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RADIATION-INDUCED OXIDATION OF AQUEOUS ACETIC ACID-OXYGEN SOLUTIONS¹

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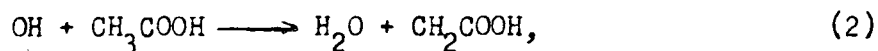
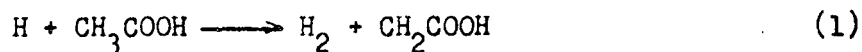
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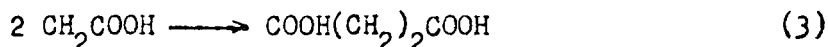
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INTRODUCTION

In the radiolysis of oxygen-free acetic acid solutions, the primary radicals H, OH are removed via the steps

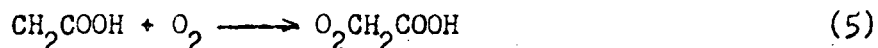


and the resultant organic intermediate CH_2COOH is removed in turn by the combination reaction



to yield succinic acid as the principal organic product (1).

If dissolved oxygen is present, the competing processes



lead to a suppression of the succinic acid production and a concomitant oxidation of the acetic acid molecule. Products of this oxidation include: glyoxylic, glycolic, and oxalic acids, formaldehyde, and carbon dioxide. The present paper reports (i) experimental evidence for the formation of these products (ii) product yield measurements for several different conditions of irradiation (iii) a consideration of the intermediate processes ensuant to steps 4,5 above.

EXPERIMENTAL

Irradiation

Studies were made with γ -rays from Co^{60} and with helium ion, proton, and neutron beams from the Crocker Laboratory 60-inch cyclotron.

A 2000 curie cobalt source was used for the γ -irradiations. Solutions (3 ml) were exposed under oxygen (5 ml) at one atmosphere in sealed pyrex tubes. Contents were shaken at intervals to prevent depletion of oxygen in the solution during exposure. The irradiation dose rate was

$\sim 7.8 \times 10^{18}$ ev/ml-min.

The all-glass cells used in the helium ion and proton irradiations were of the tubular, aerated type previously described (2). Target solutions (10 ml) were aerated continuously with oxygen during exposure. Product yields obtained at beam intensities of .01 microampere and below were essentially independent of the gas flow-rate at values above 30-40 ml/min. Details of the target assembly, beam monitoring circuits and dosimetry methods have been given (1,2). Energy of the helium ions and protons incident on the cell window were 40 Mev and 10 Mev respectively. Corrections for energy loss were calculated from range-energy data (3).

Neutrons were produced by bombardment of beryllium with 24-Mev deuterons. Solutions (10 ml) were exposed under oxygen (10 ml) at one atmosphere in pyrex tubes mounted uniformly in a motor-driven reel situated a standard distance from the source. Experimental techniques including methods used in establishing the dosimetry have been reported elsewhere (4,5).

Materials

Water from a Barnstead still was re-distilled in pyrex first from alkaline permanganate and then from dilute phosphoric or sulfuric acid. Baker and Adamson reagent grade glacial acetic acid was re-distilled twice. The middle fraction (~ 30%) was retained each time. The C¹⁴-labeled acetic acid was purified chromatographically on a silicic acid column (see below).

Analysis

The analytical scheme of the present study is very similar to that developed as part of our recent work on the synthesis of higher molecular weight products in the radiolysis of aqueous solutions of formic acid (6).

The present discussion will emphasize those modifications found to be necessary in adapting the methods to the acetic acid-oxygen system. Other experimental details may be found in the earlier paper.

1. Organic acids: Acid products were determined by methods of partition chromatography adapted from the work of Marvel and Raxis (7) and Bulen, Varner and Burrell (8). Water adsorbed on silicic acid acts as the immobile phase. Chloroform containing increasing amounts of butyl alcohol is used as the developing liquid.

In the preliminary studies, 10 ml volumes of oxygen-aerated 0.25 M acetic acid containing 100 to 200 microcuries of $\text{CH}_3\text{C}^{14}\text{OOH}$ (or $\text{C}^{14}\text{H}_3\text{COOH}$) were irradiated with 40-Mev helium ions at a beam intensity of .01 micro-ampere. The solutions were distilled to dryness in vacuo at room temperature to remove acetic acid. The non-volatile fraction was chromatographed using the standard survey method of Bulen, Varner and Burrell (8). Solvents in sequence were 5, 15, 20, 25, 35, and 50% (v/v) n-butyl alcohol in chloroform saturated with 0.5 N sulfuric acid. Appropriate aliquots of each 10 ml fraction of the effluent were neutralized with a few drops of .01 N sodium hydroxide, evaporated to dryness, and assayed for C^{14} activity. The specific activity of the target solution was set so that any acid produced in significant yield would give a product peak with a total C^{14} activity of several hundred counts per second and an associated titer of less than .1 ml of .01 N sodium hydroxide. Two major activity peaks were observed at radiation doses as low as 1×10^{18} ev/ml.

The position of peak I indicated that the C^{14} activity of this fraction could be associated with succinic acid and/or glyoxylic acid. These acids are eluted very close together in the standard survey method. Usually separation of such pairs can be accomplished by changing the

elution procedure. However, no adequate separation of succinic and glyoxylic acids could be accomplished, although numerous control runs were made under various column conditions. The composition of peak I was established as follows. A sample of the C^{14} activity plus added succinic acid and glyoxylic acid in milligram amounts was treated with 2,4-dinitrophenylhydrazine-hydrochloric acid solution (9) to form the glyoxylic acid hydrazone derivative. The solution was evaporated to dryness in vacuo and the residue was chromatographed with 25% n-butyl alcohol in chloroform. The glyoxylic acid hydrazone and excess reagent were recovered in the "break-through" volume. The succinic acid was eluted on further addition of developing liquid and showed only background activity. All of the C^{14} activity of peak I was subsequently found to be retained by the glyoxylic acid hydrazone derivative after it had been separated and purified chromatographically on filter paper with a butanol-ammonia solvent system (6).

Peak II from its position on the elution curve was suspected of being oxalic acid and/or glycolic acid. Samples of the C^{14} activity plus added authentic acids in milligram amounts were chromatographed with 25% n-butyl alcohol in chloroform saturated with 0.50 N sulfuric acid. This procedure effects a satisfactory separation of the oxalic and glycolic acids (also glyoxylic acid). The activity of peak II was found to be divided into two fractions which showed exact correspondence with the titers of the added oxalic and glycolic acids. Typical co-chromatographs for this particular separation are published in reference (6).

In determining quantitative yield data, known amounts of oxalic, glycolic, and glyoxylic acids were added to the target solution immediately after irradiation, recovered as a non-volatile fraction (not

necessarily quantitatively) and chromatographed as described in the preceding paragraph. Each of the three separated acid peaks was then re-chromatographed individually and assayed for specific activity. Corrections for self-absorption were obtained experimentally for the actual counting geometry employed.

2. Carbonyl products: Carbonyl products were identified as the 2,4-dinitrophenylhydrazone derivatives. Since these can be readily detected in amounts as low as 10^{-7} moles, preliminary studies were made on target solutions that did not contain $C^{14}H_3COOH$. Aliquots of the irradiated solutions were treated with platinum black to remove hydrogen peroxide and were then added to 2,4-dinitrophenylhydrazine-hydrochloric acid solution. Hydrazones and excess reagent were extracted with chloroform and separated chromatographically on filter paper by use of the solvent systems: (i) butanol saturated with 3% aqueous ammonia, (ii) heptane (pract) saturated with methanol. The first method separates the carbonyl acid hydrazones, the second develops the "non-acid" hydrazones, i.e., those of formaldehyde, acetaldehyde, etc. (6). Only glyoxylic acid and formaldehyde derivatives were observed.

In the quantitative studies, known amounts of formaldehyde carrier were added to irradiated solutions containing $C^{14}H_3COOH$ and precipitated as the 2,4-dinitrophenylhydrazone derivative. This was washed several times with dilute base and chromatographed by method (ii). The appropriate area of the filter paper chromatogram was then extracted with methanol and assayed for C^{14} activity and for total hydrazone (6).

3. Carbon dioxide: Yield data for carbon dioxide were obtained only for the case of helium-ion irradiation. Target cells containing C^{14} -

labeled acetic acid were aerated with oxygen containing 1% carbon dioxide. The effluent gas was scrubbed with a dilute solution of sodium hydroxide. Flow was continued several minutes after irradiation to insure complete recovery of the $C^{14}O_2$. Carbonate in the sodium hydroxide trap was quantitatively recovered as barium carbonate and assayed for C^{14} activity (thick sample geometry).

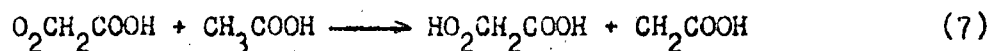
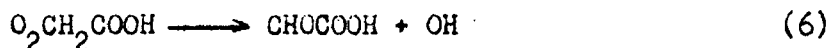
4. Peroxides: Hydrogen peroxide was routinely determined by titration with ceric sulfate in the cold (10). A series of control runs with simulated target solutions showed that the organic products of acetic acid oxidation do not interfere. Organic hydroperoxides were also measured (10,11)

RESULTS AND DISCUSSION

Table I gives the 100 ev yields or G values for the formation of organic products in oxygen-saturated 0.25 M acetic acid solution by irradiation with helium ions, protons, neutrons, and γ -rays for approximately the same total dose (ev/ml). All of the acid products appear in appreciable yield at concentrations which are lower than that of the parent solute by a factor of about 10^{-4} . This observation would suggest that the glycolic, glyoxylic, and oxalic acids, for example, are not formed in sequence through a series of consecutive oxidation steps. Support for this conclusion is to be found in the data of Table II which shows that the measured G values for the acid products are essentially independent of radiation dosage over a fairly wide range. Note also that the carbon dioxide yield data obtained with $C^{14}H_3COOH$ are consistently lower than those obtained with $CH_3C^{14}OOH$. The inference is that carbon dioxide is produced preferentially by some intermediate decarboxylation process, not through oxidation of oxalic acid. We also found that

irradiation of solutions of unlabeled acetic acid (0.25 M) containing added $C^{14}H_2OHCOOH$ (10^{-3} M) gave G values for glyoxylic acid which were less than .001. The irradiation conditions were identical with those of column 1, Table II. The foregoing observations lead to the conclusion that the radiation-induced oxidation of acetic acid occurs primarily through parallel reactions initiated by the formation of the common precursor O_2CH_2COOH via reaction 5 above.

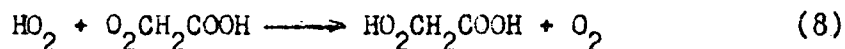
In considering possible reaction paths involving O_2CH_2COOH radicals, we note first that processes which lead to chain reactions, e.g.



probably do not contribute appreciably to the yields of observed products.

Reactions 6 and 7 in conjunction with reactions 2 and 5 respectively each initiate a chain reaction. There is, however, no evidence from the present work that more than one acetic acid molecule is removed per OH radical initially formed in the primary radiation-induced reaction.

The reaction

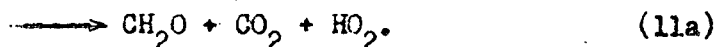
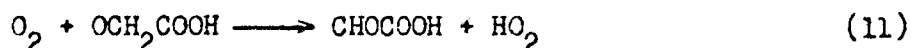
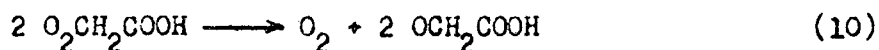


may also be ruled out since specific tests for organic hydroperoxides give an upper limit for G (ROOH) of ~ 0.3 under the conditions of the present study. This result is in agreement with the work of Weiss and co-workers (11) who have detected organic hydroperoxides as major products in several irradiated aquo-organic systems but only at the higher pH values under which conditions $HO_2(O_2^-)$ is a more effective reducing agent. At the pH of 0.25 M acetic acid we may assume that HO_2 is preferentially removed by the well established disproportionation reaction



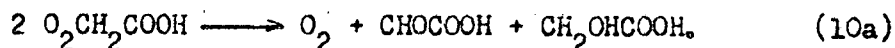
We come, therefore, to the conclusion that formation of organic products in the radiolysis of oxygen-saturated acetic acid solution occurs primarily through interactions of $\text{O}_2\text{CH}_2\text{COOH}$ radicals. The problem of elucidating the various reactions of peroxy radicals in the present study would appear to be closely related to the classical problem of formulating the mechanism of chain termination in hydrocarbon oxidation as denoted by the general reaction $2\text{RO}_2 \longrightarrow$ products. In attempting to formulate the possible interactions of $\text{O}_2\text{CH}_2\text{COOH}$ we will consider first those processes which are indicated on the basis of the more qualitative evidence, and will then attempt to ascribe relative importance in terms of the quantitative results obtained under the several experimental conditions studied.

The simplest mechanism for the formation of the aldehyde functions, glyoxylic acid and formaldehyde is given by the sequence:



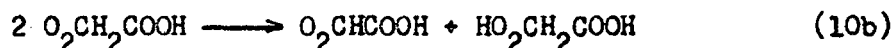
Reaction of the type 10 has been considered by Vaughn and co-workers to be of importance as a chain ending process in the low-temperature oxidation of hydrocarbons (12). More recently, Jolley employed the equivalent of reactions 10, 11, and 11a in interpreting studies of the photochemically-induced oxidation of diethylketone (13).

The removal of $\text{O}_2\text{CH}_2\text{COOH}$ may also be written as a type of disproportionation reaction to give glyoxylic and glycolic acids directly, i.e.,



Evidence for reaction of the type 10a has recently been given by Russell (14).

The presence of oxalic acid as an initial product is somewhat more difficult to account for. Bach (15) observed a rather similar phenomenon in radiolysis studies of liquid hydrocarbon systems containing dissolved oxygen. It was found that organic acids (in addition to carbonyls and organic peroxides) are produced initially as a linear function of radiation dosage. The author interprets the formation of the carboxyl function in terms of the early studies of Rieche and Meister (16) who showed that organic free-radicals of the type $RCHO_2$ undergo isomerization according to $RCHO_2 \longrightarrow RCOOH$. The formation of oxalic acid as an initial product in the present work could be interpreted on the assumption that a small fraction of the O_2CH_2COOH radicals undergo hydrogen abstraction



followed by isomerization



The correspondingly small amount of organic hydroperoxide formed in step 10b would be below the experimentally observed upper limit for hydroperoxide production, i.e., $G(ROOH) \leq 0.3$.

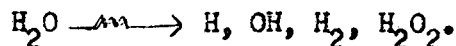
Disregarding for the moment the question of absolute product-yields, it is seen that the helium-ion, proton, and γ -ray data (Table I) are generally consistent with a mechanism in which reaction 10 represents the principal path for removal of O_2CH_2COOH . The lower yields of oxalic and glycolic acids are interpreted simply by ascribing proportionately lower rates to the parallel steps 10a and 10b. Note, however, that the results obtained with neutrons show glyoxylic and glycolic acids to be

formed in almost equivalent amounts for this particular irradiation condition. Obviously, the latter result is not consistent with the idea that the yields of oxalic, glyoxylic, and glycolic acids are wholly determined by the relative rates of parallel paths 10, 10a, and 10b. This apparent anomaly is resolved, however, if we include in the reaction scheme the recognized hydrolytic process



Reaction of the type 13 has been proposed by Sworski (17), and by Phung and Burton (18) as a mechanism for the formation of phenol in the radiolysis of aqueous benzene-oxygen solutions. We postulate that the relatively higher yield of glycolic acid from neutron irradiation in the present study may be attributed to an effect of dose rate on the relative rates of reactions 10, 10a, and 10b as compared to 13. The former, being of second order in $\text{O}_2\text{CH}_2\text{COOH}$ would, of course, be favored over the pseudo first-order reaction 13 at the higher dose rates. In the helium ion and proton irradiations the dose rate was $\sim 5 \times 10^{18}$ ev/ml-min, in the γ -ray irradiations about 7.8×10^{18} ev/ml-min. The corresponding value in the neutron runs was $\sim 1 \times 10^{17}$ ev/ml-min.

The absolute yields of observed final products can be related only approximately to the primary radical and molecular product yields for water decomposition. The notation of Dewhurst and Burton is used here to represent the initial chemical reaction (19),



The 100-ev yields of initial products are denoted $G_W(\text{H})$, $G_W(\text{OH})$, $G_W(\text{H}_2)$, $G_W(\text{H}_2\text{O}_2)$. Hart has shown that the aqueous formic acid-oxygen dosimeter provides a convenient chemical system for the determination of these

values because of the relative simplicity of the radiation-induced oxidation mechanism (20). Data are available for Co^{60} γ -rays (20) and for the 10-Mev proton beam used in the present study (5); the following primary yield values may be taken (i) γ -rays: $G_W(\text{H}) \simeq G_W(\text{OH}) \simeq 3.0$, $G_W(\text{H}_2) \simeq G_W(\text{H}_2\text{O}_2) \simeq 0.4$; (ii) 10-Mev protons: $G_W(\text{H}) \simeq G_W(\text{OH}) \simeq 2.4$, $G_W(\text{H}_2) \simeq G_W(\text{H}_2\text{O}_2) \simeq 0.6$. Although the specific yields of H, OH, H_2 , and H_2O_2 are somewhat dependent on the nature of the solute, such effects are relatively small (21) and introduce no serious limitations in the application of the above data to the present system.

Now the scheme proposed for the radiation-induced oxidation of acetic acid predicts that the sum $G(\text{CH}_3\text{COOH}) + G(\text{CH}_2\text{OHCOOH}) + 2G(\text{COOH})_2 + G(\text{CH}_2\text{O})$ should approximate $G_W(\text{OH})$. It is readily apparent from inspection of the data obtained in 0.25 M acetic acid (Table I) that G for total organic product as defined above is considerably less than $G_W(\text{OH})$ for both the γ -ray and proton irradiations. The discrepancy would seem to be considerably greater than the uncertainties referred to regarding the assumed $G_W(\text{OH})$ values. There is, of course, the possibility that all OH radicals available in the bulk of the solution are not removed by reaction with acetic acid in 0.25 M solutions. This is considered unlikely, however, in view of the fact that $G(\text{H}_2\text{O}_2)$ was found to decrease but a few percent when the acetic acid concentration was decreased by a factor of 5. On the other hand, it is quite possible that we have not identified all organic products formed in the radiation-induced oxidation of the acetic acid molecule. An interesting possibility which we are now investigating is that dialkyl peroxide derivatives are produced via reaction of type $2\text{RO}_2 \longrightarrow \text{ROOR} + \text{O}_2$.

This reaction has frequently been cited as a path for removal of RO_2 radicals in hydrocarbon oxidation (22). Dialkyl peroxides are relatively inert and are not detected by methods employed in the determination of the hydroperoxides, $ROOH$.

SUMMARY

Radiation-induced oxidation of acetic acid in oxygenated aqueous solution yields glycolic, glyoxylic, and oxalic acids, formaldehyde, and carbon dioxide. Formation of these products apparently occurs through parallel processes initiated by formation of a common precursor, viz, the peroxy radical, O_2CH_2COOH . There is no evidence for a chain reaction. Possible reaction paths for removal of O_2CH_2COOH are treated. The experimental results are shown to be consistent with the concept that the removal steps involve: $2RO_2 \longrightarrow$ products, $RO_2 + H_2O \longrightarrow$ products. A detailed mechanism is presented.

ACKNOWLEDGEMENTS

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Table I

Product yields in the radiolysis of oxygen-saturated 0.25 M acetic acid solutions by various types of radiation

Radiation	100-ev yield, G ^a			
	Helium ions ^b (40 Mev)	Protons (10 Mev)	Neutrons ^c (10 Mev)	Gamma rays ^d (Co ⁶⁰)
Dose(ev/ml) ^e	4.31×10^{19}	1.50×10^{19}	1.29×10^{19}	1.80×10^{19}
Hydrogen peroxide	1.82	2.58	2.82	-
Glyoxylic acid	0.54	1.10	0.75	1.35
Glycolic acid	0.10	0.39	0.65	0.45
Oxalic acid	0.13	0.22	0.10	0.28
Formaldehyde	0.10	0.20	0.10	-

^a Data are average values based on the results of at least 2 runs for each condition. Duplicate runs were reproducible to within 10%.

^b Although the results reported for the helium ion irradiations were obtained at a somewhat higher dose, the data given represent initial G values (see Table II) and may be compared directly with the other data shown.

^c The neutron spectrum had a population maximum at about 10 Mev. Dose was based on measurements made with the formic acid dosimeter. Assumptions involved in the use of this system for evaluating dose to dilute aqueous solutions is described in references 4,5.

^d Based on $G(\text{Fe}^{+3})=15.6$ for the Fricke Dosimeter (23).

^e Calculated in each case as total dose/total volume of irradiated solution.

Table II

Effect of dose on product yields in the radiolysis of
oxygen-saturated 0.25 M acetic acid solutions
by 40-Mev helium ions

Dose: (ev/ml)	100-ev yield, G		
	4.31×10^{19}	1.29×10^{20}	4.31×10^{20}
Glyoxylic acid	0.54	.60	0.35
Glycolic acid	0.10	.11	0.11
Oxalic acid	0.13	.12	0.19
Formaldehyde	0.10	-	-
Carbon dioxide			
CH ₃ C ¹⁴ OOH	0.07	0.15	0.20
C ¹⁴ H ₃ COOH	0.006	0.009	0.03

FOOTNOTES

- 1 This work was performed under the auspices of the Atomic Energy Commission.
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