Title

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In their study of the alpha-ray radiolysis of fatty acids, Honig,[1] Sheppard and Burton,[2] Breger,[3] and Whitehead, Goodman, and Breger[4] reported virtually no water to be formed in the radiolysis of the lower fatty acids, and the last authors reported the yield of water to increase with increasing alkyl chain length of the acid to a maximum at palmitic acid.

It has proven difficult for this author to correlate such an increase in specificity of a radiolytic decomposition with increasing chain length, therefore a study has been made of this point by helium-ion irradiations of liquid acetic and propionic acids.

Glacial acetic acid (Baker and Adamson 99.5% glacial) was dehydrated by refluxing 3 days with triacetyl borate,[5] and distilled through a 15-plate adiabatic column. The progress of the dehydration was followed by periodically taking small portions of distillate and determining the water content by both freezing point and titration with Karl Fischer reagent. The final material had a melting point of 16.67° (Lit.,[6] 16.52°), and a water content of 0.022 mg/ml. Eastman White Label Propionic acid was dried over anhydrous sodium sulfate and distilled;[7] fp, - 20 ± 1°, bp, 141° (Lit.,[5] - 20.8°, 140.80°). The water content by titration with Karl Fischer reagent was 0.52 mg/ml.

These acids were carefully degassed and irradiated at 25°C in glass cells of the type described by Garrison, Haymond, and Weeks[8] with about 32-Mev helium ions impingent on the liquid. After irradiation the gases were collected as described previously,[9] and all liquid fractions combined. Aliquots of the liquid residue were titrated with Karl Fischer reagent to determine the water content.[10] The increase in water content on irradiation was taken as the yield of water. The results of the gas-phase and liquid-phase analyses are shown in Table I.

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It is apparent from these results that far from being negligible, water is a major product from the radiolysis of acetic and propionic acids. Since the authors cited looked only for water in the gas phase (mass-spectrometer analyses), and water is soluble in the lower aliphatic acids, it is not surprising that water was not seen. The reported increase in water observed in the gas phase with increasing molecular weight acid parallels the decrease in solubility of water in these same acids. The inverse correlation reported[4] may thus be an analytical artifact resulting from the method of measurement.

The yields of products other than water are comparable to those reported by Whitehead, Goodman, and Breger,[4] considering the wide differences in experimental conditions under which the irradiations were made. The results for acetic acid are directly comparable and almost identical to values found by extrapolating the data of Garrison, Bennett, Cole, Haymond, and Weeks[11] for acetic acid solutions in water to glacial acetic acid. Since these latter authors worked in water solution, water as a product was not determined. The existence of water as a radiolysis product lends support to the conception that the reaction mechanisms postulated by these latter authors for concentrated acetic acid solutions can be extrapolated to the case of glacial acetic acid. The proof of this conception will require additional data on other products in the liquid phase.

The author hereby expresses his appreciation to Mrs. Bobby Mohler and Mr. Laurin Tolman for aid in the mass-spectrometer analyses and to Dr. J. G. Hamilton and the late Mr. Bernard Rossi of the Crocker Laboratory for aid in the cyclotron irradiations.

Table I. Yields[a] of some products produced in the helium-ion radiolysis of liquid acetic and propionic acids.

Acid energy input ev/ml	Acetic acid[b] 27.4×10^{20}	Propionic acid 40.2×10^{20}
Product	G	G
H_2	0.52	0.79
CO	0.38	0.28
CH_4	1.38	0.53
C_2H_2	--	0.33
C_2H_4	--	0.64
C_2H_6	0.85	1.07
C_3H_6	--	0.01
C_3H_8	--	0.02
C_4H_8[c]	--	0.01
$n\text{-}C_4H_{10}$	--	0.69
CO_2	4.04	3.94
H_2O	2.15	1.58

[a] Yields, G, are molecules of product specified formed per 100 ev energy input.

[b] Other products from acetic acid identified in the gas phase but not quantitatively measured are acetaldehyde, acetone, and methyl acetate.

[c] Mixture of butene-1 and butene-2.