533. *Effects of γ-Radiation. Part III.* Quantitative Studies of the Products from Glycollic Acid.*

By P. M. Grant and R. B. Ward.

The decomposition of glycollic acid solutions induced by γ-radiation *in vacuo* and in the presence of oxygen has been followed quantitatively. The concentrations of glycollic, glyoxylic, tartaric, oxalic, and formic acid, formaldehyde, and carbon dioxide have been measured directly, and by new colorimetric methods in the cases of glycollic and glyoxylic acid. A mass balance for carbon has been obtained, and degradation pathways are advanced to explain the results.

It has been shown * that the main non-volatile degradation products formed on γ-irradiation of glycollic acid in dilute aqueous solution in the presence and in absence of oxygen are glyoxylic, tartaric, and oxalic acid, the effect of oxygen being to reduce greatly the yield of tartaric acid.

In this work an attempt has been made to determine the above-mentioned products, together with the volatile products, directly and *in situ* by methods which, within the system studied, are specific for each product. This has involved developing methods for colorimetric determination of glycollic and glyoxylic acid, and finding suitable conditions for the estimation of tartaric and oxalic acid by adaptations of previous methods. The colorimetric methods adopted for glycollic and glyoxylic acids are based on two " spot " tests developed by Eegriwe, using 2 : 7-dihydroxynaphthalene and 2 : 3 : 4-trihydroxybenzoic acid respectively.[1,2,3]

2 : 7-Dihydroxynaphthalene in concentrated sulphuric acid solution, gives with glycollic acid a violet colour when heated for 30 min. in a stoppered tube at 100°. The calibration curve was not quite linear (Table 3), necessitating the use of the curve to convert Spekker readings into glycollic acid content. Standard determinations were included since the colour varied a little (reading ±0·01) for different preparations of the reagent. Measurement of known mixtures of the radiation products showed that both glyoxylic and oxalic acid slightly increased the optical density, while tartaric acid decreased it. The effect of oxalic acid is negligible; the effects of glyoxylic and tartaric acid may be ignored when their respective proportions do not exceed 20% and 50% of the glycollic acid in the sample. When present in equal amounts (Table 3) the estimated error was +11·2% and −4·1% respectively.

2 : 3 : 4-Trihydroxybenzoic acid and glyoxylic acid in the presence of sulphuric acid at 50° (30 min.) gave a blue colour. The calibration curve was linear (Table 4), but standard determinations were included. Very considerable variation in colour was found with various samples of sulphuric acid (Table 4), indicating that some contaminant, *e.g.*, iron or selenium, present in traces was essential for development of the colour. The reagent, furthermore, tended to be unstable in sulphuric acid. Best results were obtained when finely powdered solid reagent was added to the aliquot part of glyoxylic acid solution in a test-tube, followed by a measured volume of sulphuric acid. The test-tube was then stoppered, shaken, and immersed in a water-bath at 50°. In mixtures of known composition the presence of an equal quantity of oxalic acid had no detectable effect. Tartaric acid decreased the colour formed to a small extent, the effect at equal concentrations was to introduce an error in the glyoxylic acid determination of −2·6% (Table 4). Glycollic

* Part II, preceding paper.

[1] Eegriwe, *Z. analyt. Chem.*, 1932, **89**, 123.
[2] *Idem, ibid.*, 1934, **100**, 325.
[3] Feigl, " Spot Tests," Vol. II, Organic Applications, 4th English Edn., Elsevier Publ. Co., Amsterdam, 1954, pp. 249, 253.

TABLES 1 & 2. *Irradiation of glycollic acid solutions.*

Time (hr.)	Total dose (10^{18} ev ml.$^{-1}$)	Glycollic acid destroyed mmole/l.	(%)	Radiation product yields: Glyoxylic acid hydrate (mmole/l.)	Oxalic acid dihydrate (mmole/l.) (corr.)	Tartaric acid (corr.) (mmole/l.)	Tartaric acid Mol. conv.†	Formaldehyde (mmole/l.)	Formaldehyde Mol. conv.†	Formic acid (mmole/l.)	Formic acid Mol. conv.†	Carbon dioxide (mmole/l.)	Carbon dioxide Mol. conv.†	Carbon balance data: Total glycollic acid accounted for (mmole/l.)	Discrepancy (%)
						TABLE 1. *Irradiation in a vacuum.*									
0·25	0·57	0·066	0·5	0·0217	—	0·018	0·036	0·01	0·005	—	—	—	—	—	—
0·5	1·15	0·132	1·0	0·0353	—	0·039	0·078	0·01	0·005	0·01 *	0·005 *	0·01 *	0·005 *	0·128	−3
0·75	1·7	0·172	1·3	0·0484	—	0·065	0·130	0·012	0·006	—	—	—	—	—	—
1·0	2·3	0·238	1·8	0·0641	—	0·079	0·158	0·014	0·007	0·02 *	0·01 *	0·021	0·0105	0·250	+5
1·5	3·4	0·369	2·8	0·0945	—	0·117	0·234	—	—	—	—	—	—	—	—
2·0	4·6	0·475	3·6	0·1185	—	0·145	0·290	0·015	0·008	0·03 *	0·015 *	0·0345	0·0173	0·449	−5
2·5	5·7	0·607	4·6	0·128	—	0·192	0·383	—	—	—	—	—	—	—	—
3·0	6·9	0·74	5·6	0·145	—	0·237	0·473	—	—	—	—	0·0543	0·0272	—	—
4·0	9·2	0·96	7·3	0·165	—	0·337	0·673	0·014 *	0·007 *	0·05 *	0·025 *	0·0613	0·0307	0·901	−6
5·0	11·5	1·20	9·1	0·201	0·0092	0·425	0·850	—	—	—	—	0·0843	0·0422	—	—
8·0	18·5	1·73	13·1	0·251	0·0382	0·66	1·31	0·013	0·007	0·09 *	0·045 *	0·138	0·069	1·72	−1
10·0	23	2·05	15·5	0·278	0·0530	0·88	1·76	—	—	—	—	—	—	—	—
12·0	27·5	2·31	17·5	0·283	0·0728	0·97	1·93	0·013 *	0·007 *	0·15	0·075	0·205	0·1025	2·47	+7
18·0	41	3·14	23·8	0·278	0·145	1·37	2·74	—	—	—	—	0·295	0·148	—	—
24·0	55	3·88	29·4	0·272	0·259	1·72	3·43	0·013	0·007	0·28	0·14	0·363	0·182	4·29	+11
						TABLE 2. *Irradiation in oxygen.*									
0·25	0·57	—	—	0·0263	—	—	—	0·009	0·005	—	—	0·0198	0·0099	—	—
0·5	1·150	0·092	0·7	0·0540	—	—	—	0·011	0·006	0·04 ‡	0·02 ‡	0·032	0·016	0·096	+4
0·75	1·70	—	—	0·0842	—	—	—	0·012	0·006	—	—	0·055	0·0275	—	—
1·0	2·3	0·172	1·3	0·106	—	—	—	0·018	0·009	0·063	0·032	0·072	0·036	0·183	+6
1·5	3·4	0·264	2·0	0·156	—	—	—	—	—	—	—	0·117	0·0585	—	—
2·0	4·6	0·36	2·7	0·202	—	—	—	0·017	0·009	0·15	0·075	0·153	0·0765	0·363	+1
2·5	5·7	0·435	3·3	0·238	—	—	—	—	—	—	—	0·188	0·094	—	—
3·0	6·9	0·53	4·0	0·276	—	—	—	—	—	—	—	0·216	0·108	—	—
4·0	9·2	0·69	5·2	0·324	—	0·0061	0·0122	0·018 ‡	0·009 ‡	0·30	0·15	0·316	0·158	0·653	−5
5·0	11·5	0·83	6·3	0·388	—	0·0082	0·0164	—	—	—	—	0·378	0·189	—	—
8·0	18·5	1·23	9·3	0·552	0·0138	0·0132	0·0264	0·019	0·01	0·53	0·27	0·633	0·317	1·189	−3
12·0	27·5	1·77	13·4	0·711	0·0461	0·0198	0·0396	0·018 ‡	0·009 ‡	0·95	0·48	1·06	0·53	1·816	+3
18·0	41	2·47	18·7	0·870	0·135	0·0343	0·0686	—	—	—	—	1·71	0·86	—	—
24·0	55	3·10	23·5	0·962	0·286	0·0383	0·0766	0·017	0·009	1·68	0·84	2·50	1·25	3·42	+10

* Determined from Fig. 1. ‡ Determined from Fig. 2. † Molar conversion: mmole of glycollic acid required to produce observed yield of the particular component on the basis of complete conversion solely into this component.

acid, however, when present to the extent of 1000 parts of glycollic acid to one part of glyoxylic acid, introduced an error in the glyoxylic acid estimation of only +1·4%.

Tartaric acid was determined by means of its uptake of periodate.[4] At room temperature over-oxidation occurred, which was reduced by oxidation at 5° and still further by addition of glycollic acid. There was no interference by oxalic acid; glyoxylic acid showed a tendency to increase the periodate uptake, even at 5°. Addition of glycollic acid (100 times the amount of tartaric acid present) reduced the oxidation of glyoxylic acid at 5° to a negligible value (Table 5), probably because it increased acidity.

Oxalic acid was determined by precipitation of the calcium salt. To prevent co-precipitation of calcium tartrate, the tartaric acid (previously estimated as above) was destroyed by treating the sample for oxalic estimation with a 10% molar excess of sodium metaperiodate before precipitating the calcium oxalate with calcium chloride. The calcium oxalate was washed and estimated titrimetrically with potassium permanganate. Analysis of known mixtures under standard conditions showed that the values obtained

FIG. 1.

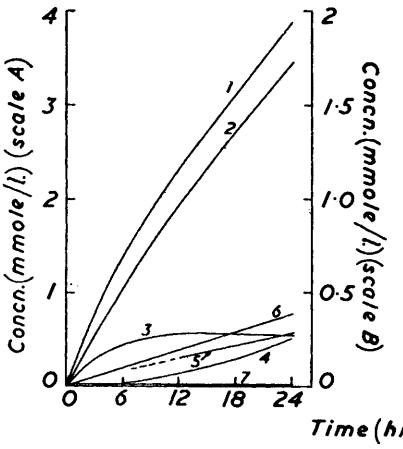


FIG. 2.

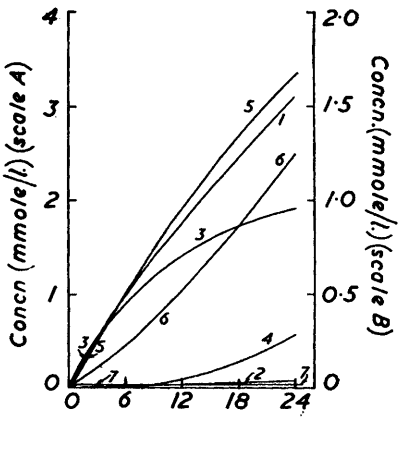


FIG. 1. *γ-Irradiation of glycollic acid solutions* in vacuo. (*Dose rate*, 2·3 × 10^{18} ev ml.$^{-1}$ hr.$^{-1}$). *Scale A*: 1, *Glycollic acid destroyed*. *Scale B*: 2, *Tartaric acid*; 3, *glyoxylic acid*; 4, *oxalic acid*; 5, *formic acid*; 6, CO_2; 7, CH_2O.

FIG. 2. *γ-Irradiation of glycollic acid solutions in oxygen*. (*Dose rate as for Fig.* 1.) *Scale A*: *curves* 1 *and* 6. *Scale B*: *curves* 2—5 *and* 7. *Numerals as for Fig.* 1.

were consistently about 5 mg. below the true value. This correction for solubility and manipulation was therefore used in each determination.

Early analyses of irradiated solutions showed that more glycollic acid was being destroyed than was accounted for by the glyoxylic, tartaric, and oxalic acid formed, indicating additional volatile products. Attention was turned to formaldehyde, volatile acids (determined as formic acid), and carbon dioxide. Formaldehyde was determined by means of chromotropic acid.[5] Only glyoxylic acid interfered and this was not serious while the glyoxylic acid content of the irradiated solution remained small.

Volatile acid was determined by estimating the acidity in the frozen sublimate obtained on freeze-drying of the irradiated solution. Appreciable quantities of glycollic acid collected in the sublimate, so this was measured by the 2:7-dihydroxynaphthalene method, and its acidity component subtracted from the total acidity of the sublimate: the difference was expressed as formic acid.

Carbon dioxide was determined by passing a stream of nitrogen through the boiling

[4] Dyer, "Methods of Biochemical Analysis, Vol. III," Interscience Publ., Inc., New York, 1956 p. 111.

[5] MacFadyen, *J. Biol. Chem.*, 1945, **158**, 107.

solution. The gas stream then passed through a reflux condenser into a two-stage sintered-glass trap containing barium hydroxide. The carbon dioxide was estimated by back-titration of the barium hydroxide solution to phenolphthalein.

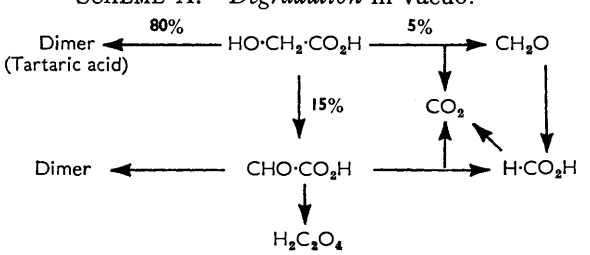
The results of these analyses are summarised in Tables 1 (evacuated system) and 2 (oxygenated system). Concentrations of the products are shown in Figs. 1 and 2. The carbon balance was obtained by adding together the amounts of glycollic acid required to yield the observed products and expressing this as a percentage excess (positive) or deficiency (negative) compared with the observed destruction of glycollic acid. In some cases certain quantities have been obtained, where indicated, by measurement from Figs. 1 and 2.

The small discrepancies in the carbon balance are considered to indicate an effectively complete analysis. As the degradation proceeds, at least three factors tending to produce high results become apparent. Increasing yields of tartaric acid and further radical addition to produce trimer molecules will each cause high values for tartaric acid. Also, all calculations for the non-volatile products were based on the assumption that there is no change in weight of the non-volatile solute, since the increase in weight associated with the formation of glyoxylic acid and oxalic acid approximately balanced the formation of volatile components. However, the yield of the volatile components becomes proportionally larger as the reaction proceeds, so estimates of non-volatile products exceed the true value, particularly in the oxygenated system. Detailed numerical analysis of the systems showed that no significant error would be introduced until after approximately 12 hr., and the error introduced then is of the same order as the observed discrepancy in the carbon balance in both systems.

It is concluded, therefore, that the discrepancies in the carbon balance, while at times larger than would be expected from experimental error, can be explained logically.

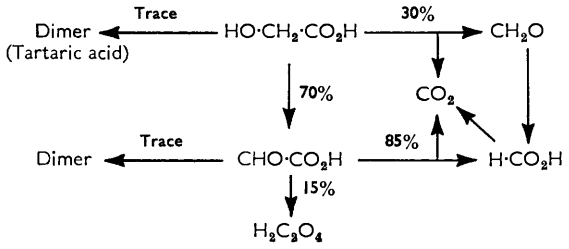
The results obtained in the absence of oxygen agreed completely with the mechanisms advanced in the preceding paper. Some 80% of the glycollic acid destroyed reappeared as tartaric acid, which behaved as a relatively stable product. Approximately 15% was converted into glyoxylic acid, while the remaining 5% formed carbon dioxide and either formaldehyde or formic acid. Since the content of formaldehyde rapidly reached a stationary low level within 1 hr. while the formic acid increased continuously, the acid was produced from the relatively unstable formaldehyde. The tartaric acid appeared to undergo little change, its rate of formation closely following the decreasing glycollic acid concentration. Glyoxylic acid was less stable and reached a stationary level after 9 hr. Oxalic acid appeared as a typical secondary product (Fig. 1) and glyoxylic acid had been shown (preceding paper) to give oxalic acid on irradiation *in vacuo*, as well as products of higher molecular weight. The rates of formation of formic acid and carbon dioxide were too great to be accounted for merely by the yield directly from glycollic acid, and also the yields increased with time, suggesting their formation to be partly primary and partly secondary. These observations indicated that some of the glyoxylic acid was degraded to carbon dioxide and formic acid. Since the mechanisms suggested should yield formic acid and carbon dioxide in almost equimolecular quantities, the progressively increasing divergence in Fig. 1 indicates that degradation of formic acid gives carbon dioxide, as illustrated in Scheme A.

SCHEME A. *Degradation* in vacuo.



The degradation in oxygen had a similar course except (cf. preceding paper) that there was very little formation of C–C linkages (including polymerisation [6]) since peroxy-radicals are formed.[7] This made it possible to estimate the relative extent of degradation of glyoxylic acid by the two pathways. The degradation may be expressed as in Scheme B. It will be seen that relatively a greater proportion of C–C linkages are broken. Higher levels of glyoxylic acid and formaldehyde are established, as would be expected from the greater proportions produced. Since a very much higher proportion of relatively labile products is formed than in the evacuated system (where tartaric acid accounted for 80%), a larger proportion of the solvent-radical yield is consumed in effecting secondary and tertiary degradations, as may be seen from the higher yields of carbon dioxide and formic acid. This results in a lower overall rate of degradation of glycollic acid, although the total amount of oxidation is larger in the oxygenated system.

SCHEME B. *Degradation in presence of oxygen.*



EXPERIMENTAL

Analytical Methods.—(i) *Determination of glycollic acid.* 0—100 μl. of glycollic acid solution (0·5 mg./ml.) were placed in a test-tube by using an Agla Micrometer Syringe and made up (if necessary) to 100 μl. with water (100—0 μl.). 10 ml. of a freshly prepared solution of 2 : 7-dihydroxynaphthalene [1] in concentrated sulphuric acid (10 mg./100 ml.) were added, the tubes were stoppered, swirled, and then heated in a boiling-water bath for 30 min. The tubes were cooled and the violet colour measured in 1 cm. cells, in a Hilger " Spekker " spectrophotometer, with a yellow-green filter (No. 605; 550 mμ). A solution with glycollic acid solution omitted [but containing water (100 μl.)] was used as the control (Table 3).

TABLE 3. *Calibration of glycollic acid: interference tests.*

Glycollic acid alone (μg.)	" Spekker " reading	Glycollic acid (μg.)	Glyoxylic acid hydrate (μg.)	Oxalic acid dihydrate (μg.)	Tartaric acid (μg.)	" Spekker " reading
2·5	0·058	25·0	—	—	—	0·605
5·0	0·131	25·0	5·0	—	—	0·619
12·5	0·329	25·0	12·5	—	—	0·634
25·0	0·605	25·0	25·0	—	—	0·673
37·5	0·797	25·0	—	12·5	—	0·606
50·0	1·001	25·0	—	25·0	—	0·609
		25·0	—	—	12·5	0·596
		25·0	—	—	25·0	0·580
		25·0	2·5	2·5	2·5	0·608
		25·0	8·3	8·3	8·3	0·613
		12·5	—	—	—	0·329
		12·5	12·5	12·5	12·5	0·374

The interference of glyoxylic, oxalic, and tartaric acid was ascertained by adding suitable volumes (0—50 μl.) of aqueous solutions of these acids (0·5 mg./ml.) to 25 or 50 μl. of 0·05% glycollic acid solution. The volumes were made up to 100 μl. and the glycollic acid determined (Table 3). Standard determinations were necessary with each batch of estimations, the variation between batches being $< \pm 0{\cdot}01$.

(ii) *Determination of glyoxylic acid.* 0—100 μl. of glyoxylic acid hydrate solution (0·5

[6] Barker, Grant, Stacey, and Ward, *J.*, 1959, 2648.

[7] Johnson, Scholes, and Weiss, *J.*, 1953, 3091; Dewhurst, Samuel, and Magee, *Radiation Res.*, 1954, **1**, 62; Garrison, Haymond, and Weeks, *ibid.*, p. 97.

mg./ml.) was placed in a test-tube by means of a micrometer syringe and made up to 100 μl. with water. Finely powdered 2 : 3 : 4-trihydroxybenzoic acid [2] (25·0 mg.) was added, followed by concentrated sulphuric acid (10 ml.). The mixture was shaken for about 15 sec. and immersed, stoppered, into a water-bath at 50°. After 30 min. the tube was cooled, and the blue colour measured in 1 cm. cells, in a " Spekker " spectrophotometer with yellow filters (No. 606; 575 mμ). A solution with glyoxylic acid solution omitted [but containing water (100 μl.)] was used as control (Table 4).

TABLE 4. *Calibration of glyoxylic acid: interference tests.*

Glyoxylic acid hydrate alone (μg.)	" Spekker " reading
2·5	0·072
5·0	0·124
12·5	0·302
25·0	0·588
37·5	0·850
50·0	1·047

Glyoxylic acid hydrate (μg.)	Glycollic acid (μg.)	Oxalic acid dihydrate (μg.)	Tartaric acid (μg.)	" Spekker " reading
25·0	—	—	—	0·588
25·0	1,700	—	—	0·586
25·0	4,400	—	—	0·594
25·0	20,000	—	—	0·596
25·0	—	5·0	—	0·582
25·0	—	25·0	—	0·585
25·0	—	—	5·0	0·586
25·0	—	—	12·5	0·576
25·0	—	—	25·0	0·573
12·5	—	—	—	0·302
12·5	5,000	18·75	18·75	0·308
25·0	Various samples of sulphuric acid supplied by Messrs. Peyton and Son			0·570—0·621
25·0	B.D.H. " AnalaR " sulphuric acid			0·238
25·0	B.D.H. " MAR " sulphuric acid			0·029

The interference of glycollic, oxalic, and tartaric acid was ascertained by adding dry glycollic acid (0—20 mg.) and suitable volumes of aqueous solutions of oxalic acid dihydrate and tartaric acid (0·5 mg./ml.) to 25 or 50 μl. of 0·05% glyoxylic acid hydrate solution. The volumes were made up to 100 μl. and the glyoxylic acid determined. Standard determinations were necessary with each batch of estimations. The colour produced was reduced very markedly when samples of sulphuric acid purer than available commercial grades were used. The reduction in colour with " AnalaR " and " MAR " reagent grades is shown in Table 4.

(iii) *Determination of tartaric acid.* The samples were dissolved in water (*ca.* 30 ml.). 0·1M-Sodium metaperiodate (10 ml.) was added and the solution made up to 50 ml. with water. The solutions were kept throughout at 5°. Aliquot parts (5 ml.) were removed at intervals, and sodium hydrogen carbonate (0·5 g.), an excess of 0·02N-sodium arsenite (20 ml.) and 20% aqueous potassium iodide (1 ml.) were added. The excess of arsenite was titrated after 10 min. with 0·021N-iodine (sodium–starch glycollate). A control determination was made without the tartaric acid. The periodate consumption was then determined from the difference titre. The results for some known mixtures are shown in Table 5, which also shows the improvement due to lowering the reaction temperature to 5°. Analytical results were determined after 5 min., and the value divided by 1·03 to correct for the slight over-oxidation.

TABLE 5. *Calibration of tartaric acid: interference tests.*

Temp.	Tartaric acid (mg.)	Glycollic acid (mg.)	Glyoxylic acid hydrate (mg.)	Oxalic acid dihydrate (mg.)	Periodate uptake (mmole per mmole of tartaric acid) at: 5 min.	15 min.	30 min.	60 min.
15°	20·0	—	—	—	1·36	1·83	2·18	2·48
15	50·0	—	—	—	1·15	1·40	1·68	1·80
15	—	5000	—	—	0·0011 *	0·0014 *	0·0017 *	0·002 *
15	—	—	50·0	—	0·2 *	0·35 *	0·5 *	0·64 *
15	—	—	—	50·0	Nil	Nil	Nil	Nil
15	50·0	5000	—	—	1·02	1·08	1·18	1·30
15	50·0	5000	50·0	50·0	1·13	1·25	1·32	1·57
5	50·0	5000	50·0	50·0	1·03	1·06	1·09	1·13
5	25·0	5000	25·0	10·0	1·02	1·05	1·09	1·11
5	25·0	500	10·0	10·0	1·05	1·08	1·12	1·16

* Expressed as uptake in mmole per mmole of solute.

(iv) *Determination of oxalic acid.* This was effected after the tartaric acid content had been ascertained. The sample was dissolved in water, and 0·1N-sodium metaperiodate added until 1·1 mmole of the oxidant were present for each mmole of tartaric acid. The solution was heated to 60°, and 5% calcium chloride hexahydrate solution (50 ml.) added. The solution was neutralised with aqueous ammonia and kept for 10 min., and glacial acetic acid (5 ml.) was added. The solution was stirred for 10 min., then filtered through a No. 4 sintered-glass crucible, and the precipitate was washed with water, 4N-acetic acid, and again water, and was extracted with 2N-sulphuric acid (10 × 10 ml.); the extract was titrated with 0·0954N-potassium permanganate at 60°.

Four solutions, each containing glycollic acid (4 g.), glyoxylic acid hydrate (50 mg.), tartaric acid (50 mg.) and oxalic acid dihydrate (severally 100, 50, 25, and 10 mg.) were estimated to contain 94·0, 47·5, 20·6, and 4·4 mg. of oxalic acid dihydrate respectively. Under carefully controlled conditions a loss of *ca.* 5 mg. was obtained in each determination irrespective of the oxalic acid content. Corrected estimations for the above solutions would therefore be 99 (99%), 52·5 (105%), 25·6 (102%), and 9·4 (94%), respectively.

(v) *Determination of formaldehyde.* Aliquot parts (1 ml.) of solution were heated at 100° for 30 min. with chromotropic acid reagent.[5] The colour was determined with a " Spekker " spectrophotometer (yellow filter, No. 606). The formaldehyde was then found from a calibration curve determined from known amounts of formaldehyde. Suitable control determinations showed glyoxylic acid to interfere, but only when its concentration was excessive: correction was made.

(vi) *Determination of formic acid.* A suitable volume of the irradiated solution was freeze-dried and the sublimate titrated with standard alkali. Glycollic acid in the sublimate was determined as described above, and the difference in these two determinations was expressed as formic acid. The other acids (glyoxylic, tartaric, and oxalic) present in the irradiated solutions were absent from the sublimate.

(vii) *Determination of carbon dioxide.* Nitrogen was passed into the irradiation vessel containing the solution which had been irradiated *in vacuo*. The gas, after passing through the solution and a reflux condenser, was bubbled through a two-stage sintered-glass absorption vessel containing N-barium hydroxide. The solution was boiled for an hour to expel carbon dioxide, which was estimated by back-titration of the alkali with 1·02N-hydrochloric acid (phenolphthalein). When oxygen was passed through the solution during irradiation, the waste gas-stream was passed through the absorption vessel containing barium hydroxide throughout the irradiation.

Preparation of Irradiated Samples.—0·1% Glycollic acid solution (4 l.) was prepared for irradiation and irradiated *in vacuo* and in the presence of oxygen as described in the preceding paper. A sample (*ca.* 5 ml.) was removed for determination of glycollic acid and formaldehyde, and the remainder freeze-dried for determination of glyoxylic, tartaric, and oxalic acid. A further batch was freeze-dried for determination of formic acid, and another 4 l. of irradiated solution was used to measure the carbon dioxide.

Analytical Results.—The analyses are summarised in Tables 1 and 2. The *G* values for the various products are given in Table 6.

TABLE 6. *G Values.*

Product	Vac.	In O_2	Product	Vac.	In O_2
Glycollic acid	−6·1	−4·5	Carbon dioxide	0·5	1·9
Glyoxylic acid	1·5	2·75	Formic acid	0·5	1·6
Tartaric acid	2·1	0·04			

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CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

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