatively unimportant even at carbonate concentrations as high as one-tenth that of the formic acid. Presumably, the solvated electron is removed in alkaline formic acid solutions through Reaction (5).

In this connection it is of interest to note that a reaction mechanism formally equivalent to the sequence (1) through (5) can be derived on the assumption that the electron formed in Step (1) undergoes dissociative capture to yield the hydride ion,

$$H_2O + e \longrightarrow H^- + OH\ . \qquad (2a)$$

The appearance of H^- at an electron-impact potential of 5.6 ev has been associated by Laidler with a repulsive state of the H_2O^- molecule ion.[7] Factors influencing the relative yields of Processes (2) and (2a) have been treated by Magee and Burton.[8]

---

[5] J. T. Allan and G. Scholes, Nature 187, 218 (1960).

[6] W. M. Garrison and G. K. Rollefson, Discussions Faraday Soc. 12, 155 (1952).

[7] K. J. Laidler, J. Chem. Phys. 22, 1740 (1954).

[8] J. L. Magee and M. Burton, J. Am. Chem. Soc. 73, 523 (1951).

Disposition of H^- may be formulated in terms of the competing steps

$$H^- + H_2O \longrightarrow H_2 + OH^- , \qquad (5a)$$

$$H^- + H_3O^+ \longrightarrow H + H_3O . \qquad (3a)$$

Reaction (5a) has recently been identified experimentally in electron-impact studies by Muschlitz and Bailey.[9] The proposal that H atoms could be liberated in the bulk of the solution through Step (3a) is predicted on the hypothesis that electron transfer in aqueous solution may occur at large separations.[10]

[9] E. E. Muschlitz and T. L. Bailey, J. Phys. Chem. 60, 681 (1956).

[10] A. Farkas and L. Farkas, Trans. Faraday Soc. 34, 1120 (1938).

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.