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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 $HCOONa$ —0.01 M $NaHC^{14}O_3$, (II) 0.1 M $HC^{14}OONa$ —0.01 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.

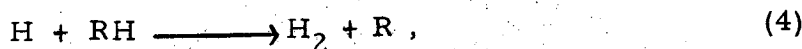
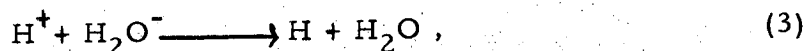
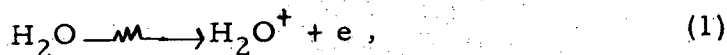
ON pH EFFECTS IN THE RADIOLYSIS OF AQUO-ORGANIC SYSTEMS*

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

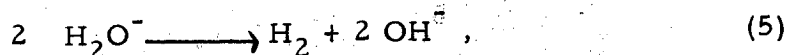
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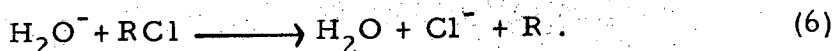
Recent studies of pH effects in the radiolysis of aqueous solutions have demonstrated the existence of two types of reducing species in irradiated water. The indications are that these species correspond to the solvated electron, H_2O^- , and the H atom.^{1, 2} Hayon and Weiss have proposed that the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



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



or through capture by solute, e. g.,



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 elsewhere⁴ in terms of an effect of pH on the relative rates of the two reactions

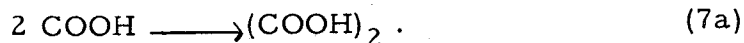
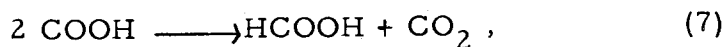
*This work was done under the auspices of the U. S. Atomic Energy Commission.

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

²E. 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.

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

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

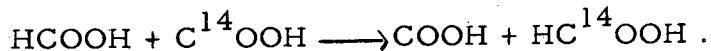


Allan and Scholes, on the other hand, have recently proposed that carbon dioxide is produced under all conditions of pH (through an unspecified mechanism),⁵ and that it is subsequently removed through a back reaction between carbonate and the solvated electron,



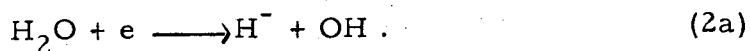
followed by (7a) or the equivalent. Although carbon dioxide in aqueous solution is known to be reduced to formic and (or) oxalic acid under various conditions of radiolysis,^{5,6} there is a question as to whether or not Reaction (8) could account for the fact that the "steady-state" concentration of 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 $\text{NaHC}^{14}\text{O}_3$ and (II) 0.1 M $\text{HC}^{14}\text{OONa}$ - .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 $(\text{C}^{14}\text{OOH})_2$ were determined because of the possibility of the step



At a dose of 9×10^{18} ev/ml, we obtained, with Solution (I), the values $G(\text{HC}^{14}\text{OOH}) \approx 0.14$, $G(\text{C}^{14}\text{OOH})_2 \approx .01$. Solution (II) under the same conditions of irradiation gave $G(\text{C}^{14}\text{OOH})_2 \approx 1.5$. 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,



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

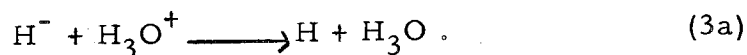
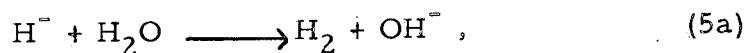
⁵J. T. Allan and G. Scholes, *Nature* 187, 218 (1960).

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

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

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

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



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

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

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

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