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June 13, 1952

Berkeley, California

HIGH ENERGY HELIUM-ION IRRADIATION OF FORMIC ACID IN AQUEOUS SOLUTION*

Warren M. Garrison, Donald C. Morrison,
Herman R. Haymond, and Joseph G. Hamilton

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Berkeley and San Francisco

June 13, 1952

Several years ago Fricke, Hart, and Smith¹ measured the amounts of hydrogen and carbon dioxide formed by x-ray induced reactions in aqueous solutions of formic acid over a wide range of pH values and solute concentrations. To account for the observed gas yields, they suggested that under certain conditions both oxalic acid and formaldehyde may be formed in addition to hydrogen and carbon dioxide. Recently, as part of a general study^{2,3} of the radiation induced synthesis of organic substances in aqueous solutions, we have found that oxalic acid, formaldehyde, and at least eight other organic compounds are produced by high energy helium-ion bombardment of hydrogen-saturated aqueous formic acid solutions. The present preliminary communication

* This report is based on work performed under Contract No. W-7405-eng-48-A for the Atomic Energy Commission.

¹ H. Fricke, E. J. Hart, and H. P. Smith. J. Chem. Phys., 6, 229 (1938).

² W. M. Garrison, D. C. Morrison, J. G. Hamilton, A. A. Benson, and M. Calvin. Science, 114, 416 (1951).

³ W. M. Garrison, and G. K. Rollefson, Discussions Faraday Soc., 11, (1952), in press.

describes briefly the experimental techniques and observations. A more detailed report of this work will be forthcoming.

Air-free aqueous solutions of C^{14} -labelled formic acid⁴ were irradiated in all-glass target cells with the 40 Mev helium-ion beam of the 60-inch cyclotron at the Crocker Laboratory. Hydrogen gas was bubbled through the solution during exposure and then passed through dilute sodium hydroxide solution to recover carbon dioxide which was subsequently assayed as $BaC^{14}O_3$. After irradiation the target solution was distilled to dryness in vacuo at room temperature. The $HC^{14}HO$ in the distillate was isolated and assayed as the methone-formaldehyde derivative.² A two-dimensional paper chromatogram of the non-volatile fraction was prepared⁵ and radioautographed. One major spot and eight other spots of lesser intensity could be seen in the original radioautogram which is reproduced in Figure 1. The region containing the major part of the activity was eluted with 0.1 N hydrochloric acid. The activity in an aliquot of this solution co-precipitated quantitatively on lanthanum oxalate after repeated washing and recrystallization from dilute nitric acid. To further identify this major non-volatile product as oxalic acid a second aliquot was co-chromatographed with added oxalic acid on a silica column by a partition chromatography method similar to one recently reported.⁶ The correspondence of oxalic acid titre and C^{14} activity in the eluant is shown in Figure 2. A 300 microcurie sample of the $HC^{14}OOH$ used in these experiments was analyzed in exactly the same way as the bombarded solutions; the control showed no activity other than $HC^{14}OOH$. Decay of the activity in the products could

⁴ We wish to thank Dr. Bert M. Tolbert for supplying the $HC^{14}OOH$ used in these experiments.

⁵ A. A. Benson, J. A. Bassham, M. Calvin, T. C. Goodale, V. A. Hass, and W. Stepka. J. Am. Chem. Soc., 72, 1710 (1950).

⁶ W. A. Bulen, J. E. Varner, and R. C. Burrell, Anal. Chem., 24, 187 (1952).

not be detected over a period of several months.

Each of the 10 ml target solutions contained 300 microcuries of HC^{14}OOH and were .009 N in total formic acid. The helium ions incident on the solution had an energy of 35 Mev. Bombardments were made at a beam current of 0.10 microampere for a period of 3.0 minutes to give a total exposure of .005 microampere hour. Yield data are summarized in Table I.

TABLE I

| Product | G (molecules/100 e.v.) | |
|----------------|------------------------|-----------------------|
| | (1) | (2) |
| Carbon dioxide | | 0.75 |
| Oxalic acid | 0.023 | 0.027 |
| Formaldehyde | 0.61×10^{-3} | 0.56×10^{-3} |

Acknowledgements

We wish to thank Mrs. Jeanne Gile-Melchert and Mrs. Harriet Powers for their assistance in the column separations, Mr. Boyd Weeks for his help in the target assembly, and the staff of the 60-inch cyclotron at the Crocker Laboratory for the bombardments.

Legends for Figures

Figure 1. Radioautogram of non-volatile products.

Figure 2. Elution curve of major non-volatile product with added oxalic acid.



ZN318

Fig. 1

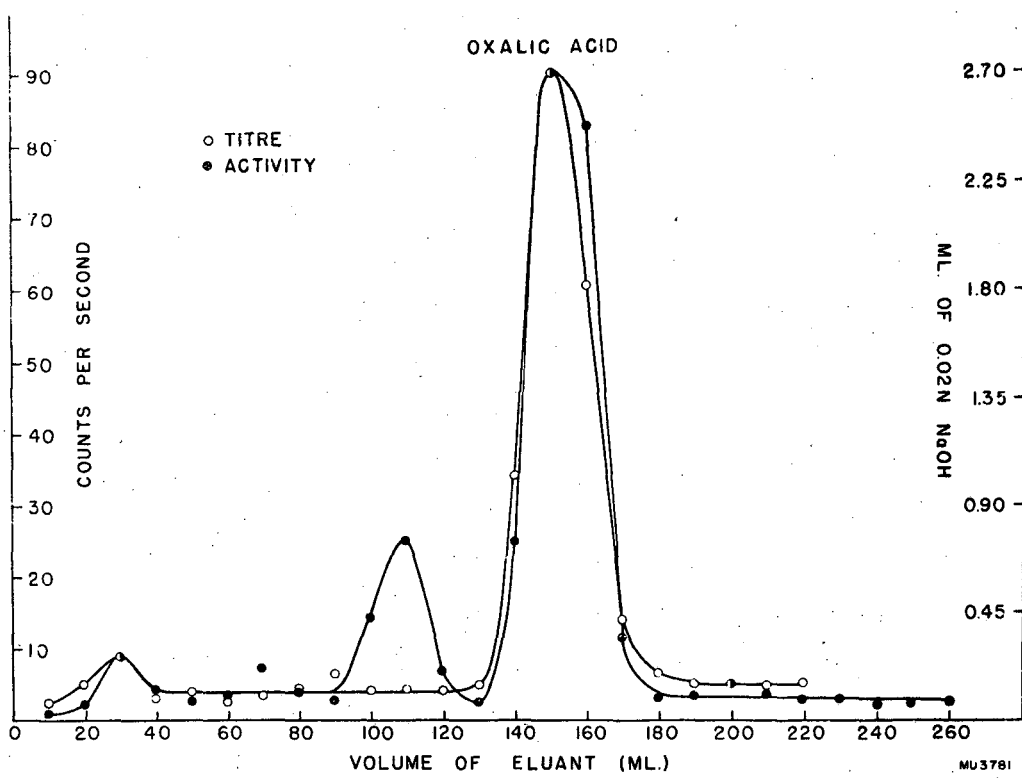


Fig. 2