High Energy Helium Ion Irradiation of Aqueous Acetic Acid Solutions[1,2]

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A study has been made of products formed in solutions of acetic acid by reactions resulting from irradiation with cyclotron-produced helium ions having an energy of 35 Mev. The non-gaseous products are principally dibasic and tribasic acids. Succinic acid is the main product at radiation doses below 1×10^{20} ev./ml. Tricarballylic, malonic, malic and citric acids in addition to succinic acid are produced at the higher dose levels. A proposed mechanism accounts for the quantitative observations at the lower dose levels.

According to present concepts[3-8] of the mechanism of radiation-induced reactions in dilute aqueous solutions, the primary chemical effect of radiation is the dissociation, by ionization and excitation, of water molecules to give hydrogen atoms and hydroxyl radicals. The observed chemical changes in irradiated solutions are attributed to subsequent reactions of the H and OH radicals with one another and with solute molecules. The relative amounts of those radicals that combine to form H_2 and H_2O_2 and of those that react with a particular solute depend upon the specific ionization density of the effective radiation. Most of the radicals formed along the track of a fast electron, e.g., in regions of low ion density, diffuse into the bulk of the solution and are available for reaction with solute molecules. In regions of high ion density, e.g., in heavy particle tracks, radicals are formed locally in high concentration. Under these conditions many of the H and OH radicals are not subsequently available for reaction with dissolved organic material because they combine to form H_2 and H_2O_2 before they have time to diffuse into the bulk of the solution.[4]

By reason of the fundamental relationships between ionization density and radiation yield in chemical and biological systems,[4,8,9] it has seemed desirable to us to investigate the qualitative and quantitative effects of heavy particle radiation on aqueous solutions containing organic solutes, particularly those of possible biological interest, and to establish the dependence of the observed effects upon the type of particle and its energy. The present paper[10] reports a study of products formed in dilute aqueous acetic acid solution by irradiation with high-energy helium ions from the 60-inch cyclotron at the Crocker Laboratory. The greater part of this study was directed toward the problems associated with the separation, identification and quantitative determination of the non-gaseous products. Some indication of the possible nature of this fraction is suggested in studies of the effects of X-rays on aqueous acetic acid published several years ago by Fricke, Hart and Smith.[11,12] They suggested on the basis of indirect evidence obtained from gas analytical data and from pH measurements that succinic or glycolic acid could be the principal non-gaseous product. No direct chemical evidence was reported. In the present work a detailed investigation of non-volatile acid products was undertaken. Recently developed methods of partition chromatography on silicic acid columns were extensively employed. Product identification was greatly facilitated by the addition of CH_3C^{14}-OOH to the target solutions.

Experimental

Two different types of all-glass target cells were used in studies involving the identification and yield determination of non-volatile products. Cell no. 1 had a solution capacity of approximately 10 ml. One side of the cell was drawn in to give a window which had an average thickness of 3 mil over the bombarded area. A stream of gas (oxygen or helium) was forced through a fritted-glass disc to stir the solution during irradiation and to control the oxygen concentration in the bulk of the solution. Cell no. 1 was supported in a bracket which was attached through a snout to the target shutter assembly shown in Fig. 1. Quantitative yield data were obtained using cell no. 2 which had a solution capacity of approximately 80 ml. Oxygen or helium was passed through an inlet during irradiation. The replaceable glass windows had an average thickness of from 1 to 3 mil and were supported in a standard-taper joint which was an integral part of the cell and in turn fitted over the tapered metal snout of the target shutter assembly.

An expanded diagram of the target shutter assembly is shown in Fig. 1. The cyclotron beam entered the front plate (1) and was delimited by the water-cooled aperture (2). The defined beam then passed through a 1 mil aluminum foil (4) which was retained in position by the plate (3) and the shutter arrangement (5, 5a). The irradiation period could be accurately controlled by the shutter (5b). The beam monitoring circuit is shown schematically. The maximum error in beam current measurement was ±0.3%.

The energy of the helium ion beam was evaluated from range-energy relationships and from calorimetric data. Absorption measurements in aluminum gave a calculated[13,14] value of 40.2 Mev. for the mean energy of the "naked" helium ion beam. The calorimetric method, to be reported in detail elsewhere, gave an average beam energy of 40.4 Mev. Energy degradation in the aluminum window (4), in the cell window, and in the air space between was calculated from theoretical range-energy data.[13,14]

(1) Presented before the Division of Physical Chemistry, 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September 14–19, 1952.

(2) The work reported in this paper was performed under Contract No. W-7405-eng-48-A for the Atomic Energy Commission.

(3) J. Weiss, Nature, 153, 748 (1944).

(4) (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); (c) E. R. Johnson and A. O. Allen, THIS JOURNAL, 74, 4147 (1952).

(5) E. J. Hart, ibid., 73, 68 (1951); J. Phys. Chem., 56, 594 (1952).

(6) F. S. Dainton, ibid., 52, 490 (1948).

(7) J. L. Magee and M. Burton, THIS JOURNAL, 73, 523 (1951).

(8) J. L. Magee, ibid., 73, 3270 (1951).

(9) D. E. Lea, Brit. J. Radiol. Suppl., 1, 59 (1947); "Actions of Radiation on Living Cells," Cambridge University Press, London, 1946.

(10) See also: (a) W. M. Garrison and G. K. Rollefson, Discussions Faraday Soc., 12, 155 (1952); (b) W. M. Garrison, D. C. Morrison, H. R. Haymond and J. G. Hamilton, THIS JOURNAL, 74, 4216 (1952).

(11) H. Fricke and E. J. Hart, J. Chem. Phys., 2, 824 (1934).

(12) H. Fricke, E. J. Hart and H. P. Smith, ibid., 6, 229 (1938).

(13) W. A. Aron, B. G. Hoffman and F. C. Williams, AECU-663 (1949).

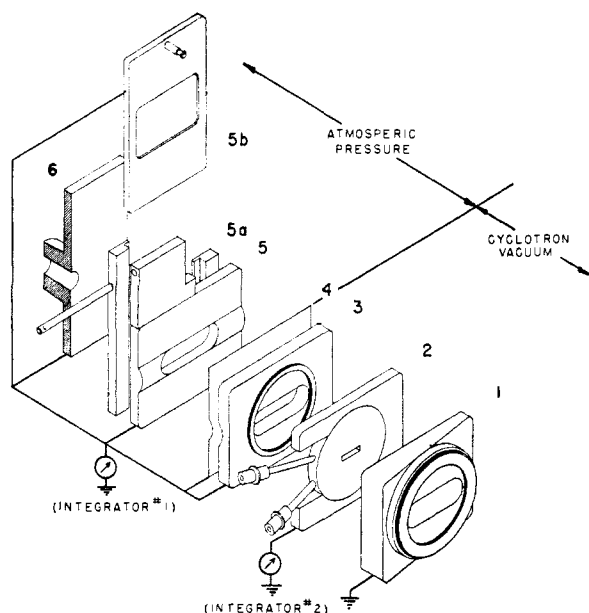(14) B. Rossi and B. Jones, private communication.

Fig. 1.—Target shutter assembly and beam monitoring circuit.

Hydrogen peroxide and organic peroxides were determined separately using a modification of the method of Greenspan and MacKellar[15] which is based on the observation that hydrogen peroxide, unlike organic peracids and hydroperoxides, is oxidized at temperatures from 0 to 10° by ceric sulfate. Organic peroxides are then reduced with potassium iodide in excess and the solution is titrated with standard thiosulfate. In the present study, an aliquot of the target solution was added to an equal volume of 6 N sulfuric acid and the resultant solution was titrated in the cold with 0.01 N ceric sulfate-1.0 N sulfuric acid solution to the ferroin end-point. Potassium iodide was then added in excess and the solution was titrated with 0.01 N sodium thiosulfate; in no case did the thiosulfate titer amount to more than 0.05 ml. Control analysis of simulated target solutions containing acetic acid, hydrogen peroxide and peracetic acid were reproducible to within ±1%.

Separation and identification of acid products was accomplished by application of recently developed methods of partition chromatography.[16-18] The column dimensions and methods of column preparation in the present work were a duplication of those developed by Marvel and Rands.[16] The developing liquids had the following composition:

1, chloroform
2, 5% n-BuOH–95% CHCl₃ v./v.   9, 50% n-BuOH–50% CHCl₃ v./v.
3, 10%   90%   10, 70%   30%
4, 15%   85%   11, 80%   20%
5, 20%   80%   12, 85%   15%
6, 25%   75%   13, 90%   10%
7, 30%   70%   14, 95%   5%
8, 40%   60%   15, 100%   0

Several different solvent sequences were employed depending upon the particular analytical problem involved. Unless otherwise stated, the solvents listed below were water saturated. Method A is essentially the standard separation procedure reported by Marvel and Rands.[16]

Method A, 100 ml. each solvents 1 through 10; B, 20 ml. each solvents 1 through 7, 100 ml. each solvents 8 through 10; C, 20 ml. each solvents 1 through 7, 100 ml. each solvents 8 through 10, 20 ml. each solvents 11 through 15; D, 20 ml. each solvents 1 through 4, 100 ml. each solvents 5 through 8; E, 20 ml. each solvents 1 through 3, 100 ml.

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

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

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

(18) A. C. Neish, *Can. J. Research*, **B27**, 6 (1949).

each solvents 4 through 6; F, 100 ml. each solvents 5 through 7; G, 100 ml. each solvents 1, 3, 5, 7, 8 and 9; all solvents saturated with 0.5 N hydrochloric acid; H, 350 ml. 35% n-butanol–65% chloroform saturated with 0.5 N hydrochloric acid; I, 400 ml. 25% n-butanol–75% benzene saturated with 0.1 N hydrochloric 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. The CH_3-$C^{14}OOH$ was prepared from the sodium salt by distillation *in vacuo* from phosphoric acid solution.[19]

Results and Discussion

In preliminary studies, 80-ml. volumes of 0.25 M acetic acid containing from 150 to 200 microcuries of $CH_3C^{14}OOH$ were irradiated in cell no. 2 with 35 Mev. helium ions at a beam intensity of 1.0 microamperes. Oxygen was bubbled through the solutions during exposure. After irradiation, the target solutions were distilled to dryness *in vacuo* at room temperature. The non-volatile fraction was dissolved in 2–3 ml. of butanol and chromatographed using method A which was employed as the general survey method in the present work. A 1-ml. aliquot of each 10 ml. of the effluent was evaporated to dryness in a porcelain dish under a heat lamp and assayed for C^{14} activity. The top curve in Fig. 2 shows a typical elution curve for a total dose of 44.6 × 10^{20} ev./ml. The lower curve in Fig. 2 gives the corresponding titers obtained by titrating with 0.02 N sodium hydroxide the remaining 9 ml. of each 10-ml. eluant volume. The similarities between the two curves shown in Fig. 2 indicate that the C^{14} activity corresponds to labeled non-volatile acids produced in the bombardment. At lower radiation doses fewer product peaks were observed. Below a dose of 1 × 10^{20} ev./ml., peak (I) only appeared.
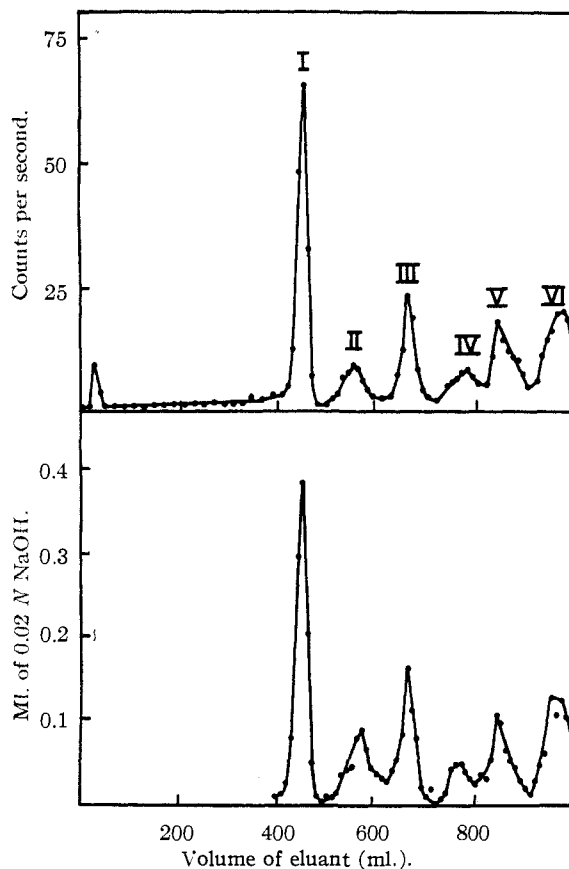

Fig. 2.—Chromatographic separation of non-volatile fractions: method A; radiation dose, 44.6 × 10^{20} ev./ml.

Acids corresponding to peaks (I) and (III) were the main products in the dose range of 1×10^{20} ev./ml. to approximately 10×10^{20} ev./ml. Above this level all of the peaks seen in Fig. 2 were present in the elution curves. For the identification studies reported below products in peaks (I) through (VI) of higher specific activity were obtained by irradiating, in cell no. 2, 10-ml. volumes of 0.25 M acetic acid solution containing 250 to 300 microcuries of CH_3C^{14}-OOH. In this way it was possible to isolate the product peaks in amounts which gave C^{14} counting rates of several hundred counts per second and a titer of less than 0.01 ml. with 0.01 N sodium hydroxide.

A sample of C^{14} activity associated with (I) was co-chromatographed with added authentic succinic acid using method E. An exact correspondence of C^{14} activity and titer was obtained. A second sample of (I) was co-chromatographed with authentic succinic acid using method G. Exact correspondence between activity and titer was again obtained. These data are summarized in Fig. 3. Milligram amounts of (I) were subsequently isolated from 500 ml. of 0.25 M acetic acid solution which received a total bombardment of 40×10^{20} ev./ml. After two recrystallizations from ether (I) melted at 182–184°. A mixture of (I) and authentic succinic acid melted at 182–184°.
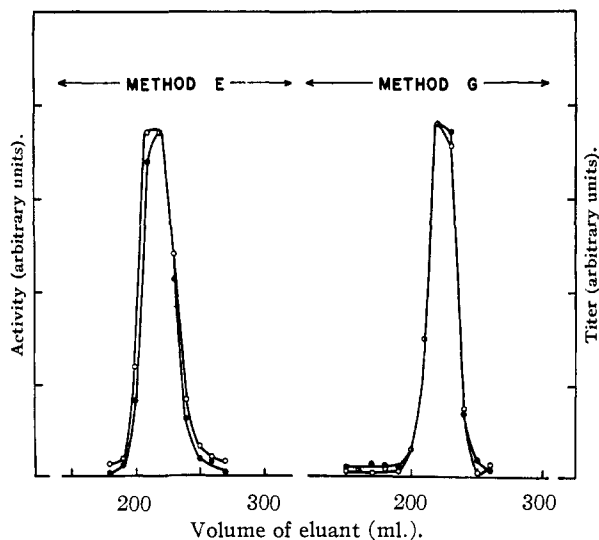

Fig. 3.—Co-elution of fraction I with authentic succinic acid: O, activity; ●, titer.

Fraction (III) was originally suspected of being glycolic acid. An aliquot of C^{14} activity in (III), however, did not co-elute with added authentic glycolic acid using chromatographic method A. Subsequent work showed (III) to be tricarballylic acid. A correspondence of activity and titer was obtained in co-chromatographs of (III) with authentic tricarballylic acid using three different methods of partition chromatography as shown in Fig. 4.

Fractions (II), (V) and (VI) were found to contain malonic, malic and citric acid, respectively. Only those methods used in the isolation and identification of malonic acid in (II) will be presented in detail because the results obtained were essentially duplicated in the identification of malic and citric acids using similar procedures. Because the peak effluent volume of (II) corresponded approximately with that reported for malonic acid, a sample of C^{14} activity from (II) was co-chromato-

graphed with authentic malonic acid using method A. The elution curve is shown in Fig. 5. Similar curves were obtained for (V) with malic acid and for (VI) with citric acid using methods B and C, respectively. The small displacement in the relative position of the titer and activity curves shown in Fig. 5 was found to be a result of the fact that (II) contains several as yet unidentified acids which co-elute with malonic acid when chromatographic method A is used. This may be observed in Fig. 6 which shows an elution curve obtained by co-chromatographing a sample of (II) with added malonic acid using method G. Part of the C^{14} activity associated with (II) is seen to correspond with malonic acid. A sample of this fraction (II-1) was then chromatographed using method F. The correspondence of activity and titer is shown in Fig. 7. Peaks (V) and (VI) were both fractionated using method H and each was found to contain several acids in addition to malic and citric as indicated above. In subsequent work it was possible to separate malonic acid in milligram amounts from (II) by fractional crystallization from ether–benzene mixtures. Identification was based on melting point and mixed melting point determinations. The isolated product (II-1) melted at 132–133°. A mixture of (II-1) with authentic malonic acid melted at 132.5–134°. Aniline and p-toluidine salts of (II-1) were prepared and these showed no depression in melting point when mixed with authentic material.

Cell no. 2 was used for the quantitative studies. In the determination of radiation yields for succinic and tricarballylic acids, the target solutions were evaporated to dryness in vacuo at room temperature. The non-volatile acids were chromatographed using method A. Each 10-ml. volume of the eluant was titrated directly with standard 0.01 N or 0.02 N aqueous sodium hydroxide to the phenolphthalein end-point after the addition of 15 ml. of methanol and 5 ml. of water to give a homogeneous solution. The total milliequivalents of product acid were calculated for the succinic and tricarballylic peaks after correcting for a small background titration. Control determinations of succinic and tricarballylic acids in simulated acetic acid target solutions gave recoveries of 97 to 102%. Figure 8 gives the concentrations of succinic and tricarballylic acids as a function of dose in 0.25 M acetic acid solution irradiated with 35 Mev. helium ions at a beam intensity of one micro-
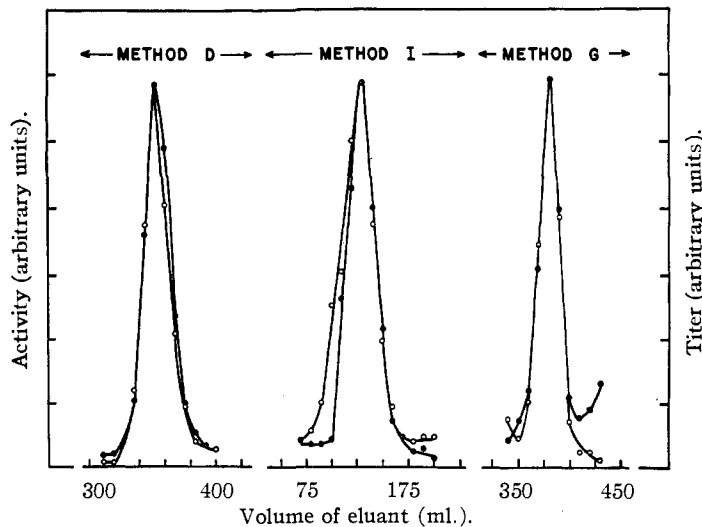

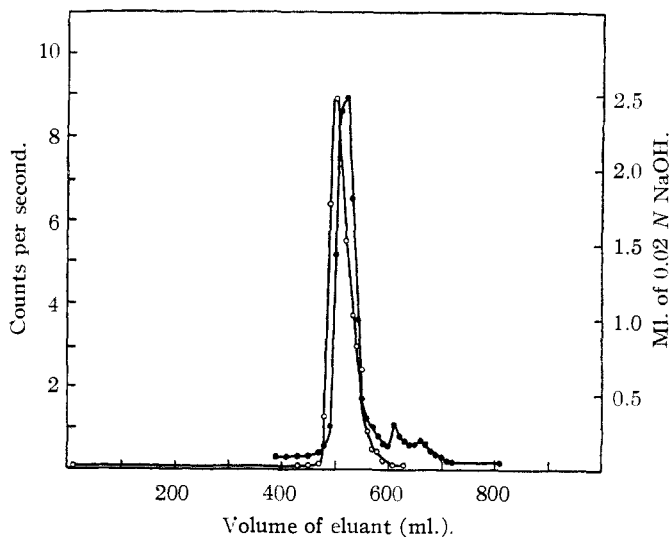Fig. 4.—Co-elution of fraction III with authentic tricarballylic acid.

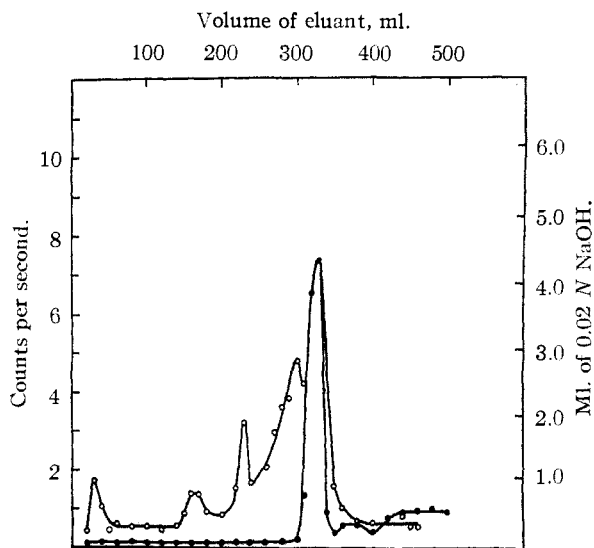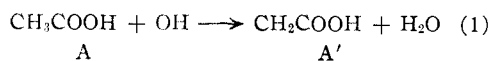Fig. 5.—Co-elution of fraction II with authentic malonic acid: method A.

Fig. 6.—Co-elution of fraction II with authentic malonic acid: method G.

Fig. 7.—Co-elution of fraction II-1 with authentic malonic acid: method A.

The data suggest that the CH_2COOH radical is formed by the reaction

$$CH_3COOH + OH \longrightarrow CH_2COOH + H_2O \quad (1)$$
$$A A'$$

Succinic and tricarballylic acids are then formed by the sequence

$$2CH_2COOH \longrightarrow \begin{array}{cc} CH_2 & CH_2 \\ | & | \\ COOH & COOH \end{array} \quad (2)$$
$$S$$

$$\begin{array}{cc} CH_2 & CH_2 \\ | & | \\ COOH & COOH \end{array} + OH \longrightarrow \begin{array}{cc} CH_2 & CH \\ | & | \\ COOH & COOH \end{array} + H_2O \quad (3)$$
$$S^1$$

$$\begin{array}{cc} CH_2 & CH \\ | & | \\ COOH & COOH \end{array} + CH_2COOH \longrightarrow$$

$$\begin{array}{ccc} CH_2 & CH & CH_2COOH \\ | & | \\ COOH & COOH \end{array} \quad (4)$$
$$T$$

Since succinic acid and tricarballylic acid are

ampere; oxygen was bubbled through the solution during the irradiation. The effluent gas was passed through a Dry Ice trap and then through a series of two scrubbing traps containing standard 0.05 N sodium hydroxide solution. The amount of carbon dioxide produced was a linear function of the dose; the radiation yield was 0.070 carbon dioxide molecule/100 ev. The corresponding hydrogen peroxide concentrations as determined by the ceric sulfate method are shown in Fig. 9. Organic peroxides were not detected.
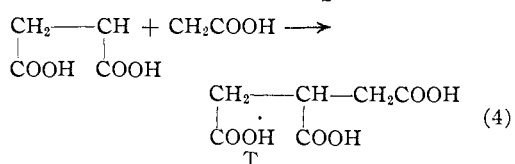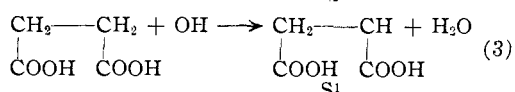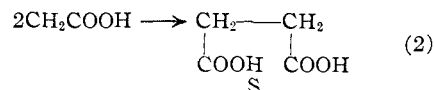
The production of succinic acid and tricarballylic acid is most readily accounted for by assuming that the CH_2COOH radical is formed as an intermediate.[20] In separate experiments it was found that (1) the radiation yields of succinic and tricarballylic acids in 0.25 M acetic acid are not changed appreciably if helium instead of oxygen is bubbled through the solution during irradiation and that (2) these acids are not produced in 0.25 M acetic acid solution containing 1.0 M ferrous sulfate.

(20) I. M. Kolthoff and A. I. Medalia, This Journal, 71, 3784 (1949).

the principal products below a dose level of 1×10^{21} ev./ml. it should be possible to apply the proposed mechanism to this dose region. If we employ the usual procedures for deriving a rate law from a mechanism and assume that the rates of change of radical concentrations are small compared to their rates of production and removal we obtain the relationships

$$d(S)/dt = k_2(A')^2 - k_3(S)(OH)$$
$$d(T)/dt = k_4(A')(S')$$
$$k_1(A)(OH) = 2k_2(A')^2 + k_4(A')(S')$$
$$k_3(S)(OH) = k_4(A')(S')$$

from which the following expression is readily obtained

$$\frac{k_1}{k_3} = \frac{(S)}{(A)}\left[2\frac{d(S)/dt}{d(T)/dt} + 3\right] \quad (5)$$

According to the proposed mechanism the rate of formation of tricarballylic acid should be initially zero. This is in agreement with the results of pre-
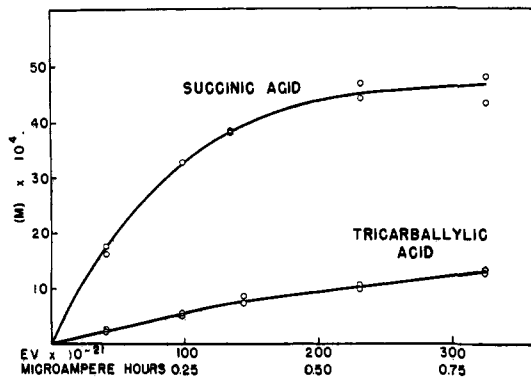
Fig. 8.—Production of succinic and tricarballylic acid.

viously mentioned product identification studies in which the acid products formed at low radiation dose levels were determined by C^{14} counting methods, viz., (1) below a dose of 1×10^{20} ev./ml. succinic acid only is formed (2) succinic and tricarballylic acids are the main products in the range 1×10^{20} ev./ml. to approximately 1×10^{21} ev./ ml. and (3) above 1×10^{21} ev./ml. other acid products begin to appear. Therefore equation 5 would not be valid above a radiation dose of 1×10^{21} ev./ ml. The effect of acetic acid concentration, radiation intensity and added succinic acid on the radia-
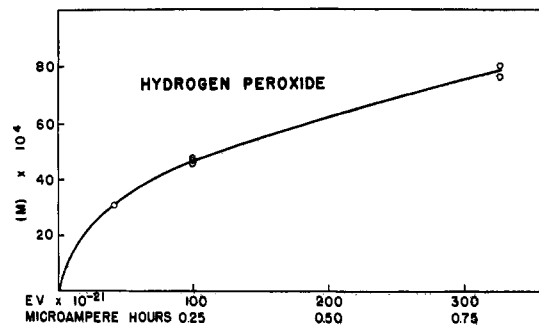
TABLE I

RADIATION YIELDS OF SUCCINIC ACID AND TRICARBALLYLIC ACIDS

Target volume, 75 ml; dose, 0.20 μa. hr.[a]

	Succinic acid	Yield (G_S)	Tricarballylic acid	Yield (G_T)	k_1/k_3
	Concn., $M \times 10^4$	mole/ 100 ev.	Concn., $M \times 10^4$	mole/ 100 ev.	$\times 10^2$ Calcd.(5)
A. Effect of acetic acid concentration: beam current, 1 microampere					
Acetic acid concn., M					
0.0625	8.85	0.049	1.95	0.011	8.54
	9.35	.052	2.26	.013	8.44
0.125	17.7	.098	5.73	.032	6.50
	16.83	.093	3.37	.020	8.75
0.25	26.0	.144	4.0	.022	8.32
0.50	40.7	.226	4.86	0.27	8.08
	37.6	.209	5.01	.028	6.80
1.0	49.6	.274	3.96	.022	6.97
	49.6	.274	4.12	.024	6.73
B. Effect of intensity; acetic acid, 0.25 M					
Beam intensity μa					
1.0	26.0	0.144	4.0	0.022	8.32
0.5	26.8	.149	4.5	.025	8.0
	26.2	.145	4.21	.0234	8.07
0.2	26.4	.147	2.97	.0165	10.89
	25.6	.143	2.60	.0145	11.61
C. Effect of added succinic acid: acetic acid, 0.25 M; succinic acid, 0.003 M; beam current, 1 microampere					
	48.6	0.102	8.99	0.049	10.51
	44.1	0.078	6.26	0.035	11.10

[a] With 35.0 Mev. helium ions a dose of 0.20 μa. hr. in a 75-ml. volume corresponds to an energy dissipation of 1.05 $\times 10^{21}$ ev./ml. Because of small differences in window thickness between target cells, the energy of helium ions absorbed in the solution varied slightly (<3%) depending on the particular cell window used. The corrected energies calculated from range–energy data, were used in the calculation of G_S.

Fig. 9.—Production of hydrogen peroxide.

tion yields of succinic acid and tricarballylic acid are shown in Tables IA, IB and IC. The values for k_1/k_3 were calculated by equation 5 using the approximation that the change in acid product concentration $(M_1) - (M_0)$ corresponds to the slope $d(M)/dt$ at the product concentration $(M_0) + [(M_1) - (M_0)]/2$. The calculated ratio is reasonably constant over the range of conditions studied. Experiments now in progress at lower dose levels give values for k_1/k_3 in substantial agreement with those found in Table I.

The decrease in radiation yield for both succinic acid and tricarballylic acid with acetic acid dilution (Table IA) indicates that reactions 1 and 3 are not the only processes involved in the removal of OH radicals. The falling off in succinic acid yield is apparently not caused by competing secondary reactions involving succinic acid and tricarballylic acid since their radiation products do not appear in appreciable amounts at a dose of 1×10^{21} ev./ml. Furthermore, since the succinic acid yield is independent of intensity (Table IB) and approaches a limiting value at the higher acetic acid concentrations it would appear that the reactions competing for OH removal are not H + OH = H_2O or OH + OH = H_2O_2. Although it is not possible at the present time to give a complete mechanism of the reactions involved, it is of interest to note that an explanation of the observed intensity and dilution effects can be obtained in terms of the mechanism proposed by Allen and co-workers[4] for the decomposition of water by ionizing radiation. Two different primary reactions apparently occur when aqueous solutions are irradiated, viz.

$$H_2O \longrightarrow H + OH \qquad (6)$$
$$2H_2O \longrightarrow H_2O_2 + H_2 \qquad (7)$$

Reaction 7 represents the formation of products by combination of like radicals in regions of high ionization density along the track of the ionizing particle and 6 represents the production of radicals which escape combination in the track and which are available for reaction with decomposition products or added solute in the bulk of the solution. The relative rates of reactions 6 and 7 are determined by the ionization density properties of the effective radiation. If we consider a competition in which OH radicals produced in 6 react in the bulk of the solution either with products (P) resulting from reaction 7 or with acetic acid (A) we have

$$k_6 I = k_P(P)(OH) + k_1(A)(OH) \qquad (8)$$

where k_6 is the free radical yield of reaction 6, k_P

the rate constant for the reaction of OH with P and I the radiation intensity. For low radiation doses the equation for the formation of succinic acid becomes

$$d(S)/dt = \alpha k_1(A)(OH)$$

where $\alpha \leq 1/2$. Substituting in equation 8 and taking (P) as a constant we obtain

$$\frac{1}{G_S} = \frac{1}{\alpha k_6}\left[1 + \frac{C}{(A)}\right] \qquad (9)$$

where G_S is the experimentally observed radiation yield for succinic acid and C is a constant involving (P). A plot of $1/G_S$ against $1/(A)$ for the data in Table IA is shown in Fig. 10. A straight line is obtained which if extrapolated to $1/(A) = 0$ gives $\alpha k_6 = 0.38$.[21] This corresponds to the case in
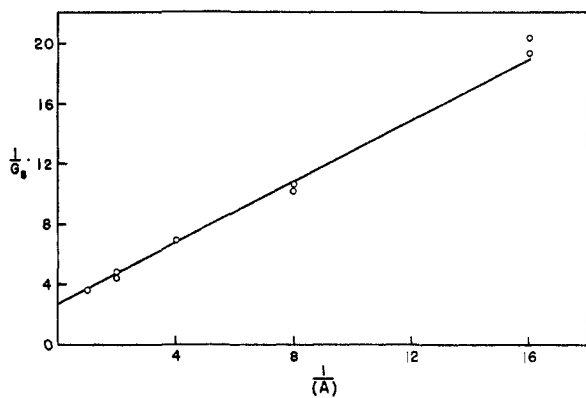

Fig. 10.—Effect of acetic acid concentration, (A), on the succinic acid yield, G_s.

(21) We are indebted to Dr. A. O. Allen for pointing out this relationship to us.

which all of the OH radicals disappear by reaction with A through reaction 1. Then $k_6 > 0.76$ which is a minimum value for the free radical yield of reaction 6. The same relationship between G_S and (A) given in equation 9 could conceivably be obtained if P were an impurity. This situation is considered unlikely because of the relatively large amount of products formed in comparison to the possible impurity concentration and because the amount of P present would have to be consistently independent of (A).

At the higher radiation doses ($>10^{21}$ ev./ml.), the kinetics become considerably more complex because of the reactions of succinic and tricarballylic acids to give malic and citric acids, respectively, and several other as yet unidentified acid products. It is apparent also from the data shown in Fig. 8 that the succinic acid and tricarballylic acid are each approaching a stationary concentration at the higher dose levels. These reactions will be discussed in a later paper.

A Thermodynamic Study of the Equilibrium $2Cu(s) + H_2S(g) = Cu_2S(\gamma) + H_2(g)$

BY ALFRED A. BROOKS[1]

The equilibrium $2Cu(s) + H_2S(g) = Cu_2S(\gamma) + H_2(g)$ has been investigated between 342 and 1037° by a recirculating technique with particular effort to eliminate the effects of thermal diffusion.

Introduction

Several authors have investigated the equilibrium between copper, hydrogen sulfide, hydrogen and cuprous sulfide. A flow method was used by Jellinek and Zakowski,[2a] Britzke and Kapustinsky,[2b] and by Sudo[3] to investigate the solid Cu–Cu$_2$S system. Sano[4] and Cox[5] used a circulating method. Schuhmann and Moles[6] investigated the region of liquid copper sulfides by a flow method. The results are not in particularly good agreement and some of the data[5] show bad scattering. The flow

(1) Standard Oil Co. (Ind.), Whiting, Ind.

(2) (a) K. Jellinek and J. Zakowski, *Z. anorg. allgem. Chem.*, **142**, 1 (1925); (b) E. V. Britzke and A. F. Kapustinsky, *ibid.*, **205**, 171 (1932).

(3) K. Sudo, *Sci. Rep. R.I.T.U.*, **A2**, 513 (1950).

(4) Sano, *Nippon-Kinsoku-Gakkaishi*, **3**, 718 (1939).

(5) E. M. Cox, *et al.*, *J. Metals* 1, *Trans.*, **185**, 27 (1949).

(6) R. Schuhmann and O. W. Moles, *J. Metals* 3, *Trans.*, **191**, 235 (1951).

method has the disadvantages that at low flow rates the effects of thermal diffusion are not negligible and at high flow rates equilibrium is not well established. The circulation method has the advantage that eventually equilibrium must be reached but has the disadvantage of producing relatively small samples. In addition, with some pump designs the linear flow rate may be so slow that thermal diffusion is an important error. In the present study an attempt was made to eliminate some of these disadvantages.

Experimental

Apparatus.—A schematic sketch of the apparatus is shown in Fig. 1. Variations in the entrance area and in the pumping rate were sufficient to change the linear velocity of the entrance gas from 67 to 6.7 cm./sec. and that of the exit gas from 23 to 11 cm./sec. A differential thermocouple was placed beside the Pt–PtRh measuring thermocouple and in the charge crucible. Changes in pumping rate from 10