[CONTRIBUTION FROM THE CROCKER LABORATORY, RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Indirect and Direct Action of Heavy Particle Radiation on Acetic Acid in Aqueous Solution[1,2]

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Chemical reactions induced by heavy-particle irradiation of acetic acid–water mixtures in the concentration range 0.0625 to 16 *M* have been studied. The principal products formed in dilute, oxygen-free acetic acid solutions at radiation doses below 5×10^{20} e.v./ml. are hydrogen, hydrogen peroxide and succinic acid. Carbon dioxide, methane, ethane and carbon monoxide are also produced. The radiation yields of all products increase with acetic acid concentration in the range 0.0625 to 1.0 *M*. With increasing acetic acid concentration above 1.0 *M* a continuous decrease in *G* values for hydrogen, hydrogen peroxide and succinic acid is observed. Values for the latter two products decrease essentially to zero in 16 *M* acetic acid. Radiation yields of carbon dioxide, methane, ethane and carbon monoxide, however, increase continuously with acetic acid concentration. With the exception of ethane, *G* values for these products show a linear dependency on acetic acid concentration. Mechanisms are proposed for both the indirect and direct action of radiation on the acetic acid molecule.

Introduction

Investigation of the chemical effects of ionizing radiation on aquoörganic systems has been largely restricted to studies of dilute aqueous solutions in which it may be assumed that radiation energy is absorbed exclusively by water molecules. Under these conditions, chemical changes in the solute occur *via* an indirect action of radiation which is generally attributed to the formation of the chemically reactive H and OH free radicals.[3] Such studies of aqueous solutions containing organic solutes at low concentration have provided basic information on the elementary processes involved in the decomposition of water by radiation and have, at the same time for a number of systems, established detailed mechanisms for the chemical changes induced by reaction of H and OH radicals with dissolved organic material. These results have, in turn, provided both a qualitative and quantitative basis for the interpretation of various radiation biological effects.[4] Of significance also in the elucidation of these phenomena are radiation studies of aquoörganic systems in which an appreciable fraction of the radiation energy is absorbed by direct interaction with the organic component. Radiation studies of such systems are of interest, not only because information on the radiation chemistry of a particular mixture is obtained, but also, and of more general significance, because an additional source of information on the nature of the elementary radiation processes occurring both in water and in organic compounds is made available.

It was on the basis of these considerations that the present radiation study of acetic acid–water mixtures was initiated. Previous work in this Laboratory has shown[5] that succinic acid is the principal product of the indirect radiation chemical action induced in dilute acetic acid solutions by 35-Mev. helium ion irradiation at radiation doses below 5×10^{20} e.v./ml. Carbon dioxide and methane were found to be minor products from dilute solutions and to increase in yield with increasing acetic acid concentration. This earlier work, which involved primarily the identification of radiation products, indicated that the acetic acid–water system would be suitable for a quantitative study of the indirect and direct action of radiation on the organic component of an aquoörganic system. In the present work we are concerned with the nature of the radiation chemical processes involved in the formation of products in acetic acid–water mixtures over the concentration range 0.0625 to 16 *M*. The 60-inch Cyclotron at the Crocker Laboratory was used as the radiation source. Irradiations were made with helium ions and deuterons having energies of 35 and 18 Mev., respectively.

Experimental

The solutions were irradiated in all-glass target cells of a type previously described.[5a,b] The cells consisted essentially of a 250-ml. erlenmeyer flask sealed at the neck and drawn in on one side approximately 1 cm. from the bottom to give a "window" with an average thickness of from 3 to 5 mils over the irradiated area. A 10-mm. side-arm was sealed to the flask about 3 cm. above the normal liquid level. To it was connected a break-off seal for the removal of gases after irradiation. In a typical run, 105 ml. of target solution was pipetted into the cell through the side arm which was then constricted above the break-off and sealed to a vacuum manifold. A Hyvac pump in series with a carbon dioxide trap was used in the evacuation which was continued until a characteristically sharp metallic "click" could be detected when the cell was shaken. The cell was then sealed off at the constriction and irradiated. Approximately 5 ml. of liquid distilled from the cell during the degassing operation. After irradiation, the cell was again sealed to the manifold through the break-off and the target gases were transferred through a carbon dioxide trap to a gas buret by means of a Toepler pump arrangement. After the total gas volume was measured, a sample was withdrawn into a gas bulb for subsequent mass spectrometric analysis.[6] The cell was then cut from the manifold, an aliquot of the measured target volume was set aside for peroxide determinations, and the remaining solution was frozen and stored for later analysis.

During irradiation, the cell was mounted in a jig which could be rapidly vibrated along the axis of the cyclotron beam by an eccentric. The motor and shaft which drove this device were electrically isolated from the target. The jig was supported by a bracket which was attached in turn to our standard target shutter assembly. Details of the target assembly, the beam monitoring circuits and the bom-

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[2] Presented before the Division of Physical Chemistry, 126th Meeting of the American Chemical Society, New York, N. Y., September 12–17, 1954.

[3] See, for example (a) D. E. Lea, "Actions of Radiation on Living Cells," The Macmillan Co., New York, N. Y., 1947; (b) "Radiation Chemistry," *Discs. Faraday Soc.*, **12**, 1ff. (1952); (c) "Symposium on Radiation Chemistry of Aqueous Solutions," *Radiation Res.*, **1**, 1ff. (1954).

[4] *Cf.* ref. 3a also "Basic Mechanisms in Radiobiology," Natl. Res. Coun. Pub. No. 305, 1953.

[5] (a) W. M. Garrison, H. R. Haymond, D. C. Morrison and B. M. Weeks, THIS JOURNAL, **75**, 2459 (1953); (b) W. M. Garrison, H. R. Haymond and B. M. Weeks, *Radiation Res.*, **1**, 97 (1954).

[6] We are indebted to Dr. Amos Newton for the mass spectrometric data.

bardment procedure have been described in detail elsewhere.[5a,b] Absorption measurements in aluminum gave a calculated mean energy of 40.2 Mev. for the "naked" helium ion beam. A calorimetric method, to be reported,[7] gave an average beam energy of 40.1 Mev. The energy of the "naked" deuteron beam is one-half this value. Energy degradation in the 1 mil aluminum cyclotron-window, in the glass cell window, and in the air space between was calculated from theoretical range-energy data.[8] Because of small differences in window thickness between target cells, the energy of helium ions and deuterons absorbed in the solution varied somewhat (<3%) from 35 and 18 Mev., respectively, depending on the particular cell window used. The energy absorbed in the solution was calculated separately for each cell. With 35 Mev. helium ions, a dose of 0.100 microampere hour in a volume of 100 ml. gives an energy dissipation of 3.94×10^{20} e.v./ml. The corresponding value for 18 Mev. deuterons is 4.05×10^{20} e.v./ml.

Analytical methods employed in the determination of certain of the non-gaseous products were essentially those used in previous studies[5a,b]: (1) hydrogen peroxide and peracetic acid were determined separately using the method of Greenspan and MacKellar[9] which is based on the observation that hydrogen peroxide, unlike peracetic acid, can be titrated quantitatively with ceric sulfate–sulfuric acid solution in the cold. Peracetic acid is then reduced with excess potassium iodide, and the iodine is titrated with standard thiosulfate. (2) The non-volatile succinic acid fraction, separated by evaporation of the target solution *in vacuo* at room temperature, was analyzed using the method of partition chromatography reported by Marvel and Rands.[10] Water adsorbed on silicic acid acts as the immobile phase. The eluant is made progressively more polar in order to develop the more water-soluble acids. This is accomplished by adding increasing amounts of *n*-butyl alcohol to chloroform. In the present study, the effluent was collected in measured 10-ml. fractions which were titrated to the phenolphthalein endpoint with 0.01 *N* sodium hydroxide.

Carbonyl compounds were identified in the form of the 2,4-dinitrophenylhydrazone derivative. These were prepared by the method of Iddles and Jackson[11] from an aliquot of the target solution which had been previously treated with platinum black to remove hydrogen peroxide. The phenylhydrazones, which in the above procedure are formed in a 2 *N* hydrochloric acid solution containing 0.05% phenylhydrazine were extracted with chloroform and separated by a method of filter paper chromatography based on a procedure reported by Meigh.[12] Comparison of R_f values obtained for derivatives isolated from targets and for authentic 2,4-dinitrophenylhydrazones showed that acetone and acetaldehyde are the only carbonyl compounds formed in the irradiation of oxygen-free acetic acid. In 16 *M* acetic acid, the carbonyl fraction is principally acetone. In 4 *M* solutions, as estimated from the appearance of the chromatograms, the acetone/acetaldehyde ratio is approximately three. The total carbonyl concentration in irradiated solutions was determined by the method of Lappin and Clark[13] in which the optical density of a basic methanolic solution of the 2,4-dinitrophenylhydrazones is measured at 480 mμ. Both the absorption maximum and the extinction coefficient are independent of the structure and concentration of the carbonyl compound. *G* values for total carbonyl in 4 and 16 *M* acetic acid were found to be 0.25 and 1.10, respectively.

In separate experiments,[14] it was found that glycolic acid, if formed in low yield, may not be recovered in the non-volatile acid fraction. A colorimetric method developed by Calkins[15] was used to test for glycolic acid in the target solution. Aldehydes and ketones which interfere were removed by forming the 2,4-dinitrophenylhydrazone derivatives and extracting both the reagent and the derivatives with ethyl acetate. Control and blank runs showed that glycolic acid is not produced with a *G* value greater than 0.05 in the helium ion irradiation of oxygen-free 0.25 *M* acetic acid.

Water from a Barnstead still, redistilled in Pyrex from alkaline permanganate, was used in the preparation of the target solutions. Baker and Adamson reagent grade glacial acetic acid was redistilled twice; the middle fraction (approximately 30%) was retained each time. Merck reagent grade 30% hydrogen peroxide was steam distilled using doubly distilled water. Baker and Adamson reagent grade iodine and hydrogen iodide were used without further purification.

Results and Discussion

The preliminary chemical effects of radiation absorption in water and in dilute aqueous solution have been represented[16] by the two reactions

$$2H_2O \rightsquigarrow H_2 + H_2O_2 \qquad (1)$$

$$H_2O \rightsquigarrow H + OH \qquad (2)$$

The relative rates of reactions 1 and 2 are determined by the ionization density properties of the effective radiation. Recently,[17] a third primary

$$2H_2O \rightsquigarrow 2H + H_2O_2 \qquad (3)$$

reaction has been proposed to account for the fact that H_2 and H_2O_2 may not be formed in equal amounts in the primary radiation process. In the absence of added solute, H and OH radicals react with H_2O_2 and H_2, respectively, by the chain back reaction[16b]

$$H + H_2O_2 \longrightarrow H_2O + OH \qquad (4)$$

$$OH + H_2 \longrightarrow H_2O + H \qquad (5)$$

If a reactive solute is present, all of the H and OH formed in the primary process may be removed by competing reactions involving the added solute species. In dilute acetic acid solution, the radical reactions result in the production of succinic acid. Figure 1 shows radiation yields obtained in the present study for succinic acid, hydrogen and hydrogen peroxide over the acetic acid concentration range 0.0625 to 16 *M*. Figure 2 shows the corresponding yield data for gaseous products derived from acetic acid. The formation of succinic acid is attributed to the reactions[5a]

$$OH + CH_3COOH \longrightarrow CH_2COOH + H_2O \qquad (6)$$

$$H + CH_3COOH \longrightarrow CH_2COOH + H_2 \qquad (7)$$

$$2CH_2COOH \longrightarrow COOHCH_2CH_2COOH \qquad (8)$$

Evidence that 7 contributes to the production of succinic acid has been obtained from isotopic analysis of hydrogen produced in the irradiation of dilute solutions of acetic acid in D_2O. The results are compared in Table I with corresponding data obtained with H_2O solvent. Although the relative product yields in the two solutions would not be expected to be identical because of possible isotope effects, the fact that HD accounts for over 35% of product hydrogen in the D_2O case may be taken as evidence for the occurrence of 7.

As the acetic acid concentration is increased from 0.0625 *M*, it is seen in Fig. 1 that the radiation

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[7] B. M. Weeks, Ph.D. Thesis, to be published.

[8] (a) W. A. Aron, B. G. Hoffman and F. C. Williams, AECU, 663 (1949); (b) B. Rossi and B. Jones, private communication.

[9] F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

[10] C. S. Marvel and R. D. Rands, Jr., THIS JOURNAL, **72**, 2642 (1950).

[11] H. A. Iddles and C. E. Jackson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 454 (1934).

[12] D. F. Meigh, *Nature*, **170**, 579 (1952).

[13] G. R. Lappin and L. C. Clark, *Anal. Chem.*, **23**, 541 (1951).

[14] H. R. Haymond, Ph.D. Thesis, UCRL-2697, 1954.

[15] V. P. Calkins, *Ind. Eng. Chem., Anal. Ed.*, **15**, 762 (1943).

[16] (a) A. O. Allen, *J. Phys. Colloid Chem.*, **52**, 479 (1948); (b) A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *ibid.*, **56**, 575 (1952).

[17] (a) F. S. Dainton and H. C. Sutton, *Trans. Faraday Soc.*, **49**, 1011 (1953); (b) A. O. Allen, *Radiation Res.*, **1**, 85 (1954).

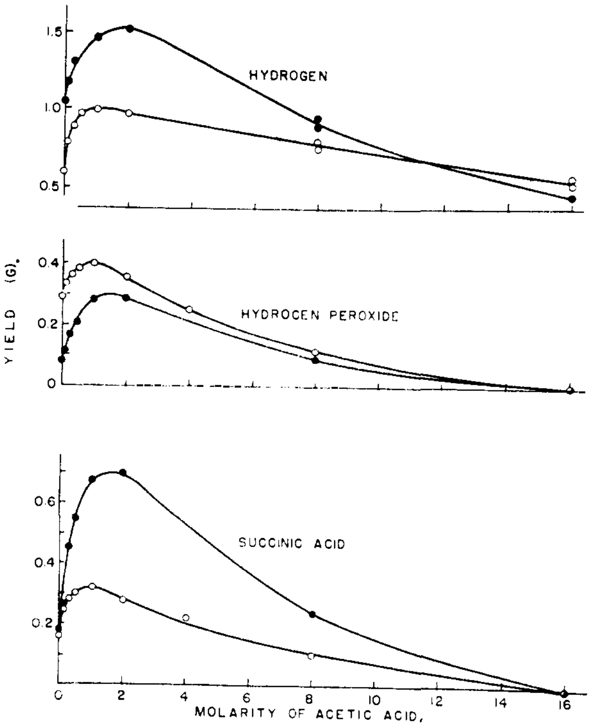

Fig. 1.—Effect of acetic acid concentration on the production of hydrogen, hydrogen peroxide and succinic acid: O, 35 Mev. helium ions; ●, 18 Mev. deuterons; beam current, 0.2 microampere; dose, 0.100 microampere hours; target volume, 100 ml.

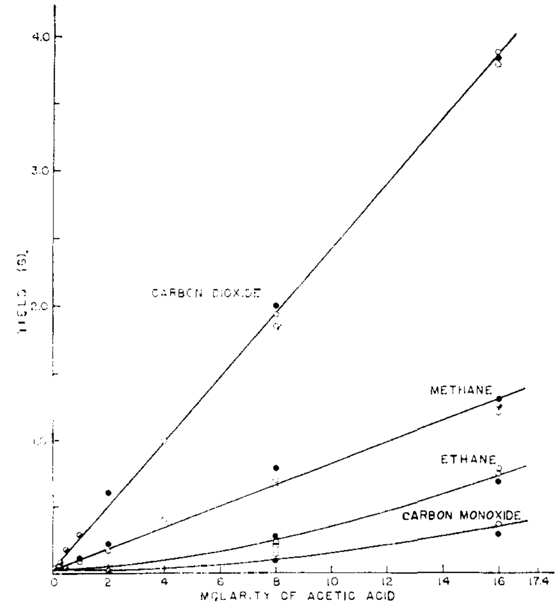

Fig. 2.—Effect of acetic acid concentration on the production of carbon dioxide, methane, ethane and carbon monoxide: O, 35 Mev. helium ions; ●, 18 Mev. deuterons; bombardment conditions, as indicated in Fig. 1.

TABLE I

COMPARISON OF RADIATION YIELDS[a] IN D_2O AND H_2O SOLUTIONS OF 0.25 *M* ACETIC ACID

Radiation, 35 Mev. helium ions; beam current, 0.2 microampere; dose, 0.100 microampere hour; target volume, 100 ml.

		Radiation yield, *G*			
		D_2O solutions[b]		H_2O solutions	
		Expt. 9–28	Expt. 10–24	Expt. 7–13	Expt. 5–8
Hydrogen	H_2	<0.005	<0.005	1.02	0.96
	HD	.26	.25	. .	. .
	D_2	.65	.70	. .	. .
Hydrogen peroxide		.35	.37	0.33	.34
Succinic acid		.27	.28	.32	.28
Carbon dioxide		.13	.13	.14	.10

[a] Radiation yields (*G*) are expressed as molecules of product per 100 e.v. of absorbed energy. [b] The D_2O was obtained from the Radiation Laboratory Bio-Organic Group through the courtesy of Dr. B. Tolbert; the hydrogen content was greater than 99 atom % D.

yields of hydrogen, hydrogen peroxide and succinic acid increase and reach a limiting value at an acetic acid concentration of from 1.0 to 2.0 *M*. These results may be interpreted on the assumption that the number of radicals involved in 4,5 decrease as the competing reactions 6,7 become more important at the higher acetic acid concentrations. The limiting *G* values observed in the 1.0 to 2.0 *M* solutions correspond to the case in which a maximum number of H and OH radicals are utilized in the net production of CH_2COOH radicals *via* 6 and 7. A larger limiting value for G_S and G_{H_2} and a lower value for $G_{H_2O_2}$ is obtained in the deuteron case in accordance with the observation that the relative number of water molecules decomposing *via* 1 as compared to 2 increases with specific ionization of the effective radiation.

Although the reactions 1 to 6 adequately describe the main qualitative features of the observed indirect action of cyclotron accelerated heavy particle radiation on acetic acid solutions at concentrations up to approximately 1 *M*, consideration of product yield in terms of recent measurements of *G* for water decomposition by other types of ionizing radiation does not indicate complete radical removal by reactions 6 and 7. It has been shown elsewhere[17b,18] that the total number of water molecules decomposed *via* 1 and 2 per 100 e.v. corresponds to a G_{H_2O} of 3.2 to 3.8 regardless of the energy or the type of the ionizing particle. Ionization density determines only the relative importance of 1 and 2. Therefore, if all available OH and H radicals were removed by reactions 6 and 7, respectively, it is obvious that higher *G* values for hydrogen and succinic acid would be observed with both the helium ion and deuteron beam regardless of the relative rates of reactions 1 and 2 in each case. The fact that the observed yields increase with acetic acid concentration and reach limiting values which do not correspond to those anticipated on the basis of complete radical removal *via* 6 and 7 indicates that back reactions are involved or that products other than those shown in Fig. 1 are formed by concurrent reactions. In a 1 *M* acetic acid solution less than 5% of the radiation energy is absorbed by direct interaction with the solute, so that the processes responsible for the low over-all yields at this concentration remain predominantly those arising as a consequence of radiation absorption in water. Since, as shown in Fig. 3, the amounts of hydrogen, hydrogen peroxide and succinic acid formed in 1 *M*

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(18) E. J. Hart, *Radiation Res.*, **1**, 53 (1954).

acetic acid are proportional to radiation dosage, it is assumed that removal of H and OH by reaction 4,5 and removal of CH_2COOH by reactions other than 8, *e.g.*, by reactions with hydrogen peroxide, are not major factors in determining the magnitude of the maximum observed values of G_{H_2}, $G_{H_2O_2}$ and G_S. That the low yields cannot be attributed to a product concentration gradient in the irradiation zone has been shown in previous studies[5b] of succinic acid production in acetic acid solutions. Irradiation of 1 *M* acetic acid in the standard "vibrating" target gave *G* values for succinic acid in close agreement with those obtained in a similar target in which a glass stirrer was rotated at 1700 r.p.m. directly behind the irradiation zone.

The above considerations regarding radiation yields may be correlated in part on the assumption that the radical combination reaction

$$H + CH_2COOH \longrightarrow CH_3COOH \qquad (9)$$

and less probably, as will be indicated in a following paragraph, the reaction

$$H + CH_3COO \longrightarrow CH_3COOH \qquad (10)$$

occur at the high radical concentration obtained under the conditions of cyclotron irradiation employed in the present study. If it is assumed that the rate of the OH reactions with acetic acid to give CH_2COOH is greater than the corresponding H reactions, it would appear probable that reaction 9, which may be assumed to have essentially zero activation energy, may occur within the beam volume element and would not be greatly dependent on the rate of flow of solution through the irradiation zone, at least within the range of flow rates attainable with present target design. Since an effect of beam intensity would be anticipated on the basis of a radical recombination reaction such as 9, a recently available low-current beam monitoring circuit is now being used in a study of product yields from dilute acetic acid at beam intensities 10^{-2} times those of the present work.

In evaluating other possible processes which may be operative in the radiolysis of dilute acetic acid solution, we consider briefly the evidence for OH reaction with acetic acid to give intermediates in addition to CH_2COOH. In recent studies[19] of oxidation of organic substances by Fenton's reagent, in which case OH radicals are formed by the Haber–Weiss mechanism $Fe^{+2} + H_2O_2 = FeOH^{+2} + OH$, it has been proposed that OH reacts with acetic acid to form the acetate radical

$$OH + CH_3COOH \longrightarrow CH_3COO + H_2O \qquad (6a)$$

Reaction 6a from an energetic point of view is apparently[20] as probable as reaction 6 which yields CH_2COOH. However, if CH_3COO radicals are formed by 6a, they cannot be involved in any secondary reaction which results in their decomposition to give carbon dioxide. This conclusion follows from the fact that the carbon dioxide yields are linearly dependent on the acetic acid concentration. Of the possible CH_3COO reactions, in addition to 10, only 10a can be eliminated unequivocally on the basis of experimental evidence obtained in the present study.

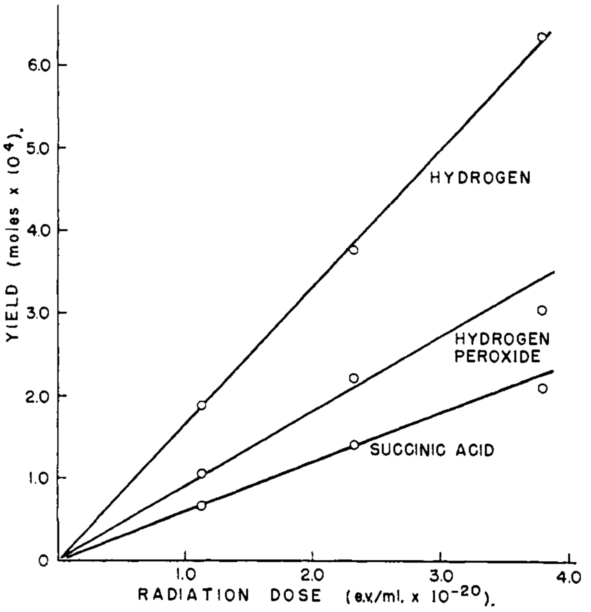

Fig. 3.—Production of hydrogen, hydrogen peroxide and succinic acid in 0.25 *M* acetic acid as a function of radiation dose: radiation, 35 Mev. helium ions; bombardment conditions, as indicated in Fig. 1.

$$CH_3COO + CH_2COOH \longrightarrow CH_3COOCH_2COOH \qquad (10a)$$

$$2CH_3COO \longrightarrow (CH_3CO)_2O_2 \qquad (10b)$$

$$CH_3COO + CH_3COOH \longrightarrow CH_3COOH + CH_2COOH \qquad (10c)$$

The production of acetylglycolic acid (CH_3COOCH_2COOH), a high boiling compound, was not observed in the chromatographic analysis of the non-volatile acid fraction nor was its hydrolysis product, glycolic acid,[21] detected in any of the target solutions. If reaction 10b occurs, hydrolysis of the acetyl peroxide would result in the production of peracetic acid. No organic peroxides were found by analytical procedures known to detect acetyl peroxide and peracetic acid in amounts equivalent in the present study to a *G* value of greater than 0.01. The possibility that acetyl peroxide and/or peracetic acid are formed but are present at low stationary state concentrations as a consequence of the reactions

$$(CH_3CO)_2O_2 + H \longrightarrow CH_3COOH + CH_3COO$$

$$CH_3CO_2OH + H \longrightarrow CH_3COO + H_2O$$

cannot, however, be eliminated on the basis of the present data. The absence of a *p*H effect in the production of succinic acid as shown in Table II indicates either that (a) the acetate ion and the undissociated acetic acid molecule are equally effective in the removal of OH radicals if attack occurs both at the carboxyl group and at the methyl group, or that (b) OH attack occurs preferentially at the methyl group or, less likely, as indicated above, at the carboxyl group in which case the CH_2COOH radicals would be formed *via* reaction 10c.

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[19] (a) I. M. Kolthoff and A. I. Medalia, THIS JOURNAL, **71**, 3777 (1949); (b) **71**, 3784 (1949).

[20] (a) F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins University Press, Baltimore, 1935; (b) N. Uri, *Chem. Revs.*, **50**, 375 (1952).

[21] G. Senter and T. S. Ward, *J. Chem. Soc.*, **101**, 2538 (1912).

TABLE II

EFFECT OF *p*H ON RADIATION YIELDS[a] IN 0.25 *M* ACETIC ACID SOLUTIONS

Radiation, 35 Mev. helium ions; beam current, 0.2 microampere; dose, 0.100 microampere hour; target volume, 100 ml.

	Radiation yield, *G* *p*H 1	5	9	11
Hydrogen	1.20	1.05	0.98	1.0
Hydrogen peroxide[b]	0.38	0.21	.04	0.03
Succinic acid	.30	.37	.43	.40
Carbon dioxide[c]	.14			.18
Methane	.04	.04	.04	.04

[a] Radiation yields (*G*) are expressed as molecules of product per 100 e.v. of absorbed energy. [b] The low peroxide yields in alkaline solutions have been found to result from a "dark" reaction which does not form succinic acid or carbon dioxide. [c] The carbon dioxide yield reported for the solution at *p*H 11 represents the amount of product recovered after the solution was acidified in a closed system; carbon dioxide values at *p*H 5 and 9 were not measured.

In regard to the reactions of H with acetic acid other than 7, the data of Table I on HD formation in D_2O solutions of acetic acid together with the discussion above concerning evidence for CH_3CO_2 formation indicate that the reaction

$$CH_3COOH + H \longrightarrow CH_3CO_2 + H_2 \qquad (7a)$$

is unimportant as a competing process for H removal. The reaction

$$H + CH_3COOH \longrightarrow CH_4 + COOH \qquad (7b)$$

cannot occur because it would result in the formation of methane as a principal product of indirect action in dilute acetic acid solution. The reaction of H with acetic acid *via*

$$CH_3COOH + H \longrightarrow CH_3C(OH)_2 \qquad (7c)$$

can also be excluded as a major competing process for H removal on the basis of data obtained some years ago in a study of gaseous products formed by the action of X-rays on dilute aqueous solutions of a number of organic substances.[22] In the case of acetic acid, it was found that the hydrogen yield increased with acetic acid concentration and approached a limiting value corresponding approximately to that which would be expected[18] on the assumption that all H atoms formed in the primary radiation process react with acetic acid to form hydrogen. Dosage rates in the present study are, however, in the order of 10^2 times those used in obtaining the above X-ray data.

The observed decrease in the radiation yield of succinic acid, hydrogen and hydrogen peroxide with increasing acetic acid concentration above 1 *M* is attributed in part to the fact that a decreasing fraction of the total absorbed energy is dissipated *via* reactions 1, 2 and 3. The relationship between acetic acid concentration and the radiation yield of carbon dioxide, methane, ethane and carbon monoxide as seen in Fig. 2 can be accounted for on the basis that these products are formed principally by reactions induced by direct interaction of radiation with acetic acid molecules over the entire concentration range of from 0.0625 to 16 *M*. Almost identical *G* values for these products were obtained with 35 Mev. helium ions and with 18 Mev. deuterons. Examination of Fig. 2 also shows that the combined yield of carboxyl carbon as carbon dioxide plus carbon monoxide is greater than the yield of methyl carbon as methane and ethane. This difference in 16 *M* acetic acid corresponds to a *G* of 1.5. It is apparent from this relationship that non-gaseous products also are formed. Both acetone and acetaldehyde have been identified by chromatographic separation of the 2,4-dinitrophenylhydrazone derivatives and by mass spectrometric analysis[6] of a volatile sample which was separated from an irradiated solution by fractional distillation.

To obtain additional information on the nature of the elementary processes involved in the formation of products by direct action of radiation on acetic acid in acetic acid–water mixtures, irradiations were made of acetic acid solutions containing iodine and iodine plus hydrogen iodide. Iodine is known to react with certain radicals *via* displacement reactions of the type $R + I_2 = RI + I$,[23] while iodide is effective in "quenching" other radical reactions by the process $R + I^- = R^- + I$.[16] Data for 16 *M* acetic acid solutions containing iodine and iodine plus hydrogen iodide are shown in Fig. 4. Irradiation conditions were identical with those used in obtaining the data of Fig. 2. In Fig. 4, it is seen that both methane and ethane yields decrease with increasing iodine concentration, and level off at an iodine value of approximately 0.02 *M*. An increase in iodine concentration up to the limiting solubility value of 0.05 *M* does not result in further decrease. The carbon dioxide and hydrogen yields are relatively unaffected. The effects of 0.25 *M* hydrogen iodide plus iodine from 0.10 to 0.25 *M* shown in Fig. 4 indicate only a small additional effect of hydrogen iodide on carbon dioxide production from 16 *M* acetic acid. The effects of hydrogen iodide plus iodine (0.25 *M* HI, 0.10 *M* I_2) on product yields over the entire acetic acid concentration range 0.0625 to 16 *M* are shown in Figs. 5 and 6. The dotted lines represent the corresponding data of Fig. 2. The carbon dioxide values remain essentially unchanged except for a small decrease at the higher acetic acid concentration. The methane yield dependency on acetic acid concentration remains linear, although the slope of the yield-concentration curve is decreased by about 50%. Ethane production is strongly quenched, particularly in dilute acetic acid solutions, while carbon monoxide yields are unaffected over the entire acetic acid concentration range. Succinic acid is not produced in these solutions at any acetic acid concentration.

Although the chemical action of radiation in dilute solution can be described adequately in terms of free radical processes, it becomes necessary in evaluating the mechanism of radiation induced reaction at the higher acetic acid concentrations to consider the possible contributions of shorter-lived ionic species formed from both water and acetic acid molecules. In the case of liquid water, it has been proposed[3a,16b] that H and OH

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[22] H. Fricke, E. J. Hart and H. P. Smith, *J. Chem. Phys.*, **6**, 229 (1938).

[23] (a) W. H. Hamill and R. H. Schuler, THIS JOURNAL, **73**, 3466 (1951); (b) R. C. Petry and R. H. Schuler, *ibid.*, **75**, 3792 (1953).

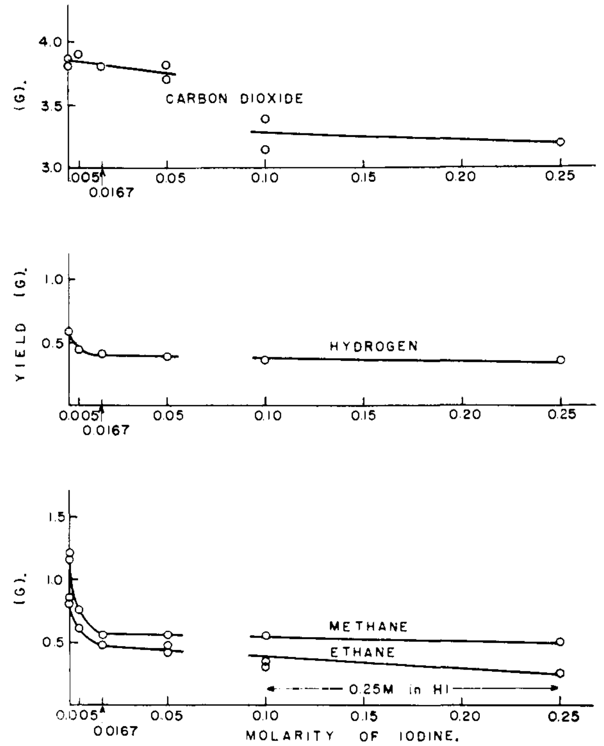

Fig. 4.—Effect of iodine and iodine plus hydrogen iodide on product yields in 16 *M* acetic acid: radiation, 35 Mev. helium ions; bombardment conditions, as indicated in Fig. 1.

are formed from ionic intermediates by the reactions

$$H_2O \rightsquigarrow H_2O^+ + e^- \quad (11)$$

$$H_2O^+ \longrightarrow H^+ + OH \quad (12)$$

$$e^- + H_2O \longrightarrow H + OH^- \quad (13)$$

where reaction 11 represents the primary ionization act. Reactions 12 and 13 are assumed to proceed in liquid water by utilizing the hydration energy of H^+ and OH^- ions. The electron formed in 11 is considered to be captured by a neutral water molecule *via* 13 at some distance from the parent ion. It has been pointed out that since hydration furnishes the necessary dissociation energy for 12 and 13, these processes can occur only as quickly as the water dipoles can orient to form the hydration layer.[24] The relaxation time for dipole orientation in water is 10^{-11} second, and it is presumed that this value represents a minimum time for the occurrence of 12. It has been estimated that reaction of the "solvated" electron *via* 13 may require as long as 10^{-9} second.[24a] These considerations indicate that reactions of electrons and H_2O^+ ions with solute may be of increasing importance in the most concentrated solutions. Recently, however, it has been proposed[24b,25] that in a condensed phase the coulomb field of the parent ion is strong enough to prevent escape of the ejected electron, and that the electrons produced simultaneously with the ions M^+ are recaptured within 10^{-13} second to give the reaction

$$M^+ + e^- \longrightarrow M^* \quad (14)$$

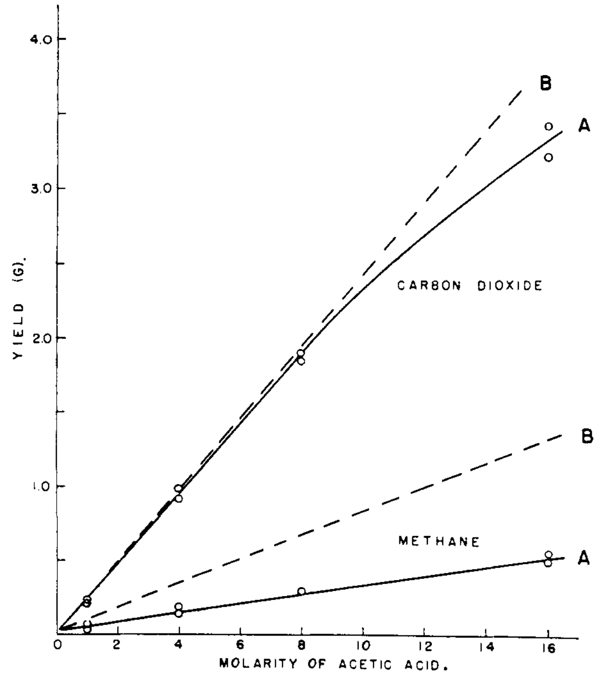

Fig. 5.—Effect of iodine plus hydrogen iodide on the production of carbon dioxide and methane in acetic acid solutions 0.0625 to 16 *M*: radiation, 35 Mev. helium ions; bombardment conditions, as indicated in Fig. 1 (A), 0.1 *M* I_2 + 0.25 *M* HI; (B) data from Fig. 2.

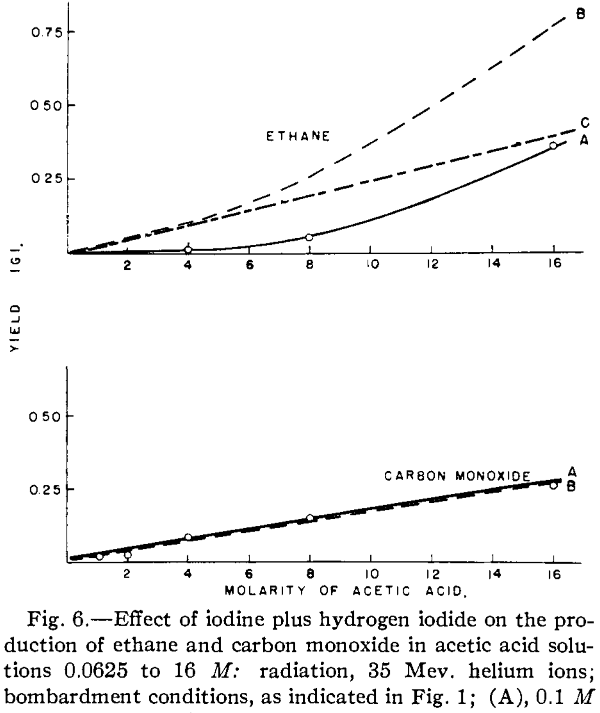

Fig. 6.—Effect of iodine plus hydrogen iodide on the production of ethane and carbon monoxide in acetic acid solutions 0.0625 to 16 *M*: radiation, 35 Mev. helium ions; bombardment conditions, as indicated in Fig. 1; (A), 0.1 *M* I_2 + 0.25 *M* HI; (B) data from Fig. 2; (C), (B)-(A).

If the latter model is correct, radiation effects in many systems may originate from excited molecules produced in the primary absorption act and in the recombination processes represented by 14. In the case of water, radical formation may occur predominantly *via*

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[24] (a) R. L. Platzman, ref. 4, Part II; (b) H. A. Dewhurst, A. H. Samuel and J. L. Magee, ref. 3c, p. 62.

[25] M. Burton, J. L. Magee and A. H. Samuel, *J. Chem. Phys.*, **20**, 760 (1952).

$$H_2O^* \longrightarrow H + OH \qquad (15)$$

rather than by reactions 12,13.

In dilute aqueous solutions, the principal consequences of radical production by 12,13 as compared to 15 would be in the difference in spatial distribution of H and OH along the particle track.[24a] Radical formation by each mechanism would occur in dilute solution before charged intermediates could react with solute molecules. In concentrated solution, however, the possibility of solute molecules reacting with ionic intermediates becomes an important consideration. It is particularly of interest in the case of aquoörganic mixtures, since reactions of the type A + H and A + e are less likely to form identical products if A is an organic rather than an inorganic substance. A similar situation exists for the possible reactions A + H_2O^+ and A + OH.

Possible electron capture processes involving acetic acid include

$$\begin{aligned} CH_3COOH + e^- &\longrightarrow CH_3CO_2^- + H \qquad (16)\\ &\longrightarrow CH_3CO + OH^- \qquad (16a)\end{aligned}$$

If H atoms are formed by reaction of electrons with acetic acid molecules *via* 16, much higher *G* values for hydrogen would be observed in concentrated acid solutions in view of the fact that H has been shown to react with acetic acid by hydrogen abstraction. The possibility that 16a competes with the electron capture processes 13 above cannot be disregarded on the basis of evidence obtained in the present study. However, since diacetyl is not produced at any acetic acid concentration, the CH_3CO radical, if formed by 16a or by any dissociation reaction, must be removed by a process other than dimerization. In regard to the reaction of H_2O^+ with acetic acid, it is concluded on the basis of the observed linear dependency of carbon dioxide and methane yields on acetic acid concentration, that charge transfer is not involved in the formation of the major gaseous products derived from acetic acid.

Mass spectrometric evidence as to the nature of the intermediate charged species formed by direct action of radiation on the acetic acid molecule indicates that the processes 17, 17a and 17b occur in acetic acid vapor at low pressures with about an equal probability and account for a major fraction of the observed charged fragments

$$\begin{aligned} CH_3COOH &\rightsquigarrow CH_3COOH^+ + e^- \qquad (17)\\ &\rightsquigarrow CH_3 + COOH^+ + e^- \qquad (17a)\\ &\rightsquigarrow CH_3CO^+ + OH + e^- \qquad (17b)\end{aligned}$$

In a recent discussion[26] of mass spectrometric data from the radiation chemical viewpoint, it has been pointed out that in the irradiation of a condensed as compared to an attenuated gas, energy goes with high probability to yield the lowest excited and ionized states. Process 17 may, therefore, be assumed to be favored over 17a and 17b in solution. In considering the possible subsequent reactions or intermediate ionic species formed in 17, 17a and 17b, it has been assumed in the absence of any specific evidence for charge transfer reactions as described in the preceding section, that ejected electrons are recaptured by the molecule ion or ion fragment and that the chemically reactive intermediates are excited molecules and free radicals. It is from this viewpoint that the following discussion of direct action is presented.

The fact that the methane yield dependency on acetic acid concentration remains linear with the addition of iodine and cannot be decreased below a minimum value with increasing iodine concentration indicates that methane, in iodine-free solutions, is formed by two different reactions, each of which has a rate directly proportional to the acetic acid concentration. The data also show that one of these reactions is quenched by the addition of iodine without, at the same time, effecting the carbon dioxide yields. Since only moderate concentrations of iodine (0.02 *M*) are required, it may be assumed that the iodine-quenched reactions occur in the bulk of the solution. In considering a mechanism for methane production from the standpoint of possible radical reactions which can be quenched by iodine, it is to be noted that methane cannot be formed by reaction of H with acetic acid since, as previously mentioned, methane would then appear as a product of indirect action. Furthermore, since H atoms react with acetic acid to form H_2 and the CH_2COOH radical, it follows that the reaction of H with CH_3CO_2 in the bulk of the solution would not contribute appreciably to the methane yield. The experimental requirement for a free radical mechanism for the methane production which is quenched by iodine would appear, therefore, to involve the formation of methyl radicals either by a process such as 17a or by the process

$$CH_3COOH^* \longrightarrow CH_3 + COOH \qquad (18)$$

In the absence of iodine, to obtain the observed acetic acid concentration dependency, it is necessary that all of the methyl radicals formed in reaction 18 or possibly 17a, yield methane. However, if dissociation of acetic acid molecules to give methyl radicals occurs within a particle track, it must be presumed that as the acetic acid concentration is increased, the composition of the radical environment changes so that the combination of methyl radicals to form ethane

$$2CH_3 \longrightarrow C_2H_6 \qquad (19)$$

would be increasingly favored at the higher acetic acid concentration. No such effect of concentration on methane or ethane yields is observed. Although the ethane yield plot of Fig. 2 shows a greater than first power dependency on the acetic acid concentration, a corresponding decrease in methane at the higher acetic acid concentrations is not observed. Furthermore, comparison of the *G* values for ethane in Figs. 2 and 6 shows that the ethane production which is quenched by iodine is directly proportional to the acetic acid concentration. It is concluded, therefore, that the methane, which is quenched by iodine, does not arise from methyl radicals formed within the track environment. This would exclude reaction 17a and all other reactions which produce methyl radicals within an initial inhomogeneous distribution. Methyl radicals may, however, be produced *via* 18 through the predissociation of an excited acetic acid molecule of sufficiently long life so that dissociation may be assumed to occur outside the particle

(26) S. Gordon and M. Burton, ref. 3b, p. 88.

track. Without attempting to establish a detailed mechanism, it is seen that the experimental requirements for a free radical mechanism are met if each of the CH_3 and COOH radicals produced *via* 18 yield methane and carbon dioxide respectively, *i.e.*

$$CH_3 + RH \longrightarrow CH_4 + R \qquad (20)$$

$$R + COOH \longrightarrow RH + CO_2 \qquad (21)$$

Iodine would prevent methane formation *via* 20 without influencing carbon dioxide yields on the basis of the competing reactions

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (20a)$$

$$COOH + I_2 \longrightarrow CO_2 + HI + I \qquad (21a)$$

Methane production which is not quenched by iodine is accounted for by the ultimate molecule decomposition

$$CH_3COOH^{\ddagger} \longrightarrow CH_4 + CO_2 \qquad (22)$$

It is to be noted that a reaction scheme formally analogous to the above sequence may be obtained on the assumption that 22 occurs and that the excited acetic acid species, CH_3COOH^*, predissociates in the bulk of the solution to give

$$CH_3COOH^* \longrightarrow CH_4 + CO_2 \qquad (18a)$$

or reacts in the presence of iodine according to

$$CH_3COOH^* + I_2 \longrightarrow CO_2 + \text{products } (CH_3I + HI) \qquad (18b)$$

Ethane, as indicated in the above discussion of methane production, is apparently not produced by combination of methyl radicals. Although ethane may be formed by the reactions

$$CH_3COOH^* \longrightarrow CH_3CO_2 + H \qquad (18c)$$

$$2CH_3CO_2 \longrightarrow C_2H_6 + 2CO_2 \qquad (23)$$

evidence against the occurrence of 23 in the bulk of the solution is to be found in the fact that ethane yields from 16 *M* acetic acid are not quenched by the addition of 0.25 *M* hydrogen iodide. Iodide would be expected to react with CH_3CO_2 according to the reaction

$$CH_3CO_2 + I^- \longrightarrow CH_3CO_2^- + I$$

Ethane production which is not quenched by the addition of iodine may, however, be accounted for by the formation of CH_3CO_2 within the track volume. If ethane is formed in the bulk of the solution through a reaction of the type

$$CH_3COOH^* + CH_3COOH \longrightarrow C_2H_6 + \text{products} \qquad (18d)$$

and is quenched by reaction 18b, it is to be noted that other reactions which are proposed for CH_3COOH^* must be considered collision induced processes in order that the observed requirements regarding concentration dependencies may be met.

The fact that the carbon dioxide yields are proportional to acetic acid concentration and are not influenced by the addition of iodine indicates that this product is formed directly in a primary process or is formed from an intermediate which yields carbon dioxide both in the presence and absence of iodine. These requirements are met by either of the reaction schemes proposed for the production of methane. It cannot, however, be concluded that these reactions are the only ones involved in the production of carbon dioxide since the combined yield of carboxyl carbon as carbon dioxide plus carbon monoxide is greater than the yield of methyl carbon as methane and ethane. Acetone is the only observed product which has a methyl–carbon, carboxyl–carbon ratio greater than that of acetic acid. In 16 *M* acetic acid the difference $(G_{CO_2} + G_{CO}) - (G_{CH_4} + G_{C_2H_6})$ is approximately 1.5. The estimated acetone yield at this same concentration is greater than 1.0, so that the major part of the above difference can be accounted for by the stoichiometry

$$2CH_3COOH = CH_3COCH_3 + CO_2 + H_2O$$

Although the most obvious mechanism for acetone production involves the combination of methyl and acetyl radicals

$$CH_3 + CH_3CO \longrightarrow CH_3COCH_3 \qquad (24)$$

it may be seen on the basis of previous considerations of methane and ethane production in terms of reactions involving methyl radicals that it is unlikely that 24 occurs within the radical environment of the track or in the bulk of the solution. Other mechanisms for acetone formation also have been considered, *e.g.*

$$CH_3CO + CH_3COOH \longrightarrow CH_3COCH_3 + COOH$$

$$CH_3CO + CH_2COOH \longrightarrow CH_3COCH_3 + CO_2$$

$$CH_3COOH^* + CH_3COOH \longrightarrow CH_3COCH_3 + CO_2 + H_2O$$

Additional data, however, are needed for further discussion of these processes. It is anticipated that photochemical and radiation chemical studies now in progress will provide the information required to establish a mechanism for the production of acetone in irradiated acetic acid.

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