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### Authors

Garrison, Warren M.  
Haymond, Herman R.  
Morrison, Donald C.  
[et al.](#)

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Radiation Laboratory

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Boyd M. Weeks, and Jeanne Gile-Melchert

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HIGH ENERGY HELIUM-ION IRRADIATION OF AQUEOUS ACETIC ACID SOLUTIONS<sup>\*,†</sup>

Warren M. Garrison, Herman R. Haymond, Donald C. Morrison,  
Boyd M. Weeks, and Jeanne Gile-Melchert

Crocker Laboratory, Radiation Laboratory  
University of California,  
Berkeley, California

## SUMMARY

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  $1 \times 10^{20}$  ev/ml. Tricarballic, 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.

According to present concepts<sup>1-6</sup> 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

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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.

By reason of the fundamental relationships between ionization density and radiation yield in chemical and biological systems,<sup>2,6,7</sup> 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<sup>8</sup> 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.<sup>9,10</sup> 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

Target cells of the type represented in Figs. 1 and 2 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 (A) which had an average thickness of 3 mils over the bombarded area. A stream of gas (oxygen or helium) was forced through the fritted-glass disc (B) to stir the solution during irradiation and to control the oxygen concentration in the bulk of the solution. Cell No. 1 was supported in the bracket (C) which was attached through the snout (D) to the target shutter assembly shown in Fig. 3. Quantitative yield data were obtained using cell No. 2 which had a solution capacity of approximately 80 ml. Oxygen or helium was passed through the inlet (A) during irradiation. The replaceable glass windows (B) had an average thickness of from 1 to 3 mil and were supported in the standard-taper joint (C) which 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. 3. The cyclotron beam entered the front plate (1) and was delimited by the water-cooled aperture (2). The defined beam then passed through a one 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  $\pm 0.3\%$ .

The energy of the helium-ion beam was evaluated from range-energy relationships and from calorimetric data. Absorption measurements in aluminum.

gave a calculated <sup>11,12</sup> value of 40.4 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 40.2 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.<sup>11,12</sup>

Hydrogen peroxide and organic peroxides were determined separately using a modification of the method of Greenspan and MacKellar<sup>13</sup> which is based on the observation that hydrogen peroxide, unlike organic peracids and hydroperoxides, is oxidized at temperatures from 0 to 10°C. 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 6N sulfuric acid and the resultant solution was titrated in the cold with .01N ceric sulfate-1.0N sulfuric acid solution to the ferroin end point. Potassium iodide was then added in excess and the solution was titrated with .01N sodium thiosulfate; in no case did the thiosulfate titre amount to more than .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.<sup>14,15,16</sup> The column dimensions and method of column preparation in the present work were a duplication of those developed by Marvel and Rands.<sup>14</sup> The developing liquids had the following composition:

- |    |                                   |     |
|----|-----------------------------------|-----|
| 1- | chloroform                        |     |
| 2- | 5% n-butanol - 95% chloroform V/V |     |
| 3- | 10%                               | 90% |
| 4- | 15%                               | 85% |



5-	20% n-butanol	- 80% chloroform V/V
6-	25%	75%
7-	30%	70%
8-	40%	60%
9-	50%	50%
10-	70%	30%
11-	80%	20%
12-	85%	15%
13-	90%	10%
14-	95%	5%
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.<sup>14</sup>

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 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 Adams reagent grade glacial acetic acid was redistilled twice; the middle fraction (approximately 30 per cent) was retained each time. The  $\text{CH}_3\text{C}^{14}\text{OOH}$  was prepared from the sodium salt by distillation in vacuo from phosphoric acid solution.<sup>17</sup>

#### RESULTS AND DISCUSSION

In preliminary studies, 80 ml volumes of 0.25 M acetic acid containing from 150 to 200 microcuries of  $\text{CH}_3\text{C}^{14}\text{OOH}$  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  $\text{C}^{14}$  activity. The top curve in Fig. 4 shows a typical elution curve for a total dose of  $44.6 \times 10^{20}$  ev/ml. The lower curve in Fig. 4 gives the corresponding titres obtained by titrating with .02 N sodium hydroxide the remaining 9 ml of each 10 ml eluant volume. The similarities between the two curves shown in Fig. 4 indicate that the  $\text{C}^{14}$  activity corresponds to labelled non-volatile acids produced in the bombardment. At lower radiation doses fewer product peaks were

observed. Below a dose of  $1 \times 10^{20}$  ev/ml, peak (I) only appeared. Acids corresponding to peaks (I) and (III) were the main products in the dose range of  $1 \times 10^{20}$  ev/ml to approximately  $10 \times 10^{20}$  ev/ml. Above this level all of the peaks seen in Fig. 4 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. 1, 10 ml volumes of 0.25 M acetic acid solution containing 250 to 300 microcuries of  $\text{CH}_3\text{C}^{14}\text{OOH}$ . In this way it was possible to isolate the product peaks in amounts which gave  $\text{C}^{14}$  counting rates of several hundred counts per second and a titre of less than .01 ml with .01 N sodium hydroxide.

A sample of  $\text{C}^{14}$  activity associated with (I) was co-chromatographed with added authentic succinic acid using method E. An exact correspondence of  $\text{C}^{14}$  activity and titre was obtained. A second sample of (I) was co-chromatographed with authentic succinic acid using method G. Exact correspondence between activity and titre was again obtained. These data are summarized in Fig. 5. Milligram amounts of (I) were subsequently isolated from 500 ml of 0.25 M acetic acid solution which received a total bombardment of  $40 \times 10^{20}$  ev/ml. After two recrystallizations from ether (I) melted at  $182-184^\circ\text{C}$ . A mixture of (I) and authentic succinic acid melted at  $182-184^\circ\text{C}$ .

Fraction (III) was originally suspected of being glycolic acid. An aliquot of  $\text{C}^{14}$  activity in (III), however, did not co-elute with added authentic glycolic acid using chromatographic method A. Subsequent work showed (III) to be tricarballic acid. A correspondence of activity and titre was obtained in co-chromatographs of (III) with authentic tricarballic acid using three different methods of partition chromatography as shown in Fig. 6.

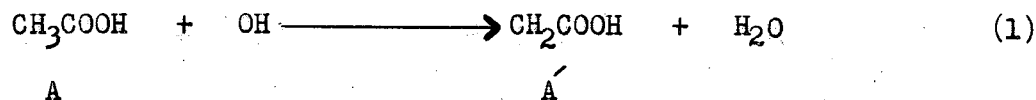
Fractions (II), (V) and (VI) were found to contain malonic, malic, and citric acid respectively. Only those methods used in the isolation and identification of malonic acid in (II) will be presented in detail because the results obtained were essentially duplicated in the identification of malic and 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-chromatographed with authentic malonic acid using method A. The elution curve is shown in Fig. 7. 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 titre and activity curves shown in Fig. 7 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. 8 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 titre is shown in Fig. 9. 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  $132-133^{\circ}C$ . A mixture of (II-1) with authentic malonic acid melted at  $132.5-134^{\circ}C$ . Aniline and para-toluidine

salts of (II-1) were prepared and these showed no depression in melting point when mixed with authentic material.

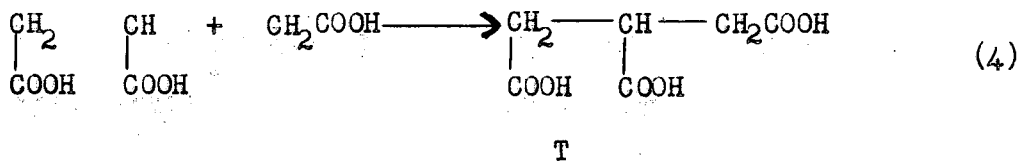
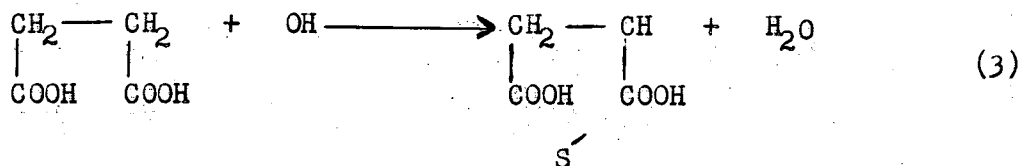
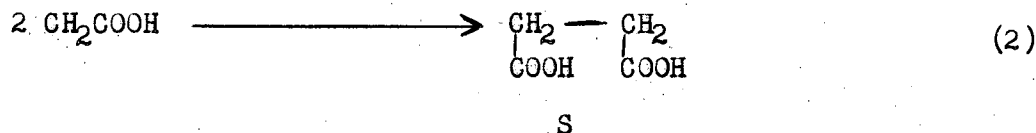
Cell No. 2 was used for the quantitative studies. In the determination of radiation yields for succinic and tricarballic acids, the target solutions were evaporated to dryness in vacuo at room temperature. The non volatile acids were chromatographed using method A. Each 10 ml volume of the eluant was titrated directly with standard .01N or .02N aqueous sodium hydroxide to the phenolphthalein end point after the addition of 15 ml of methanol and 5 ml of water to give a homogenous solution. The total milliequivalents of product acid were calculated for the succinic and tricarballic peaks after correcting for a small background titration. Control determinations of succinic and tricarballic acids in simulated acetic acid target solutions gave recoveries of 97 to 102%. Fig. 10 gives the concentrations of succinic and tricarballic 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 microampere; 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 .05 N sodium hydroxide solution. The amount of carbon dioxide produced was a linear function of the dose; the radiation yield was .070 carbon dioxide molecules/100 ev. The corresponding hydrogen peroxide concentrations as determined by the ceric sulfate method are shown in Fig. 11. Organic peroxides were not detected.

The production of succinic acid and tricarballic acid is most readily accounted for by assuming that the  $\text{CH}_2\text{COOH}$  radical is formed as an intermediate.<sup>18</sup> In separate experiments it was found that (1) the radiation yields of succinic and tricarballic 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. The data strongly suggest that the  $\text{CH}_2\text{COOH}$  radical is formed by the reaction



Succinic and tricarballic acids are then formed by the following sequence:



Since succinic acid and tricarballic acid are the principal products below a dose level of  $1 \times 10^{21}$  ev/ml it would 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:

$$\begin{aligned} d(S)/dt &= k_2 (\dot{A})^2 - k_3 (S)(OH) \\ d(T)/dt &= k_4 (\dot{A})(\dot{S}) \\ k_1 (A)(OH) &= 2k_2 (\dot{A})^2 + k_4 (\dot{A})(\dot{S}) \\ k_3 (S)(OH) &= k_4 (\dot{A})(\dot{S}) \end{aligned}$$

from which the following expression is readily obtained:

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

According to the proposed mechanism the rate of formation of tricarballic acid should be initially zero. This is in agreement with the results of previously 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  $1 \times 10^{20}$  ev/ml succinic acid only is formed (2) succinic and tricarballic acids are the main products in the range  $1 \times 10^{20}$  ev/ml to approximately  $1 \times 10^{21}$  ev/ml and (3) above  $1 \times 10^{21}$  ev/ml other acid products begin to appear. Therefore equation 5 would not be valid above a radiation dose of  $1 \times 10^{21}$  ev/ml. The effect of acetic acid concentration, radiation intensity and added succinic acid on the radiation yields of succinic acid and tricarballic acid are shown in Tables 1A, 1B, and 1C. 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  $(M_0) + \left[ (M_1) - (M_0) \right] / 2$ . 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 1.

The decrease in radiation yield for both succinic acid and tricarballylic acid with acetic acid dilution (Table 1A) 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  $1 \times 10^{21}$  ev/ml. Furthermore, since the succinic acid yield is independent of intensity (Table 1B) 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<sup>4</sup> for the decomposition of water by ionizing radiation. Two different primary reactions apparently occur when aqueous solutions are irradiated viz



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



TABLE I

Radiation Yields of Succinic Acid and Tricarballic Acids.  
Target volume, 75 ml; Dose, 0.20  $\mu$ hr<sup>a</sup>

## A. Effect of acetic acid concentration

Beam current, 1 microampere.

Acetic Acid Concen. M	Succinic Acid		Tricarballic Acid		$k_1/k_3 \times 10^2$ Calcd. (5)
	Concen. M x 10 <sup>4</sup>	Yield(G <sub>S</sub> ) mol/100ev.	Concen. M x 10 <sup>4</sup>	Yield(G <sub>T</sub> ) mol/100ev.	
0.0625	8.85	.049	1.95	.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	.027	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

a With 35.0 Mev helium ions a dose of 0.20  $\mu$ 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 per cent) depending on the particular cell window used. The corrected energies calculated from range-energy data, were used in the calculation of G<sub>S</sub>.

## B. Effect of intensity

Acetic acid, 0.25 M

Beam current microamperes	Succinic Acid		Tricarballic Acid		$k_1/k_3 \times 10^2$ Calcd. (5)
	Concen. M x 10 <sup>4</sup>	Yield mol/100ev.	Concen. M x 10 <sup>4</sup>	Yield mol/100ev.	
1.0	26.0	.144	4.0	.022	8.32
.5	26.8	.149	4.5	.025	8.0
	26.2	.145	4.21	.0234	8.07
.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, .003 M; beam current, 1 microampere.

	Succinic Acid		Tricarballic Acid		$k_1/k_3 \times 10^2$ Calcd. (5)
	Concen. M x 10 <sup>4</sup>	Yield mol/100ev.	Concen. M x 10 <sup>4</sup>	Yield mol/100ev.	
	48.6	.102	8.99	.049	10.51
	44.1	.078	6.26	.035	11.10

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

$$k_6 I = k_p(P)(OH) + k_1(A)(OH) \quad (8)$$

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

$$\frac{d(S)}{dt} = \alpha k_1 (A)(OH)$$

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

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

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 1A gives a straight line which if extrapolated to  $1/(A) = 0$  gives  $\alpha k_6 = 0.38$ .<sup>19</sup> This corresponds to the case in which all of the OH radicals disappear by reaction with A through reaction 1. Then  $k_6 \geq 0.76$  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 tricarballic 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. 10 that the succinic acid and tricarballic acid are each approaching a stationary concentration at the higher dose levels. These reactions will be discussed in a later paper.

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17. We wish to thank Dr. Bert M. Tolbert for supplying the  $\text{CH}_3\text{C}^{14}\text{OOH}$  used in these experiments.
18. I. M. Kolthoff and A. I. Medalia, *J. Am. Chem. Soc.* 71, 3784 (1949).
19. We are indebted to Dr. A. O. Allen for pointing out this relationship to us.

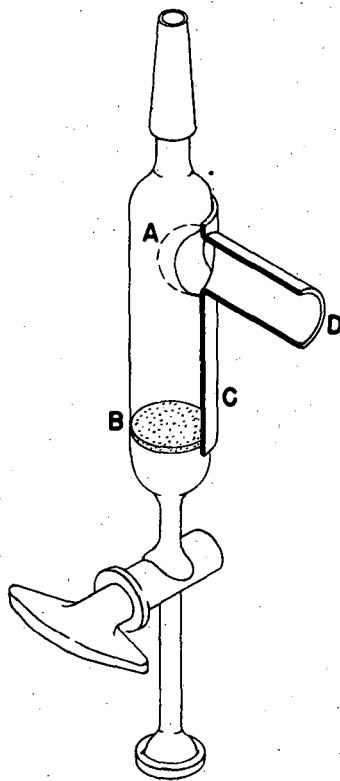


Fig. 1

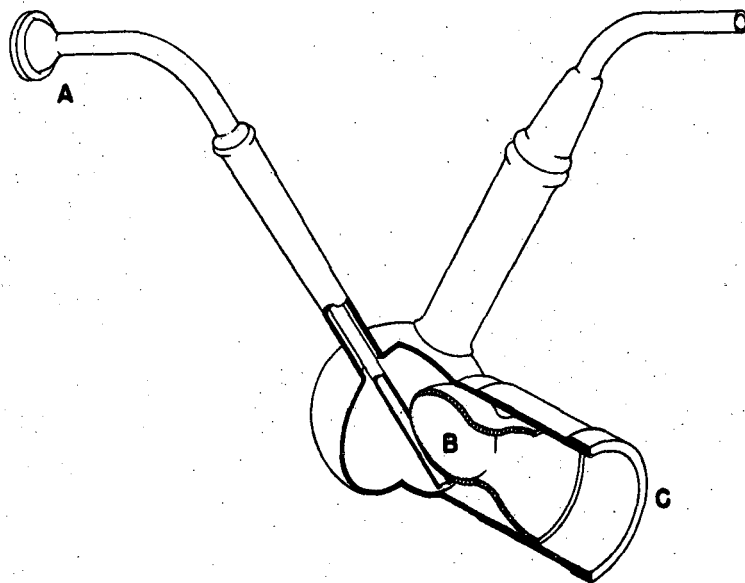


Fig. 2

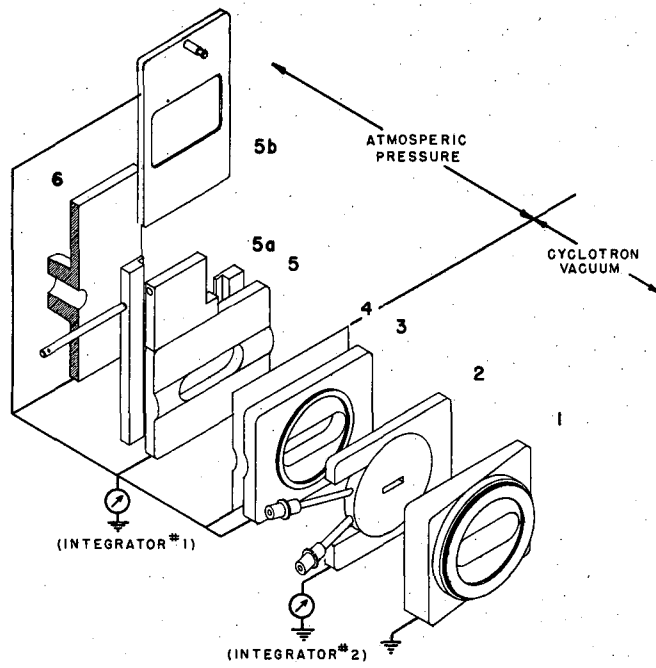


Fig. 3



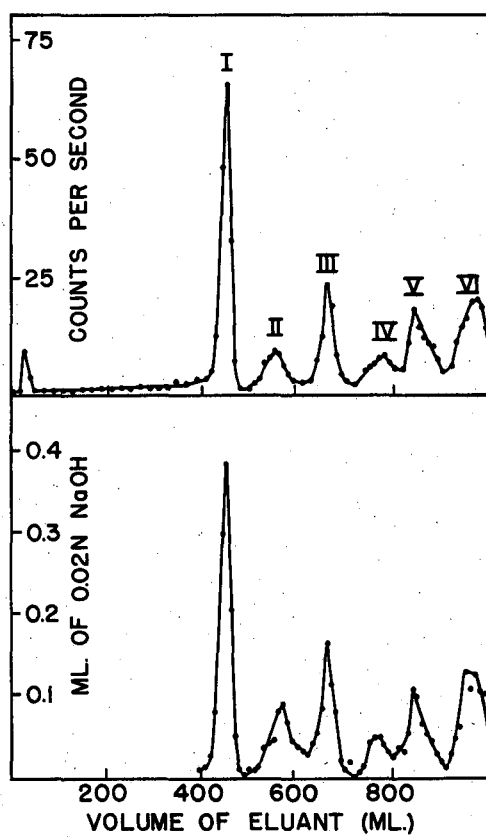


Fig. 4

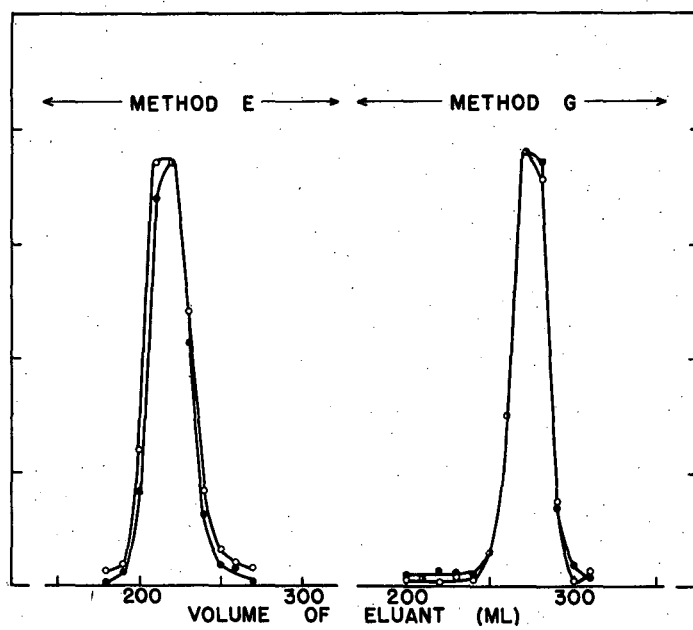


Fig. 5

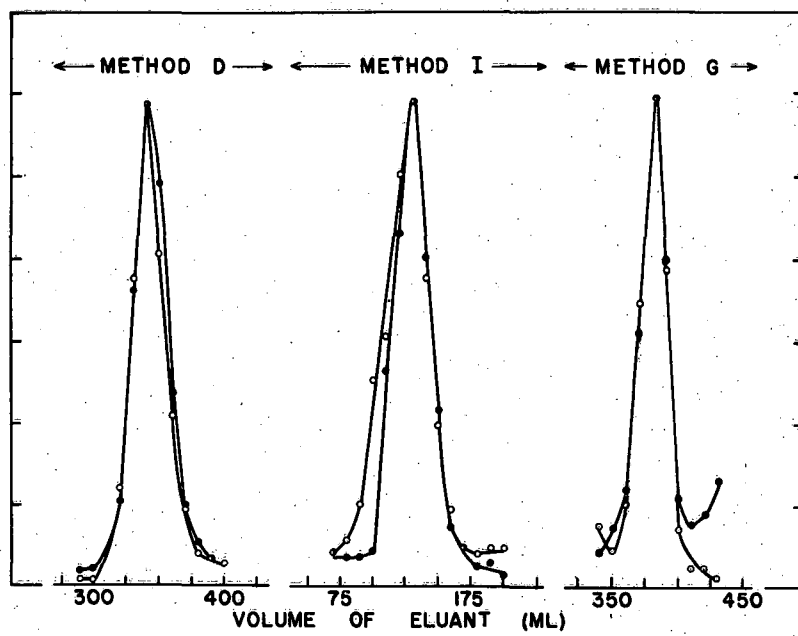


Fig. 6

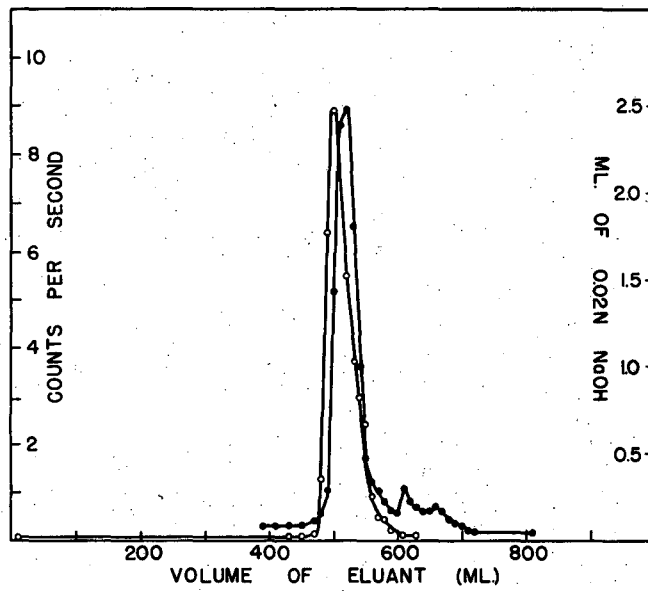


Fig. 7

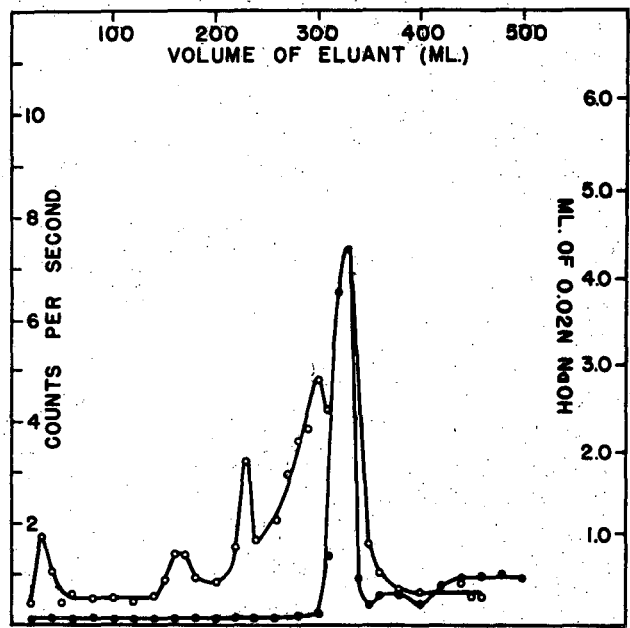


Fig. 8

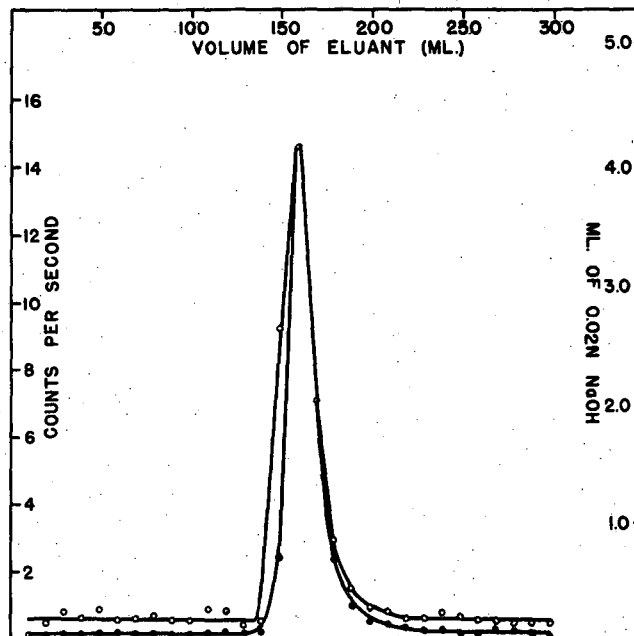


Fig. 9

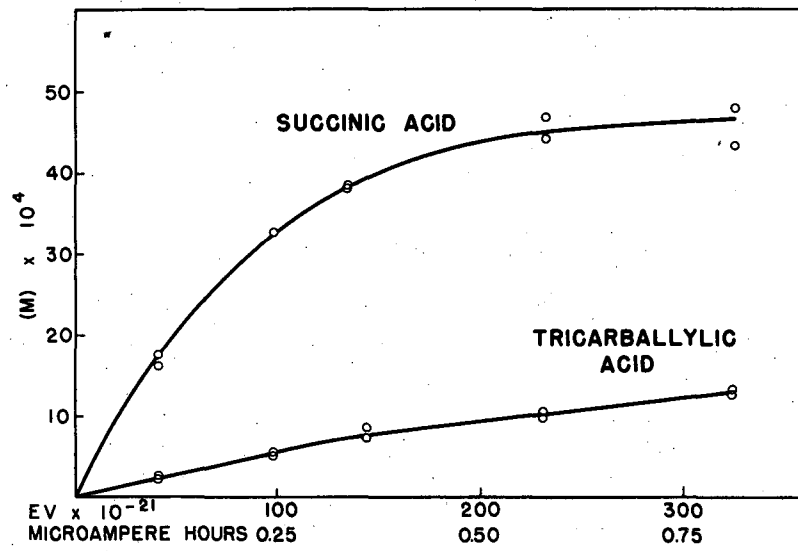


Fig. 10

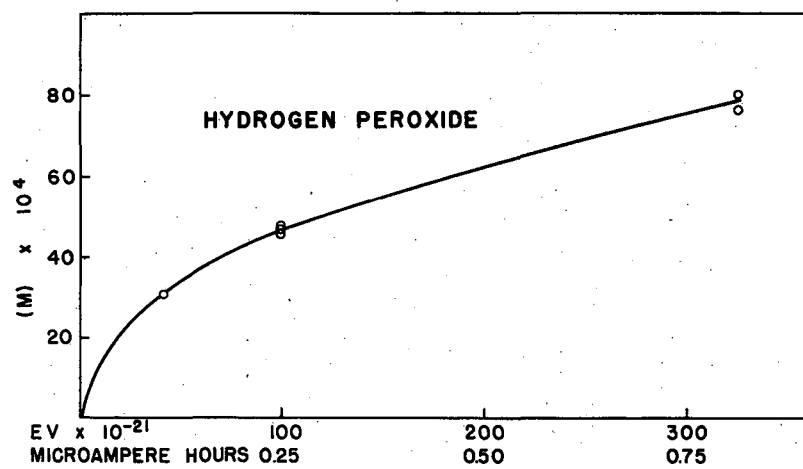


Fig. 11