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Synthesis of Products of Higher Molecular Weight in the Radiolysis of Aqueous Solutions of Formic Acid[1]

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INTRODUCTION

In an early paper on the action of X-rays on aquo-organic systems, Fricke *et al.* (*1*) reported a detailed study of the gaseous products formed in the radiolysis of aqueous solutions of formic acid. They found for oxygen-free solutions at pH 3 or below that product stoichiometry can be represented in terms of the net reaction

$$HCOOH \rightarrow H_2 + CO_2 \qquad\qquad (i)$$

over the concentration range 0.001 M to 0.05 M.

Above 0.05 M the specific yield of carbon dioxide increases, whereas the hydrogen yield remains essentially constant. The authors suggested that an additional over-all reaction, viz.,

$$2HCOOH \rightarrow HCHO + CO_2 + H_2O \qquad\qquad (ii)$$
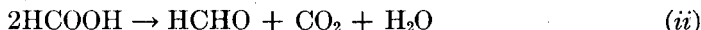
may be involved at the higher formic acid concentrations in the pH range below 3.

As the pH is increased above 3, the specific yields of both hydrogen and carbon dioxide decrease. Carbon dioxide decreases more rapidly than hydrogen, and at pH values above 7 only hydrogen is obtained. Fricke *et al.* pointed out that the simplest interpretation of this effect would be that oxalic acid is produced at the higher pH values, i.e.,

$$2HCOOH \rightarrow (COOH)_2 + H_2 \qquad\qquad (iii)$$
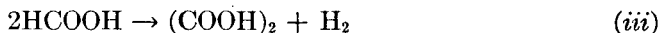
These early studies have recently been extended from the point of view of current radiation chemical theory. In a detailed study of the mechanism of indirect action in the γ-ray radiolysis of formic acid solutions, Hart (*2*) has described in-

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termediate free-radical processes that lead to the stoichiometric relationships given by equation *i*. He has also considered processes that are related to the net reaction *ii* (*3*).

We have observed that organic products in addition to those given by equations *i* to *iii* are formed in oxygen-free formic acid solutions by irradiation with cyclotron-produced helium ions at radiation doses that correspond to the removal of less than 1% of the formic acid initially present (*4*). The organic product fraction includes oxalic, glyoxylic, glycolic, tartronic, mesoxalic, and tartaric acids. These studies have since been continued as part of a more general investigation of mechanism in the radiolysis of aquo-organic systems. We describe herein our recent findings on the formic acid system and discuss the correlation of this work with the related literature.

EXPERIMENTAL PROCEDURE

Irradiation

The Crocker Laboratory 60-inch cyclotron was the radiation source. Irradiations were made with (1) 40-Mev helium ions, (2) 10-Mev protons, and (3) neutrons produced by bombardment of beryllium with 24-Mev deuterons.

The all-glass cells used in the charged-particle irradiations were of the tubular, aerated type previously described (*5*). In the present study, the target solutions (10 ml) were aerated with nitrogen (or helium) to exclude air and to effect mixing of products. Product yields obtained at beam intensities of 0.01 μamp and below were essentially independent of the gas flow rate at values above 40 cc/min. Details of the target assembly, beam monitoring circuits, and dosimetry methods have been given (*5, 6*).

In the neutron irradiations, the solutions (10 ml) were exposed in evacuated Pyrex tubes mounted uniformly in a motor-driven reel situated a standard distance from the beryllium target. The reel was rotated on a horizontal axis and was centered along the forward axis of the neutron beam. The cells were affixed in a canted position so that mixing of the contents occurred on rotation of the reel. One of the cells in each exposure contained a formic acid-oxygen dosimeter solution (*2*). This system for evaluating dose to dilute aqueous solutions under neutron irradiation has been described in detail elsewhere (*6, 7*).

Materials

Water from a Barnstead still was redistilled in Pyrex, first from alkaline permanganate solution and then from dilute phosphoric or sulfuric acid. Baker and Adamson reagent-grade formic acid was redistilled once. The $HC^{14}OOH$ and $(C^{14}OOH)_2$ were purified chromatographically on a silicic acid column (see below).

Analyses

Acids. The irradiated solutions were evaporated to dryness (*in vacuo*), and the nonvolatile products were investigated by application of methods of partition chromatography in which water adsorbed on silicic acid acts as the immobile phase. Column dimensions and techniques of manipulation were those given by Marvel and Rands (*8*). The developing liquid or eluant was made progressively more polar by adding increasing amounts of *n*-butyl alcohol to chloroform. Product peaks were located by titration and/or by C^{14} assay of measured fractions of the effluent.

The standard method of Bulen *et al.* (*9*) was used to obtain an initial separation of the nonvolatile acid products. The eluting solvents in sequence were 5, 15, 20, 25, 35, and 50 % (v/v) *n*-butyl alcohol in chloroform equilibrated with 0.5 *N* sulfuric acid. Several modifications of this general survey method were employed. These will be described from the standpoint of the particular analytical problem involved.

In the preliminary studies, 10-ml volumes of 0.25 *N* formic acid containing 100 to 200 μc of $HC^{14}OOH$ were irradiated with 40-Mev helium ions at a beam intensity of 0.01 μamp. The irradiated solutions were distilled to dryness, and the nonvolatile fraction was examined chromatographically by the standard survey method. Appropriate aliquots of each measured fraction of the effluent were evaporated to dryness in counting dishes and assayed for C^{14} activity. Four major activity peaks were observed at radiation doses as low as 1×10^{18} ev/ml of target solution. Tentative identification was made on the basis of a comparison of the peak activity positions with the published chromatographs of Bulen *et al.* (*9*). Samples of C^{14} activity from each fraction were then rechromatographed with milligram amounts of the indicated acid, and the correspondence between C^{14} activity and titer was determined. Various modifications of the standard elution procedure were used. The product activity peaks I to IV were subsequently shown to have the following composition: I, glyoxylic acid; II, oxalic acid plus glycolic acid; III, tartronic acid; IV, tartaric acid. Correspondence between C^{14} activity and titer of authentic acid was obtained in two or more different chromatographic procedures for each product. Typical co-chromatographs are shown in Figs. 1 to 4. The elution procedures are indicated in the legends.

In determining the quantitative yield data of Table I, known amounts (0.2 to 0.5 milliequivalent) of authentic acid corresponding to each of the identified products were added to the target solution immediately after irradiation. The solutions were distilled to dryness *in vacuo* and chromatographed by the standard survey procedure. The material in each of the peaks I to IV was combined and rechromatographed separately by the procedures in Figs. 1 to 4, respectively.
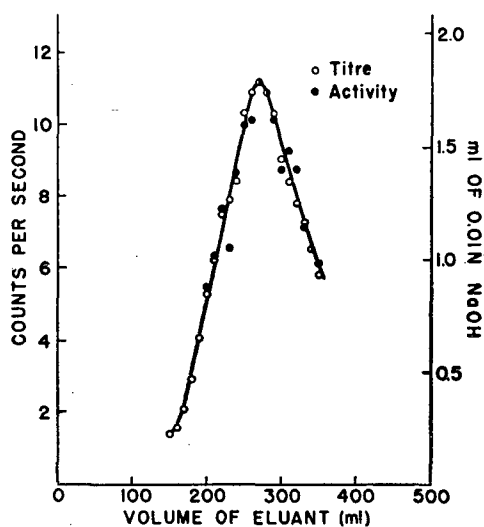
FIG. 1. Co-elution of authentic glyoxylic acid with C14 activity from fraction I. Eluant, 10% *n*-butyl alcohol–90% chloroform (v/v) saturated with 0.5 *M* sulfuric acid.
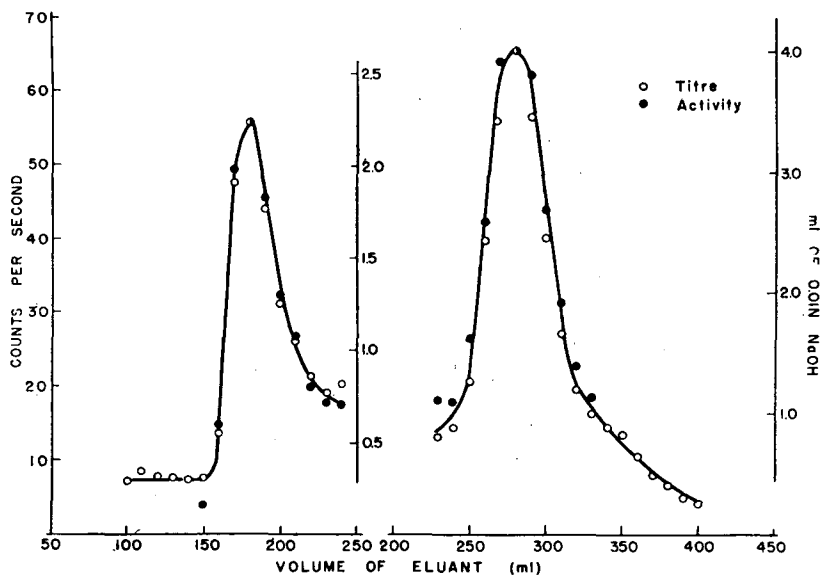

FIG. 2. Co-elution of authentic oxalic and glycolic acids with C14 activity from fraction II. Eluant, 25% isobutyl alcohol–75% chloroform saturated with 0.5 *M* sulfuric acid.
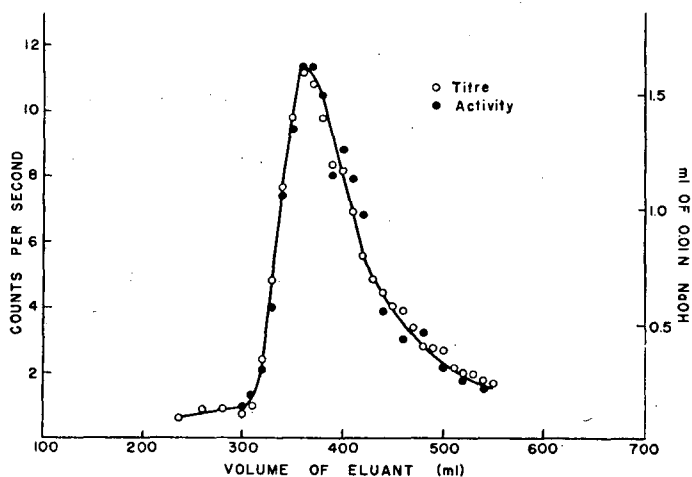
FIG. 3. Co-elution of authentic tartronic acid with C^{14} activity from fraction III. Eluant, 35% n-butyl alcohol–65% chloroform saturated with 0.5 M sulfuric acid.
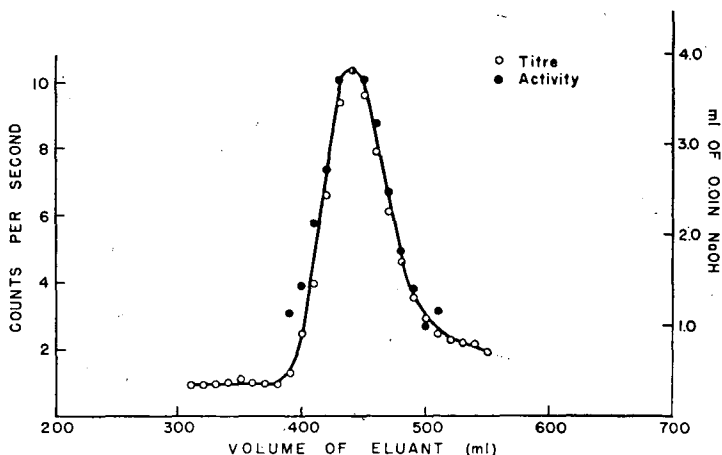
FIG. 4. Co-elution of authentic tartaric acid with C^{14} activity from fraction IV. Eluant, 50% isobutyl alcohol–50% chloroform.

Since the titer associated with the C^{14}-labeled products as formed in the target solution was negligible compared to the titer of the added carrier, G-values could be calculated directly on the basis of the specific activities of the formic acid and the separately recovered acid carriers. Control experiments showed that a constant specific activity for each acid was obtained after the series of two chromatographic separations.

TABLE I

SUMMARY OF YIELD DATA[a]

Run	Radiation	Solution	Dose		G						
			μahr	$ev/ml \times 10^{-19}$	$(COOH)_2$	$CHOCOOH$	$CH_2OHCOOH$	$CG(COOH)_2$	$CHOH(COOF)_2$	$(CHOHCOOH)_2$	H_2CO
H-1	He^{++}, 40 Mev	0.25 N HC^{14}OOH	0.00035	1.57	0.082	0.23	0.017	0.13	0.041	$\sim$0.006	<0.005
H-2	He^{++}, 40 Mev	0.25 N HC^{14}OOH	0.001	4.53	0.09	0.23	0.014	0.20	0.045	$\sim$0.004	<0.005
H-3	He^{++}, 40 Mev	0.025 N HC^{14}OOH	0.001	4.53	0.10	0.10	0.011	—	0.042	$\sim$0.003	<0.005
H-4	He^{++}, 40 Mev	0.25 N HC^{14}OOH +10^{-3} M (COOH)$_2$	0.001	4.53	0.11	0.18	0.03	0.11	0.035	$\sim$0.005	—
H-5	He^{++}, 40 Mev	0.25 N HCOOH +10^{-3} M (C^{14}OOH)$_2$	0.001	4.53	—	$\sim$0.006	<0.002	0.03	<0.004	—	—
P-1	H^{+}, 10 Mev	0.25 N HC^{14}OOH	0.0007	1.57	0.17	0.17	0.030	0.32	0.071	<0.003	<0.005
N-1	n, 10 Mev^{b}	0.25 N HC^{14}OOH	—	1.0	<0.01	0.04	<0.005	0.01	<0.005	<0.003	—
N-2	n, 10 Mev^{b}	0.25 N HC^{14}OONa	--	1.4	1.2	0.80	0.25	—	<0.01	<0.001	—

[a] Typical data are given for each condition. Duplicate runs were reproducible to within 10%.

[b] See footnotes b and c in Table II.

Carbonyls. Carbonyl products were identified in the form of the 2,4-dinitrophenylhydrazone derivatives. Since these derivatives can be readily detected visually in amounts as low as 10^{-6} mole, preliminary identification studies were made on irradiated formic acid solutions that did not contain added $HC^{14}OOH$. An aliquot of the target solution (previously treated with platinum black to remove hydrogen peroxide) was added to a 0.1 % solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid (10). Hydrazones and excess reagent were extracted quantitatively with chloroform and separated chromatographically on filter paper. The strips were sprayed with 10 % potassium hydroxide solution for increased sensitivity. Investigation of a number of different solvents as developing liquids showed that more than one chromatographic method would be required for complete separation of the product hydrazones. The following solvent systems were ultimately used in the separation and identification of the carbonyl products, formaldehyde, glyoxal, glyoxylic acid, and mesoxolic acid: method I, butanol saturated with 3 % aqueous ammonia; method II, heptane (pract.) saturated with methanol.

In method I, excess reagent and formaldehyde hydrazone are recovered at the solvent front. Glyoxal remains at the origin (with some streaking), and the carbonyl acid hydrazones are separated with intermediate R_f values. In method II, only formaldehyde hydrazone moves out of the origin (with an intermediate R_f). Excess reagent and the hydrazones of glyoxal and the carbonyl acids remain at the origin. Each of the separated product hydrazones was extracted from the paper with methanol and co-chromatographed with the authentic derivative. Product identification was confirmed in each case.

In determining the quantitative yield data of Table I, known amounts of the authentic carbonyl product compounds were added to irradiated formic acid solutions ($HC^{14}OOH$) and then treated with 2,4-dinitrophenylhydrazine reagent in excess. The resultant mixture was evaporated to dryness *in vacuo* to recover $HC^{14}OOH$. The residue containing C^{14}-labeled product hydrazones plus carriers was washed with "cold" formic acid and again evaporated to dryness. This residue was then extracted with 10 % sodium carbonate solution to remove glyoxylic acid and mesoxalic acid hydrazones (fraction A). The residue contained the formaldehyde and glyoxal derivatives (fraction B).

Fraction A, which also contained C^{14}-labeled organic acid products (glycolic acid, etc.), was acidified, evaporated to dryness, and chromatographed on a silicic acid column by the standard survey method previously described. The glyoxylic acid and mesoxalic acid hydrazones were recovered together in the "breakthrough" volume free of organic acid contamination. The carbonyl acid hydrazones were then separated chromatographically on filter paper sheets with the butanol-ammonia solvent. Formaldehyde separated from fraction B by methanol extraction was chromatographed with heptane-methanol.
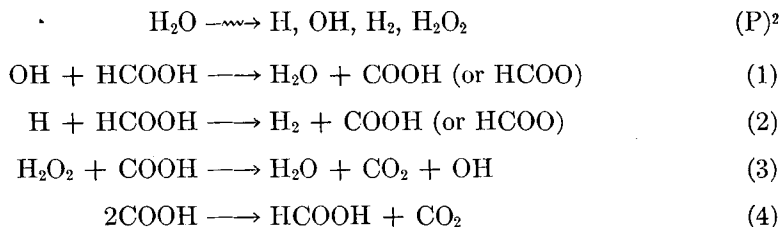
The specific activity of each of the separated hydrazone derivatives was then determined; the appropriate areas of the chromatograms were cut out and extracted with methanol. An aliquot of each solution was assayed for C^{14} activity and for total hydrazone. The latter was accomplished by mixing a sample of the methanol extract with a solution of 10 % potassium hydroxide in 80 % methanol-20 % water and measuring the optical density at the absorption maximum for the particular hydrazone in question (11). A separate calibration curve for each of the products was required. Yields were calculated from the specific activities of the initial target solution and the separately recovered hydrazones. Control experiments showed that the specific activities obtained after the above manipulations did not change when the entire sequence was repeated.

An adequate chromatographic method for separation and purification of glyoxal hydrazone could not be found. Many different solvents were tried. In all cases the glyoxal hydrazone remained at the origin or streaked badly. After repeated washings with the solvents used in methods I and II above, however, the glyoxal derivative retained appreciable C^{14} activity which appeared to approach a limiting value. The specific activity did not change appreciably on reprecipitation from pyridine-water mixtures. The glyoxal yield for helium ion irradiation (run H-1, Table I) was estimated at $G \sim 0.1$.
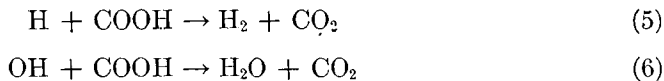
Peroxides. Hydrogen peroxide was determined by titration with ceric sulfate in the cold. Tests for organic peroxides were negative (12).

DISCUSSION

The γ-ray radiolysis of dilute, oxygen-free formic acid has been shown by Hart (2) to be in accord with the mechanism

$$H_2O \longrightarrow H, OH, H_2, H_2O_2 \tag{P}^2$$

$$OH + HCOOH \longrightarrow H_2O + COOH \text{ (or } HCOO) \tag{1}$$

$$H + HCOOH \longrightarrow H_2 + COOH \text{ (or } HCOO) \tag{2}$$

$$H_2O_2 + COOH \longrightarrow H_2O + CO_2 + OH \tag{3}$$

$$2COOH \longrightarrow HCOOH + CO_2 \tag{4}$$

The steps

$$H + COOH \rightarrow H_2 + CO_2 \tag{5}$$

$$OH + COOH \rightarrow H_2O + CO_2 \tag{6}$$

were included as an alternate for step 4. Hydrogen peroxide formed in the initial

[2] Following the notation of Dewhurst and Burton (13), we indicate the 100-ev yields of the initial products by $G_w(H)$, $G_v(OH)$, $G_w(H_2)$, and $G_w(H_2O_2)$; the yields of final products are denoted $G(\text{product})$.

reaction (P) is not observed as a net final product. Hart found that hydrogen peroxide is consumed in a chain reaction given by the sequence of steps 1, 3.

In considering the data of the present study in terms of the mechanism 1 to 6, we note first (Table II), that, whereas $G(H_2O_2)$ is, indeed, essentially zero for neutron irradiation, an appreciable yield of hydrogen peroxide is obtained in oxygen-free formic acid solutions irradiated with 10-Mev protons or 40-Mev helium ions. This effect is related to differences in effective dose rate. With neutrons, the entire sample volume was under continuous irradiation, and the solution was therefore uniformly exposed to the recoil nuclei formed in the processes of neutron attenuation. In the proton and helium ion runs, however, only a small fraction of the total target volume was instantaneously irradiated. This volume element (determined by the range of the particle and by the diameter of the beam aperture) was ~0.05 ml in the present study (see also reference 6). Under these conditions, even at beam intensities as low as 0.010 μamp, radical combination reactions (e.g., H + OH = H_2O, and reactions 4 to 6) compete effectively with the chain reaction given by the sequence 1, 3. In fact, the value[2] $G(H_2O_2) = 0.30$ obtained in the 10-Mev proton irradiation of oxygen-free formic acid (Table II) represents an appreciable fraction of the total molecular product yield for radiation of this quality. We recently measured (6) the free radical and molecular product yields for 10-Mev protons in the aqueous formic acid–oxygen dosimeter (2) and obtained the values $G_w(H_2O_2) \simeq G_w(H_2) \simeq 0.63$, $G_w(OH) \simeq G_w(H) \simeq 2.39$. In the same study (see also reference 7) we obtained the values $G_w(H_2O_2) \simeq G_w(H_2) \simeq 0.49$, $G_w(H) \simeq G_w(OH) \simeq 2.68$ for neutrons produced by bombardment of beryllium with 24-Mev deuterons under target conditions identical with those employed in the present study.

Comparison of the yield data for organic product formation given in Table I shows that it is only in the proton and helium ion irradiations that appreciable amounts of higher molecular weight products are formed in *acid* solutions. Processes

TABLE II

HYDROGEN PEROXIDE YIELDS IN THE RADIOLYSIS OF OXYGEN-FREE 0.25 N FORMIC ACID

Radiation	Energy (Mev)	Dose[a] (ev/ml $\times$ 10^{-19})	$G(H_2O_2)$
Neutrons	10[b]	~1.0[c]	<0.02
Protons	10	1.54	0.30 ± 0.02
Helium ions	40	1.54	0.42 ± 0.02

[a] Calculated in each case as total dose/total volume of irradiated solution.

[b] Produced by bombardment of beryllium with 24-Mev deuterons. The neutron spectrum had a population maximum at approximately 10 Mev. See reference 6.

[c] Based on measurements made with the formic acid–oxygen dosimeter (2). Use of this system for evaluating dose to dilute aqueous solutions under neutron irradiation is described in references 6 and 7.

in addition to reactions 1 to 6 are therefore operative in acid solutions under the conditions of charged-particle irradiation used in the present study.

In attempting to describe these processes we consider first the problem of deriving a mechanism for the formation of the two-carbon products, oxalic acid and glyoxylic acid. Now the simplest explanation for the formation of oxalic acid would appear at first hand to involve the dimerization reaction

$$2COOH \rightarrow (COOH)_2 \qquad (7)$$

On the basis of Hart's work, however, it is necessary to assume that, if COOH radicals are actually involved as long-lived intermediates, their removal must occur by disproportionation (i.e., by reactions 4 to 6) and not by dimerization. This conclusion is substantiated by our direct observation that oxalic acid is not produced in the neutron irradiation of 0.25 M HCOOH. We suggest, however, that oxalic acid could be produced via reaction 7 in the proton and helium ion irradiations if the COOH radical represents a first product of OH attack on the formic acid molecule but is relatively short-lived because of the reaction

$$COOH + HCOOH \rightarrow HCOOH + HCOO \qquad (8)$$

Reaction 7 would then be favored over reaction 8 at the higher dose rates obtained in the charged-particle irradiations. In the neutron irradiations (and under the conditions of γ-ray radiolysis employed by Hart) COOH would react preferentially via reaction 8, and the resultant HCOO radicals would undergo the disproportionation reaction 4.

In the initial phases of this study it seemed logical to assume that glyoxylic acid was formed as a secondary product through a reduction of oxalic acid, either in the bulk of the solution or in the "beam volume."

$$(COOH)_2 + H \rightarrow COCOOH + H_2O \qquad (9)$$

$$COCOOH + H \rightarrow CHOCOOH \qquad (10)$$

(or)

$$COCOOH + COOH \rightarrow CHOCOOH + CO_2 \qquad (10a)$$

If glyoxylic acid were being formed through reduction of oxalic acid in the bulk of the solution, a decrease in G for oxalic acid would be observed with increasing dose. Examination of the data for runs H-1 and H-2 (Table I) shows little change in G for oxalic acid over the dose range studied. Additional evidence against the occurrence of reactions 9 and 10 in the bulk of the solution is to be found in the results obtained on formic acid solutions containing added oxalic acid. Now in the typical run H-2, the oxalic acid concentration at the end of bombardment is approximately 2×10^{-4} M. Runs H-4 and H-5 show the results obtained on irradiation of the systems

$0.25 N HC^{14}OOH + 10^{-3} M (COOH)_2$, and $0.25 N HCOOH + 10^{-3} M (C^{14}OOH)_2$. Again note that only C^{14}-labeled products are measured in these systems. It is readily apparent from the data that a major fraction of the glyoxylic acid is not produced through reduction of oxalic acid in the bulk of the solution. We cannot conclude, however, from these studies that reduction of oxalic acid product (in systems containing no added oxalate) does not occur within the beam volume element. The instantaneous product concentration within this element may be considerably higher than the average product concentration in the bulk of the solution.[3] If such is the case, the observed yields could be essentially independent of total dose over a range of values.

Note, however, that these considerations regarding the formation of glyoxylic acid through reduction of oxalic acid are based on the assumption that oxalic acid is indeed formed as a primary product. As mentioned earlier, this would seem to require a dose rate-dependent reaction sequence such as that given by steps 7, 8. At the present time we cannot distinguish this possibility from a second reaction path, which (1) would yield glyoxylic acid as a primary product and (2) could also be dose rate-dependent. This path can be written

$$H + HCOOH \rightarrow HCO + H_2O \tag{11}$$
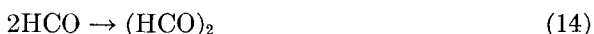
$$HCO + COOH \rightarrow CHOCOOH \tag{12}$$
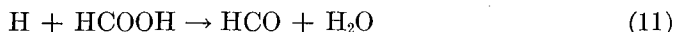
Now, the main point here is that, if HCO were formed via reaction 11, some evidence of the HCO intermediate should be found in the products of both neutron and charged-particle irradiation. It should appear as glyoxylic acid (reaction 12), as formaldehyde:
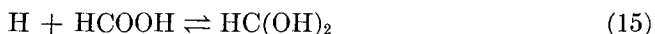
$$HCO + HCOOH \rightarrow H_2CO + COOH \tag{13}$$

(or)

$$HCO + COOH \rightarrow H_2CO + CO_2 \tag{13a}$$
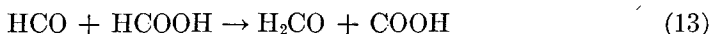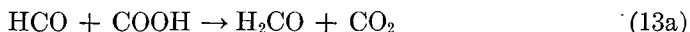
or possibly as glyoxal:

$$2HCO \rightarrow (HCO)_2 \tag{14}$$

The fact is, however, that appreciable net reduction is observed only in the charged-particle irradiations. This apparent anomaly can be resolved if for reaction 11 we write

$$H + HCOOH \rightleftharpoons HC(OH)_2 \tag{15}$$

[3] The beam of the Crocker Laboratory 60-inch cyclotron has a repetition time of 12 megacycles per second with a duty cycle of approximately 0.05. Superimposed on this is a second modulation with a repetition time of 360 cycles per second with a duty cycle of about 0.5.

i.e., assume that H adds reversibly to the formic acid molecule. The $HC(OH)_2$ radicals could then combine with COOH to give glyoxylic acid:

$$HC(OH)_2 + COOH \rightarrow CHOCOOH + H_2O \tag{16}$$

(or dimerize to glyoxal) at the high radical concentrations obtained in the charged-particle irradiations. In the neutron (or γ-ray) irradiations, the radical concentrations are lower, and H would be removed preferentially to form hydrogen via step 2.[4]

As regards the formation of glycolic, mesoxalic, tartronic, and tartaric acids in the charged-particle irradiations, we observe first that G-values in each case are essentially independent of total dose, at least within the range covered by runs H-1 and H-2.[5] This suggests, as previously noted in the discussion on oxalic and glyoxylic acid formation, that reactions responsible for these higher products also occur principally within the beam volume. Reactions of the following type are proposed for the formation of the hydroxy acids:

$$CHOCOOH + H \rightarrow CHOHCOOH \tag{17}$$

$$CHOHCOOH + COOH \rightarrow CH_2OHCOOH + CO_2 \tag{18}$$

$$CHOHCOOH + COOH \rightarrow CHOH(COOH)_2 \tag{18a}$$

$$2CHOHCOOH \rightarrow (CHOHCOOH)_2 \tag{19}$$

Similarly, mesoxalic acid is written as derived from oxalic acid via

$$(COOH)_2 + H \rightarrow COCOOH + H_2O \tag{20}$$

$$COCOOH + COOH \rightarrow CO(COOH)_2 \tag{21}$$

Only limited data on alkaline solutions have been obtained. Neutron irradiation of sodium formate solutions (pH $\sim$12) produces oxalic acid as a major product (run N-2). Glyoxylic and glycolic acids are also formed. Synthesis of products of higher molecular weight in alkaline solution is not therefore related to effects of dose rate. The simplest explanation for the formation of oxalate would seem to involve the assumption that the relative rates of reactions 4, 7 are pH-dependent. The presence of glyoxylic and glycolic acids indicates either that the over-all reaction is more complicated than that proposed or that secondary reactions involving oxalate are important in 0.25 N sodium formate at oxalate concentrations as low as 10^{-4} M.

SUMMARY

Irradiation of dilute, oxygen-free formic acid solutions with cyclotron-produced protons or helium ions leads to the synthesis of a number of products of higher

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[4] This is equivalent to saying that the intermediate $HC(OH)_2$ either decomposes to H_2 + COOH or combines with COOH, depending on the radical concentration.

[5] This situation changes at higher doses. For example, the tartronic acid yield increases from the value $G = 0.045$ at a helium ion dose of 0.001 μahr (run H-2) to $G = 0.14$ at 0.010 μahr.

molecular weight. The compounds identified include oxalic, glyoxylic, glycolic, mesoxalic, tartronic, and tartaric acids, and glyoxal. These products are not formed in appreciable yield by neutron (and γ-ray) irradiation. The observations are correlated in terms of a reaction mechanism that involves dose rate-dependent steps.

ACKNOWLEDGMENTS

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