983. *The Chemical Action of Ionising Radiations in Solution. Part XXIV.* Action of X-Rays* (200 kv) *on Aqueous Solutions of Acetic Acid and Glycollic Acid.*

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The chemical action of *X*-rays (200 kv) on deoxygenated aqueous solutions of acetic acid and glycollic acid has been studied, mainly as a function of pH and of the solute concentration, particularly to distinguish the reactions of "self-trapped" electrons ("polarons") from that of hydrogen atoms formed from the polarons by the reaction $(H_2O)^- + H^+ \longrightarrow H + H_2O$. The hydrogen atoms react by dehydrogenating α-positions to the carboxyl groups, giving molecular hydrogen; in the case of glycollic acid, the electron can attach itself to the OH group in the α-position according to: $(H_2O)^- + HO{\cdot}CH_2{\cdot}CO_2H \longrightarrow {\cdot}CH_2{\cdot}CO_2H + OH^- + H_2O$; with glycollic or acetic acid (which does not have an electron-attracting group in the α-position), the polaron can react to some extent with the carboxyl group which can then split up, leading to the formation of carbonyl radicals: in acetic acid $CH_3{\cdot}CO{\cdot}$ is formed, which leads to formation of biacetyl.

A NUMBER of papers have appeared in recent years on the radiation chemistry of simple carboxylic acids in aqueous solution, such as acetic acid,[1] formic acid,[2]

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* Part XXII, *J.*, 1959, 3913.

[1] (*a*) Garrison, Haymond, and Weeks, *Rad. Res.*, 1954, **1**, 97; (*b*) Garrison, Bennett, Cole, Haymond, and Weeks, *J. Amer. Chem. Soc.*, 1955, **77**, 2720; (*c*) Garrison, Haymond, Bennett, and Cole, *J. Chem. Phys.*, 1956, **25**, 1282.

[2] (*a*) Fricke and Hart, *J. Chem. Phys.*, 1934, **2**, 824; Hart, *J. Amer. Chem. Soc.*, 1951, **73**, 68; 1954, **76**, 4198; (*b*) Hart, *ibid.*, p. 4312; (*c*) Hart, *ibid.*, p. 4198; (*d*) Garrison, Bennett, and Jayko, *J. Chem. Phys.*, 1956, **24**, 631; (*e*) Garrison, Weeks, Ward, and Bennett, *ibid.*, 1957, **27**, 1214; (*f*) Smithies, Abstract of paper presented at International Congress of Radiation Research, Burlington, Vermont, U.S.A., 1958, p. 185; (*g*) Sutton and Galletand, *J. Chim. phys.*, 1959, **56**, 16.

hydroxy-acids (including pyruvic [3] and malic acid [4]), and mono- and tri-chloroacetic acids.[5]

Garrison *et al.*[1] found that irradiation of acetic acid with 40 Mev helium ions in air-free aqueous solutions gave hydrogen, hydrogen peroxide and succinic acid, with small yields of carbon dioxide, methane, ethane, and carbon monoxide; in oxygenated solutions, hydrogen, hydrogen peroxide, and glycollic, glyoxylic, and oxalic acid were the major products. Cobalt γ-irradiation of deaerated formic acid solutions was shown by Hart [2] to give mainly hydrogen and carbon dioxide; at higher concentration ($>10^{-1}$M), carbon monoxide and formaldehyde were also formed; in air-free solutions of formic acid at pH 4, oxalic acid is apparently also formed.[2g] Helium-ion irradiation of air-free formic acid solutions [2d] gives glyoxal, glyoxylic acid, and formaldehyde, with small amounts of carboxylic acids containing more than one carbon atom. Hydroxy-acids [3,4] yield keto-acids as the main organic product. Among the products formed in the irradiation of the chloroacetic acids [5] are hydrogen, hydrogen peroxide, and inorganic chloride; in the case of monochloroacetic acid, small amounts of glyoxylic acid, formaldehyde, and carbon monoxide were also found; in aerated solutions of monochloroacetic acid, glyoxylic acid and glycollic acid are the main organic products.

Irradiation of chloroacetic acid [5] seems to indicate that the chlorine atom has a specific influence. In view of this, we studied the irradiation of acetic acid and glycollic acid, some information on the radiation-induced reactions of these being available in the literature.

RESULTS

Irradiations were carried out with *X*-rays (200 kv) in deoxygenated aqueous solutions of the acids (see Experimental).

Fig. 1 shows the concentration dependence of the initial yields of hydrogen from 10^{-4}M- to 10·0M-glycollic acid at pH 1·0 and 4·2. Table 1 gives the corresponding yields of carbon dioxide and carbon monoxide, the latter occurring only, and in small amounts, at the higher concentrations. Glyoxylic acid was also produced from deaerated aqueous 10^{-2}—10^{-1}M-glycollic acid, the yields being greater at pH 5 than at pH 1.

TABLE 1. *Concentration dependence of the yields* (G-*values*) *of carbon dioxide and carbon monoxide in the irradiation* (X-*rays,* 200 kv) *of aqueous solutions of glycollic acid at* pH 1·0 *and* 4·5 *in the absence of oxygen.*

	Yields			
Glycollic acid	$G(CO_2)$		G(CO)	
concn. (M)	pH 1·0	pH 4·5	pH 1·0	pH 4·5
10^{-4}	0·10	0·15	—	—
10^{-3}	0·10	0·15	—	—
10^{-2}	0·10	0·15	—	—
0·1	0·15	0·35	0·02	0·02
0·5	0·35	1·10	0·07	0·09
1·0	0·71	1·93	0·09	0·14
3·0	1·44	3·53	0·13	0·26
7·0	2·35	6·26	0·25	0·34

It is readily seen from Fig. 1, that at pH 1·0, the yield of hydrogen increases up to a concentration of 10^{-2}M-glycollic acid, after which it remains about constant at $G(H_2) \sim 4{\cdot}3$ up to 10^{-1}M-glycollic acid and then decreases with further increase in solute concentration. At pH 4·5, however, $G(H_2) \sim 2{\cdot}5$ is at its maximum in 10^{-3}M-solutions and decreases continuously up to 7·0M-glycollic acid solutions.

The gaseous products from dilute aqueous acetic acid were hydrogen, methane, and carbon dioxide, with traces of carbon monoxide and ethane. Fig. 2 shows the variation of the yields of hydrogen with acetic acid concentration (10^{-4}—8·0M) which show maxima of $G(H_2)$ 3·9 at pH 1 and $G(H_2) \sim 2{\cdot}4$ at pH 4·5.

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[3] Johnson, Scholes, and Weiss, *J.*, 1953, 3091.

[4] Pratt and Putney, *Rad. Res.*, 1954, **1**, 234; 1956, **5**, 134.

[5] Hayon and Weiss, Proceedings of 2nd International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. **29**, p. 80.

Fig. 3 shows that on irradiation of air-free acetic acid solutions at pH 1·0 and 4·5 the yields of methane and carbon dioxide rise sharply with increase in acetic acid concentration. Figs. 4 and 5 show the effect of acetic acid and glycollic acid concentration, respectively, on the initial yields of hydrogen peroxide in air-free solutions at pH 1·0 and 4·5.

Fig. 1. *Dependence of the yield of hydrogen on the concentration of glycollic acid in the irradiation of deoxygenated aqueous solutions with* X-*rays* (200 kv); *dose rate* 3·37 × 10^{-7} ev/*N per min., at* pH 1·0 (○) *and* pH 4·5 (□).

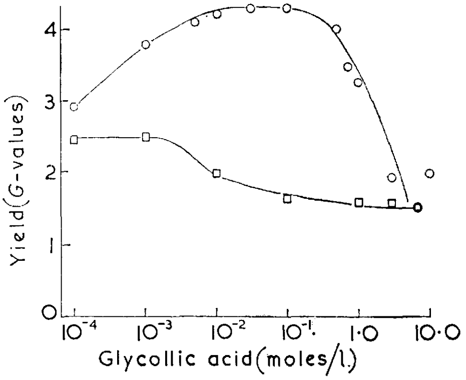
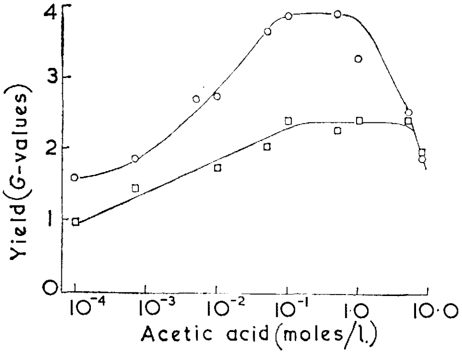


Fig. 2. *Dependence of the yields of hydrogen on the concentration of acetic acid in the irradiation of deoxygenated aqueous solutions with* X-*rays* (200 kv); *dose rate* 3·37 × 10^{-7} ev/*N per min., at* pH 1·0 (○) *and* pH 4·5 (□).



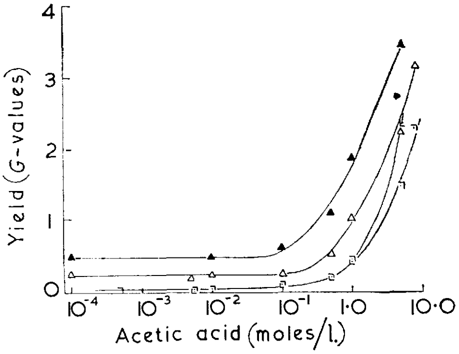


Fig. 3. *Dependence of the yields of methane and carbon dioxide on the concentration of acetic acid in the irradiation of deoxygenated aqueous solutions with* X-*rays* (200 kv); *dose rate* 3·37 × 10^{-7} ev/*N per min.*, CH_4 (⌝, pH 1·0; ⌞, pH 4·5): CO_2 (△, pH 1·0; ▲, pH 4·5).

Fig. 4. *Dependence of the yields of " molecular " hydrogen peroxide on the concentration of acetic acid in the irradiation of deoxygenated aqueous solutions with* X-*rays* (200 kv); *dose rate* 3·37 × 10^{-7} ev/*N per min., at* pH 1·0 (○) *and* pH 4·5 (□).

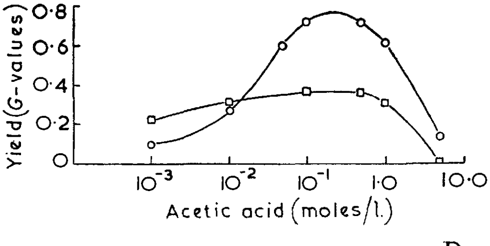
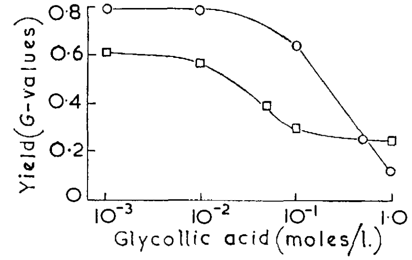


Fig. 5. *Dependence of the initial yields of " molecular " hydrogen peroxide on the concentration of glycollic acid in the irradiation of deoxygenated aqueous solutions with* X-*rays* (200 kv); *dose rate* 3·37 × 10^{-7} ev/*N per min., at* pH 1·0 (○) *and* pH 4·5 (□).



DISCUSSION

Absorption of radiation energy by water has been assumed to involve the reaction,[6] $H_2O \rightsquigarrow H + OH$, and the " molecular " process,[7] $2H_2O \rightsquigarrow H_2 + H_2O_2$.

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[6] Weiss, *Nature*, 1944, **153**, 748.

[7] Allen, *Ann. Rev. Phys. Chem.*, 1952, **3**, 57.

In the irradiation of glycollic acid solutions the following reactions have to be considered:

$$OH + HO\cdot CH_2\cdot CO_2H \longrightarrow HO\cdot CH\cdot CO_2H + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$H + HO\cdot CH_2\cdot CO_2H \longrightarrow HO\cdot CH\cdot CO_2H + H_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

In acid solutions [8] we have:

$$H + H^+ \rightleftarrows H_2^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$H_2^+ + HO\cdot CH_2\cdot CO_2H \longrightarrow HO\cdot CH\cdot CO_2H + H_2 + H^+ \quad . \; . \; . \; . \; . \quad (4)$$

Reactions (2) and (4) account for the yield of hydrogen obtained on irradiation of 10^{-2} to 10^{-1}M-glycollic acid at pH 1·0, where $G(H_2) = 4{\cdot}3$ (Fig. 1) based on taking $G_{H_2}{}^{w}$ 0·57 and $G_{H}{}^{w}$ 3·70.[9] With $>10^{-2}$M-glycollic acid at pH 1·0, not all the available hydrogen atoms undergo reactions (2) and (4), but the hydrogen yield increases with increasing solute concentration. However, at concentrations above 0·1M, the yield of hydrogen decreases again with increasing solute concentration, and the above reactions alone cannot account for the experimental results.

A similar behaviour was found on irradiation of air-free solutions of monochloroacetic acid [5] at pH 1·0: above 0·1M, the yield of hydrogen decreased, leading to a corresponding increase in the yield of inorganic chloride. It was suggested there that the precursors of the hydrogen atoms can, under certain conditions (depending on solute concentration, pH, etc.), react differently with the solute molecule.

Passage of ionising radiation through water is known to result in ionisation and excitation, giving some excited molecules (H_2O^*) and " self-trapped " electrons and holes, $(H_2O)^-$ and $(H_2O)^+$, *i.e.*, negative and positive polarons.[5]

The excited water molecules, which are apparently formed only in low yield, will dissociate:

$$H_2O^* \longrightarrow H + OH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

The polarons themselves are rather stable and behave differently from hydrogen atoms.[10] As in the reaction with monochloroacetic acid,[5] they should react with the glycollic acid according to the scheme:

$$(H_2O)^- + HO\cdot CH_2\cdot CO_2H \longrightarrow OH^- + CH_2\cdot CO_2H + H_2O \quad . \; . \; . \; . \; . \; . \quad (6)$$

It is suggested that this process is responsible for the decrease in the yield of hydrogen from $>0{\cdot}1$M-glycollic acid at pH 1·0. In very dilute solutions of glycollic acid (10^{-4}—10^{-3}M) at pH 4·2, it was found that $G(H_2) = 2{\cdot}5$. This is appreciably smaller than can be accounted for on the basis of the " molecular " hydrogen yield plus reaction (2), the yield for hydrogen atoms being taken as $G_{H}{}^{w}$ 2·9, in near-neutral solution. This difference is explained as due to favouring of reaction (6) even at lower solute concentration under conditions of the relatively high pH of 4·2. This points to a competition for the polaron according to reactions (6) and (7):

$$(H_2O)^- + H^+ \longrightarrow H_2O + H \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

Such competition have been established recently by Allan and Scholes.[11]

On irradiation of acetic acid solutions at pH 1·0, the yield of hydrogen (Fig. 2) increased steadily with increase in solute concentration from 10^{-4}M to 10^{-1}M, reaching a maximum of $G(H_2)$ 3·9. This value is less than the maximum yield of hydrogen, $G(H_2) \sim 4{\cdot}3$, expected on the basis of the number of available H atoms ($G_{H}{}^{w}$ 3·7) plus " molecular " hydrogen ($G_{H_2}{}^{w} = 0{\cdot}57$). Dehydrogenation of the methyl group by hydrogen atoms in acetic acid seems to be less favourable than that of methylene groups in glycollic or monochloroacetic acid. Indeed, on irradiation of air-free acetic acid solutions, hydrogen atoms or their precursors

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[8] Weiss, *Nature*, 1950, **165**, 728.

[9] Johnson and Weiss, *Proc. Roy. Soc.*, 1957, **240**, *A*, 189.

[10] Weiss, *Nature*, 1960, **186**, 751.

[11] Allan and Scholes, *Nature*, 1960, **187**, 218.

appear to react also with hydrogen peroxide (see Fig. 4). At >0·5M-acetic acid, the yield of hydrogen decreases with further increase in the concentration of the solute (Fig. 2), but here this decrease cannot be explained on the basis of reactions similar to reaction (6).

With carboxylic acids such as acetic acid which have no strong electron-accepting groups in the α-position, the polaron apparently reacts with the carboxyl group, *viz.*:

$$(H_2O)^- + CH_3{\cdot}CO_2H \longrightarrow (CH_3{\cdot}CO_2H)^- + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

giving an unstable ionic species which may dissociate in one of the following ways:

$$(CH_3{\cdot}CO_2H)^- \longrightarrow \left| \begin{array}{ll} \longrightarrow CH_3{\cdot}CO^- + OH & . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9a) \\ \longrightarrow CH_3{\cdot}CO{\cdot}O^- + H & . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9b) \\ \longrightarrow CH_3{\cdot}CO + OH^- & . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9c) \end{array} \right.$$

The $CH_3{\cdot}CO$ radical should afford carbonyl compounds; in fact we detected biacetyl and acetaldehyde in irradiated solutions of 1·0M-acetic acid (but not of less concentrated acid), the yield of total carbonyl corresponding to $G \sim 0{\cdot}3$, calculated on the basis of the extinction coefficient of acetaldehyde. Garrison *et al.*[1b] also found carbonyl compounds (acetone and acetaldehyde) on helium-ion irradiation of concentrated solutions of acetic acid (but not biacetyl). Hart [2b] found formaldehyde on cobalt γ-irradiation of 1·0M-formic acid solutions. In our experiments, there is some indication that acetone is formed in 1·0M-solutions at pH 4·5 but the spot obtained on the paper chromatogram was rather faint.

While hydroxyl radicals can cause dehydrogenation according to reaction (1) and (10):

$$OH + CH_3{\cdot}CO_2H \longrightarrow CH_2{\cdot}CO_2H + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

the $(H_2O)^+$ and possibly also the hydroxyl radical could oxidise the carboxyl group:

$$(H_2O)^+ + CH_3{\cdot}CO_2H \longrightarrow CH_3{\cdot}CO{\cdot}O + H_2O + H^+ \quad . \; . \; . \; . \; . \; . \quad (11)$$

this being followed by decomposition of the radical:

$$CH_3{\cdot}CO{\cdot}O \longrightarrow CH_3 + CO_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

The yield of carbon dioxide obtained on irradiation of glycollic acid and acetic acid does, in fact, increase appreciably at solute concentrations above 0·1M (Table 1 and Fig. 3). At high concentrations, in near-neutral solutions, the yields of carbon dioxide are somewhat higher than would be expected from the radicals only. This may be due to a chain reaction, as was suggested for irradiation of concentrated solutions of formic acid.[2f]

Reaction (12) can also account in part for the increase in the yield of methane on irradiation of solutions of >0·1M-acetic acid (Fig. 3), since the methyl radical can cause dehydrogenation:

$$CH_3 + CH_3{\cdot}CO_2H \longrightarrow CH_4 + CH_2{\cdot}CO_2H \quad . \; . \; . \; . \; . \; . \; . \quad (13)$$

and may dimerise:

$$2CH_3 \longrightarrow C_2H_6 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

The $CH_2{\cdot}CO_2H$ and the $HO{\cdot}CH{\cdot}CO_2H$ radical formed may also dimerise:

$$2CH_2{\cdot}CO_2H \longrightarrow (CH_2{\cdot}CO_2H)_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

$$2HO{\cdot}CH{\cdot}CO_2H \longrightarrow [CH(OH){\cdot}CO_2H]_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

$$CH_2{\cdot}CO_2H + HO{\cdot}CH{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H \quad . \; . \; . \; . \; . \quad (17)$$

It is noteworthy that tartaric acid has been detected in the γ-irradiation of deaerated aqueous solutions of glycollic acid.[12]

The yield of hydrogen obtained on irradiation of acetic acid solutions at pH 4·5 increases almost linearly up to 0·1M-acetic acid and then remains almost constant to 5·0M-solutions. In order to account for the low yields of hydrogen obtained at the lower concentrations of acetic acid at both pH 4·5 and 1·0, as compared with those from glycollic acid, one must

[12] Grant and Ward, *J.*, 1959, 2654, 2659.

assume that dehydrogenation of acetic acid by hydrogen atoms or H_2^+ ions in solutions of low pH does not occur readily and that the polaron and probably also hydrogen atoms may be involved in some other chemical reactions. The yields of " molecular " hydrogen peroxide formed on irradiation of air-free acetic acid solutions confirm this. Fig. 4 gives the initial yields of " molecular " H_2O_2 as obtained from 10^{-3} to 5·0M-acetic acid. At pH 1·0 it increases from *G* 0·1 in 10^{-3}M- to *G* 0·75 in 0·5M-acetic acid and then falls to *G* 0·15 in 5·0M-acid. This curve follows, more or less, that of the hydrogen yield at pH 1·0 (Fig. 2). The yield of hydrogen peroxide at pH 4·5 (Fig. 4) also increases with solute concentration from *G* 0·22 in 10^{-3}M-solutions to *G* 0·36 in 0·5M-acid and then decreases with further increase in acetic acid concentration.

Fig. 5 shows, for comparison, the yields of " molecular " hydrogen peroxide obtained on irradiation of glycollic acid solutions at pH 1·0 and 4·5 over the concentration range 10^{-3} to 1·0M. The yield of " molecular " hydrogen peroxide obtained on *X*-ray irradiation of dilute solutions of glycollic acid was found to be *G* 0·8 at pH 1·0 and *G* 0·62 at pH 4·5 (Fig. 5). As in the case of cobalt γ-irradiation,[13] the yield of " molecular " hydrogen peroxide on use of 200 kv *X*-rays is also smaller in neutral than in acid solution. It should be noted, however, that the yield of $G_{H_2O_2}{}^{w}$ 0·8 observed at pH 1·0 from glycollic and acetic acid is not the yield extrapolated to infinite dilution and is therefore smaller than the " true " value of $G_{H_2O_2}{}^{w}$ 1·06 obtained recently for 200 kv *X*-rays.[9,14]

The decrease in the yield of hydrogen peroxide with increase in solute concentration is explained as due to competition between the solute molecule and the precursors of hydrogen peroxide. However, the smaller yields of hydrogen peroxide obtained on irradiation at solute concentrations below 10^{-2}—10^{-1}M and at low pH, *e.g.*, in acetic acid (Fig. 4), can only be accounted for if one assumes that some reactive species (H_2O^- or H) decomposes the " molecular " hydrogen peroxide, whereas, at higher acetic acid concentrations, the hydrogen atoms or $(H_2O)^-$ react preferably with the solute.

At pH 4·5, the yield of " molecular " hydrogen peroxide obtained on irradiation of dilute solutions of acetic acid is much lower than from glycollic acid. It appears also that, in the presence of a solute which is a relatively poor acceptor of polarons and free radicals, *e.g.*, acetic acid, the back-reaction of hydrogen peroxide with the reactive species formed on irradiation is more prominent at higher than at the lower pH (Fig. 4), which suggests the reaction:

$$(H_2O)^- + H_2O_2 \longrightarrow OH^- + OH + H_2O \qquad . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

EXPERIMENTAL

Irradiations were carried out with a Victor Maximar *X*-ray therapy tube operated at 200 kv and 15 mA. The solutions (100 ml.) were irradiated in Pyrex-glass vessels, with a dose rate of $3{\cdot}37 \times 10^{-7}$ ev/*N* per ml. per min. as measured by the ferrous sulphate dosimeter, $G(Fe^{3+}) = 15{\cdot}5$. The yields of the products at solute concentration above 10^{-1}M were corrected for absorption by the solute.[15]

The *X*-radiation used had an effective wavelength of about 0·3 Å. The energy absorption per g. of the 10M-glycollic acid is 6% less than per g. of water; the density of the 10M-glycollic acid solution was found to be 1·05 (at 20°); the total energy absorption of 10M-glycollic acid solution per ml. is thus practically the same as that of water.

Triply distilled water was used throughout, obtained by distilling ordinary distilled water from potassium permanganate and then from sulphuric acid.

The solutions were evacuated by means of a mercury-diffusion pump backed by a two-stage oil-pump down to 10^{-3} mm. Hg.

" AnalaR " reagents were used. Adjustments of pH were carried out with sulphuric acid or with sodium hydroxide.

Gas Analysis.—The gases formed on irradiation were pumped from the vessel, by means of a

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[13] Allen and Holroyd, *J. Amer. Chem. Soc.*, 1955, **77**, 5852.
[14] Backhurst, Johnson, Scholes, and Weiss, *Nature*, 1959, **183**, 176.
[15] Spiers, *Brit. J. Radiol.*, 1946, **19**, 52.

Töpler pump, through a trap containing solid carbon dioxide–methanol. The gas was collected, measured, and determined by mass-spectrometry.

Determination of Hydrogen Peroxide.—The method of Egerton *et al.*[16] was used, which is based on the oxidation of ferrous to ferric thiocyanate, latter being measured colorimetrically at 450 mμ by a "Unicam" Spectrophotometer S.P. 500. Calibrations were always carried out simultaneously, a hydrogen peroxide solution standardised with titanium sulphate reagent[17] being used.

Detection of Carbonyl Compounds.—The presence of biacetyl and acetaldehyde on irradiation of aqueous solutions of glycollic acid above 0·1M at pH 1·0 and 4·5 has been confirmed by paper chromatography.[18] Total carbonyl was determined by Johnson and Scholes's method.[19]

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[*Received, March 28th,* 1960.]

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[16] Egerton, Everett, Minkoff, Rudrakanchana, and Salooja, *Analyt. Chim. Acta*, 1954, **10**, 422.

[17] Eisenberg, *Ind. Eng. Chem. Analyt.*, 1943, **15**, 327.

[18] Gasparic and Vecera, *J. Chromatography*, 1958, **1**, XVIII.

[19] Johnson and Scholes, *Analyst*, 1954, **79**, 217.