

443. *Chemical Action of Ionising Radiations in Solution. Part XXI.*
The Action of ^{60}Co γ -Radiation on Aqueous Solutions of Ethylene at
Different Pressures.*

By P. G. CLAY, G. R. A. JOHNSON, and J. WEISS.

^{60}Co γ -Irradiation of water saturated with ethylene (1 atm.), in the absence of oxygen, yields aldehydes, mainly acetaldehyde and *n*-butyraldehyde, and hydrogen peroxide, together with an oily polymer. From water, saturated with different ethylene-oxygen mixtures, the irradiation products are: acetaldehyde, formaldehyde, glycollaldehyde, hydrogen peroxide, and relatively small amounts of an organic hydroperoxide. Their formation at different ratios of [ethylene]/[oxygen], at different pH values, and in the presence of added ferrous salt has been studied. Irradiations of aqueous ethylene-oxygen solutions at higher pressures (up to 10 atm.) showed that the products and their yields, under these conditions, are not markedly different from those at lower pressures. This finding is contrary to that of Henley *et al.*^{1, 2}

RECENT investigations have provided much information about the reactions of various functional groups when compounds in aqueous solution are subjected to the action of ionising radiations.³ Little attention has been paid, however, to the reactions occurring when solutions of unsaturated compounds are irradiated in the presence of molecular oxygen, except for the polymerisation of certain vinyl compounds, which occurs on irradiation of their solutions in the absence of oxygen.^{cf. 3} We have now studied the action of ^{60}Co γ -rays on aqueous solutions of ethylene as part of an investigation into the effects of ionising radiations on simple unsaturated compounds.

RESULTS

Irradiations in the Absence of Oxygen.—Irradiation of ethylene-saturated water in absence of oxygen yielded an oily polymer and a mixture of aldehydes, in which acetaldehyde and *n*-butyraldehyde were identified by paper chromatography of their 2:4-dinitrophenylhydrazones. Some spots with R_F values greater than those of acetaldehyde and butyraldehyde

* Part XX, *J.*, 1957, 1358.

¹ Henley and Schwartz, *J. Amer. Chem. Soc.*, 1955, **77**, 3167.

² Henley, Schiffries, and Barr, *Ass. Inst. Chem. Eng. J.*, 1956, **2**, 211.

³ Collinson and Swallow, *Chem. Rev.*, 1956, **56**, 471.

were also observed, indicating that other longer-chain aldehydes were present, but these have not been identified. Hydrogen peroxide was also formed. The yields of total aldehyde and hydrogen peroxide were linear with radiation dose up to the highest doses used [$\sim 12 \times 10^{-6}(\text{ev/N}) \text{ ml.}^{-1}$] having the values: $G(\text{H}_2\text{O}_2) = 0.40 \pm 0.10$ and $G(\text{total aldehyde}) = 0.24 \pm 0.05$ at pH 1.2; and $G(\text{H}_2\text{O}_2) = 0.28 \pm 0.10$ and $G(\text{total aldehyde}) = 0.090 \pm 0.030$ at pH 5.0 (where G = number of molecules formed per 100 ev of radiation-energy absorbed).

TABLE 1. Irradiation of aqueous solutions of ethylene-oxygen mixtures at pH 1.2.

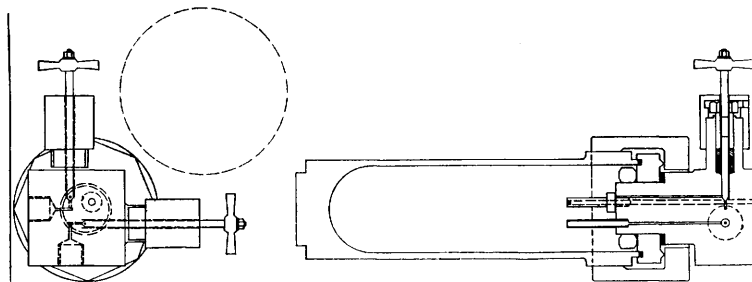
Dependence of initial yields on the [ethylene]/[oxygen] ratio in the gaseous phase (total pressure, 1 atm.). Dose rate: $1 \times 10^{-7} (\text{ev/N}) \text{ ml.}^{-1} \text{ min.}^{-1}$.

| Ratio $[\text{C}_2\text{H}_4]/[\text{O}_2]$ | G values (molecules formed per 100 ev) | | | | |
|---|--|---|------------------------|---------------------------------------|--|
| | $(\text{H}\cdot\text{CHO} + \text{CH}_3\cdot\text{CHO})$ | $\text{CH}_2(\text{OH})\cdot\text{CHO}$ | H_2O_2 | $\text{R}\cdot\text{O}\cdot\text{OH}$ | |
| 0.11 | 1.7 | 1.8 | 2.8 | 0.6 | |
| 1.00 | 2.4 | 2.4 | 2.4 | 0.4 | |
| 3.00 | 3.0 | 2.5 | 2.6 | 0.4 | |
| 9.00 | 3.0 | 2.4 | 2.4 | 0.3 | |

Some experiments were carried out in the presence of ferric ammonium sulphate, formation of ferrous ion being determined by complex-formation with *o*-phenanthroline and measurement of the absorption at 510 μ . At a concentration of $5 \times 10^{-2}\text{M}$ -ferric ion $G(\text{Fe}^{2+}) = 6.0$ and $G(\text{total aldehyde}) = 0.70$; at 10^{-3}M -ferric ion $G(\text{Fe}^{2+}) = 1.0$ and $G(\text{total aldehyde}) = 0.70$.

Irradiations in Presence of Oxygen.—The products detected in irradiated ethylene-oxygen solutions were acetaldehyde, formaldehyde, glycollaldehyde and hydrogen peroxide. An unidentified organic peroxide was also detected in low yields ($G \simeq 0.4$).

FIG. 1. Steel bomb used for irradiation of solutions of oxygen-ethylene mixtures under pressure.



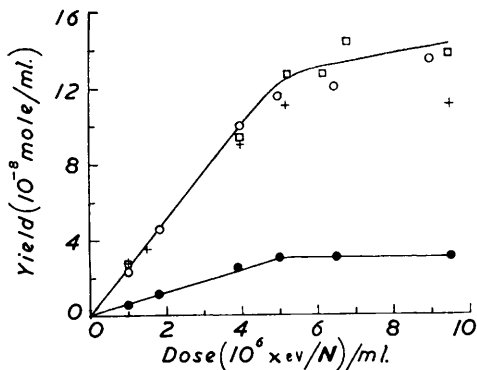
As preliminary quantitative experiments showed that the yields of the products depended, to some extent, upon the relative concentrations of ethylene and oxygen in solution we studied the effect of the ratio [ethylene]/[oxygen] on the yields. Table 1 gives the initial yields (G values) of the products at values of this ratio ranging from 0.11 to 9.0; over this range, the yields are relatively insensitive to changes in the ethylene concentration. For the quantitative experiments, therefore, a gas mixture of [ethylene]/[oxygen] = 3.0 was used, corresponding to solution concentrations of ethylene and oxygen of $3 \times 10^{-3}\text{M}$ and $3 \times 10^{-4}\text{M}$, respectively, as calculated from the known solubilities of these gases at 19°. Also, the concentration of ethylene was determined bromometrically and that of oxygen by polarography; the values obtained were in good agreement with the above calculated values.

In view of a report^{1,2} that high yields of acetaldehyde ($G \simeq 60$) were obtained when solutions of ethylene-oxygen were irradiated at pressures above 8 atm., solutions of a 1:1 mixture at a total pressure of 10 atm. have been investigated. The yields of the products obtained were: $G(\text{H}_2\text{O}_2) = 2.6$, $G(\text{acetaldehyde} + \text{formaldehyde}) = 1.3$, and $G(\text{glycollaldehyde}) = 1.5$. This confirms the results obtained on varying the ratio ([ethylene]/[oxygen]), and that, contrary to the findings of Henley *et al.*,^{1,2} this increase in the ethylene concentration does not lead to a chain reaction and has, indeed, very little effect on the yield of the products.

The yields were determined as a function of total radiation dose at pH 1.2 (Fig. 2), 2.5, 3.2, 5.5 (Fig. 3), and 7.5. At all these values the yield-dose curves were initially linear but eventually showed a relatively sharp decrease in the yield per unit dose, attributable to the utilisation, by

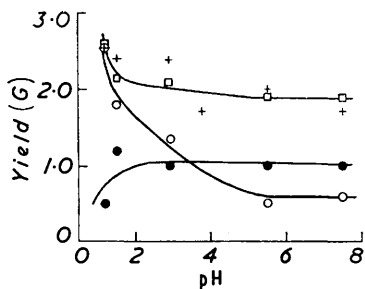
the radiation-induced reactions, of all the oxygen originally present in solution. Diffusion of oxygen into the solution is relatively slow, and when practically all the original oxygen has

FIG. 2. Irradiation of aqueous solutions of ethylene-oxygen mixtures (3:1 in the gaseous phase; total pressure 1 atm.) with ^{60}Co γ -rays.



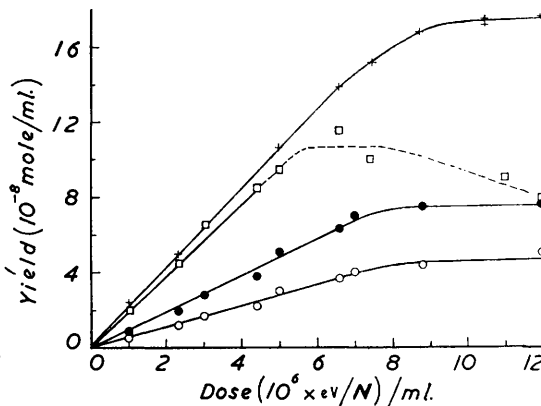
Dependence of yield of hydrogen peroxide (□), glycollaldehyde (+), acetaldehyde (○), and formaldehyde (●) on total radiation dose at pH 1.2.

FIG. 4. Irradiation of aqueous solutions of ethylene-oxygen mixtures (3:1 in the gaseous phase; total pressure 1 atm.) with ^{60}Co γ -rays.



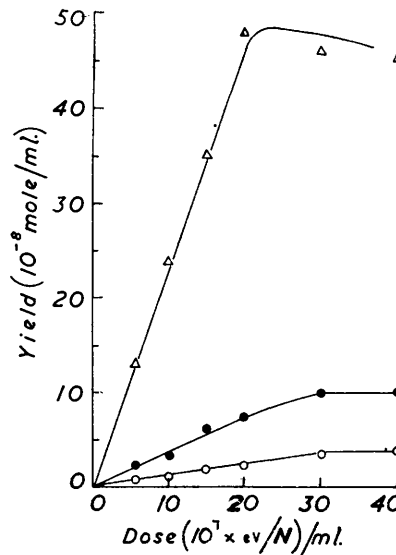
pH-Dependence of the initial yields of hydrogen peroxide (□), glycollaldehyde (+), acetaldehyde (○), and formaldehyde (●).

FIG. 3. Irradiation of aqueous solutions of ethylene-oxygen mixtures (3:1 in the gaseous phase; total pressure 1 atm.) with ^{60}Co γ -rays.



Dependence of yield of hydrogen peroxide (□), glycollaldehyde (+), acetaldehyde (○), and formaldehyde (●) on total radiation dose at pH 5.5.

FIG. 5. Irradiation of aqueous solutions of ethylene-oxygen mixtures (3:1 in the gaseous phase; total pressure 1 atm.) containing ferrous sulphate (10^{-3}M) at pH 1.2.



Yield-dose dependence of the products: ferric ion (Δ), acetaldehyde (○), and formaldehyde (●).

been used the irradiation proceeds virtually in the absence of oxygen. The results (Fig. 2) therefore indicate that all the oxygen originally present in solution is used up, at pH 1.2, after a dose of about $5 \times 10^{-6}(\text{ev/N}) \text{ ml.}^{-1}$. Since the initial oxygen concentration is $3 \times 10^{-4}\text{M}$,

this gives a value for the rate of oxygen utilisation $G(\text{O}_2) \simeq 6.0$. Similarly, at pH 5.5 $G(\text{O}_2) \simeq 4.0$.

The pH-dependence of the initial G -values for the formation of the different products is shown in Fig. 4; each value was taken from a yield-dose plot. At pH 1.2, the major products are acetaldehyde and glycollaldehyde, in almost equal amounts; as the pH is increased, the yield of these products decreases and the yield of formaldehyde increases. At pH 5.5 the major product is glycollaldehyde; less acetaldehyde and formaldehyde are formed. The total yield of organic products falls from $G \simeq 5.9$ at pH 1.2 to $G \simeq 3.6$ at pH 5.5. The yield of hydrogen peroxide also falls from $G = 2.6$ at pH 1.2 to $G = 1.9$ at pH 5.5 and remains about the same up to pH 7.5.

Ferrous sulphate (10^{-3} and 10^{-2}M) when added to the solutions (at pH 1.2), before irradiation, altered the yields of acetaldehyde and formaldehyde from the values of $G(\text{acetaldehyde}) = 2.5$ and $G(\text{formaldehyde}) = 0.5$ to 1.2 and 3.8, respectively; glycollaldehyde was not then formed. The yield of ferric ion corresponded to $G(\text{Fe}^{3+}) = 23.0$. The yields of these products, obtained in the presence of ferrous salt, were linear with dose up to the point at which all the oxygen in the solution had been consumed (Fig. 5).

DISCUSSION

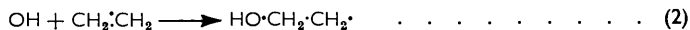
The net result of the absorption of ionising radiations by water is the formation of hydrogen atoms and hydroxyl radicals⁵ and of the molecular products H_2 and H_2O_2 .⁶ The yields are related by the stoichiometry:

$$2G^w(\text{H}_2) + G^w(\text{H}) = 2G^w(\text{H}_2\text{O}_2) + G^w(\text{OH}) \quad \dots \dots \dots (1)$$

where the coefficients $G^w(\text{X})$ refer to the yields in molecules of X per 100 ev of radiation energy absorbed by the water. There is no general agreement on the exact values of these coefficients and they probably depend on the pH of the irradiated solution and on the concentration and chemical nature of any solute present. For the present discussion, values of $G^w(\text{H}_2\text{O}_2) = 0.8$, $G^w(\text{OH}) = 2.7$, and $G^w(\text{H}) = 3.8$ will be assumed.^{7,8}

Ethylene has disadvantages as a solute in radiation studies. It is inconvenient to handle, and its relatively low solubility ($4 \times 10^{-3}\text{M}$ at 1 atm. and 15°) makes it difficult to study the effect of solute concentration on yield. The latter disadvantage is serious, since the solute concentration is an important factor in determining the processes occurring during irradiation of a solution of organic compounds.⁹ The ethylene-oxygen system, studied at concentrations between 10^{-4} and 10^{-2}M -ethylene, showed little dependence of yield on concentration, so we assumed that at the solute concentration used for most of the quantitative experiments ($3 \times 10^{-3}\text{M}$), attack on the ethylene will be due mainly to free radicals and that most of the available hydroxyl radicals will react with the ethylene. Oxygen concentration has relatively little influence on the yields, these being linear with dose under all conditions studied until all, or nearly all, the oxygen present has been consumed. However, complete removal of oxygen, either by continued irradiation or by deaeration beforehand, markedly influenced the course of the reaction.

The most probable initial reaction is addition of an OH radical, produced by irradiation to the ethylene double bond:



This type of reaction has been well established from polymerisation studies;¹⁰ the alternative reaction, suggested by Henley *et al.*,² *viz.*,

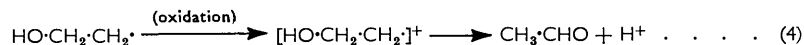


⁴ Kolthoff and Lingane, "Polarography," Vol. 2, p. 552 (New York, 1952).
⁵ Weiss, *Nature*, 1944, **153**, 748.
⁶ Allen, Hochanadel, Ghormley, and Davis, *J. Phys. Chem.*, 1952, **56**, 575.
⁷ Johnson and Weiss, *Proc. Roy. Soc.* 1957, *A.*, **240**, 189.
⁸ Hochanadel and Lind, *Ann. Rev. Phys. Chem.*, 1957, **7**, 83.
⁹ Johnson, Scholes, and Weiss, *Nature*, 1956, **177**, 883.
¹⁰ Dainton, *J. Phys. Colloid Chem.*, 1948, **52**, 490.

is unlikely on energetic grounds (cf. Walsh¹¹). In the absence of oxygen, addition of hydrogen atoms to ethylene may also occur:

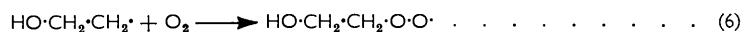
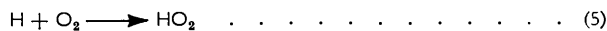


The radicals formed in reactions (2) and (3) may react with monomeric ethylene resulting in polymerisation, and the oily polymer observed in absence of oxygen is presumably so formed. Oxidation of the radical formed in reaction (2), which may occur to some extent as an alternative to reaction of the radical with ethylene, could yield, for example, acetaldehyde:

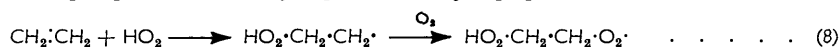
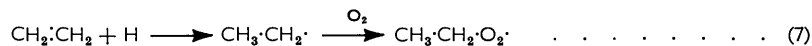


Oxidative termination of the polymerisation could produce higher aldehydes (butyraldehyde, etc.). The enhancement of the aldehyde yields at low pH suggests that the species H_2^+ may be involved in the oxidation step.¹² The effect of ferric ion, which increases the yield of acetaldehyde, is attributable to the enhancement of reaction (4) at the expense of the polymerisation (cf. Dainton¹³). No detailed study of these reactions has been made.

Oxygen in the irradiated solution qualitatively alters the course of the reaction: it will add to hydrogen atoms and to the free radical formed in reaction (2):



If one molecule of oxygen is required for the formation of each molecule of organic product and of hydrogen peroxide, the extent of oxygen consumption would correspond to $G(\text{O}_2) = 7.4$ at pH 1.2, and $G = 4.2$ at pH 5.5 [these figures allow for a "molecular yield" of hydrogen peroxide of $G^w(\text{H}_2\text{O}_2) = 0.8$, which would be formed without using any oxygen]. The observed values for oxygen utilisation at pH 5.5, *viz.*, $G(\text{O}_2) = 4.0$, is in quite good agreement with the above assumption and this confirms also that the measured products are the only ones formed here. At pH 1.2 the agreement between the observed value, *viz.*, $G(\text{O}_2) = 6.0$, and that calculated is less satisfactory. There are no reasons to believe that the products at this pH are different; rather does this discrepancy reflect some ambiguity regarding the molecular oxygen consumption in the formation of acetaldehyde, whose yield is greater at the lower pH. While reaction (7) followed by some reduction step would require one molecule of O_2 per acetaldehyde molecule, formation of acetaldehyde *via* the radical $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ (eqn. 2), with subsequent dehydrogenation by O_2 to give HO_2 , would proceed without net consumption of molecular oxygen. The experimental values for consumption of oxygen lie in each case within the calculated limits derived from these two routes; *i.e.*, for pH 1.2, $G(\text{O}_2) \sim 5.0-7.5$ and for pH 5.5 $G(\text{O}_2) \sim 3.9-4.2$. The relatively high total yield of organic product ($G \simeq 5.9$, at pH 1.2) is greater than the maximum value which may be assumed for $G(\text{OH}) (\simeq 3.6)$ under these conditions. The occurrence of a short-chain reaction, involving primary attack by OH radicals only, could lead to a total yield greater than that corresponding to $G^w(\text{OH})$, but is unlikely in view of the observed small dependence of the yield on ethylene concentration. Therefore, it appears that the high yields, particularly in acid solution, are associated with attack on ethylene by either hydrogen atoms and/or HO_2 radicals:¹⁴



Even in the presence of oxygen, certain organic solutes can, under suitable conditions, compete for the hydrogen atoms produced in the radiolysis.

¹¹ Walsh, *Trans. Faraday Soc.*, 1946, **42**, 282.

¹² Weiss, *Nature*, 1950, **165**, 728.

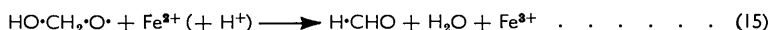
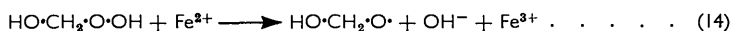
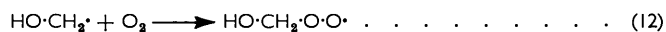
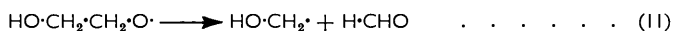
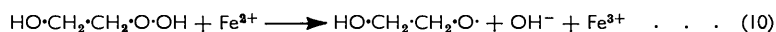
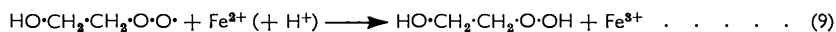
¹³ Collinson, Dainton, and McNaughton, *Trans. Faraday Soc.*, 1957, **53**, 489.

¹⁴ Hargrave and Morris, *ibid.*, 1956, **52**, 89.

The observed products, glycollaldehyde, acetaldehyde, and formaldehyde, presumably arise from mutual oxidation-reduction reactions between the possible primary species $\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{O}$ and $\text{HO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{O}$, but little is known about the reactions of such radicals. These reactions appear to be markedly influenced by the pH of the irradiated solutions. Yields of the primary products from water are probably pH-dependent. Also, participation of hydrogen atoms and/or the HO_2 radical may lead to pH-dependent reactions owing to the different possibilities for reaction of this radical and its anion O_2^- ($\text{HO}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^-$) and to the equilibrium $\text{H} + \text{H}^+ \rightleftharpoons \text{H}_2^+$.

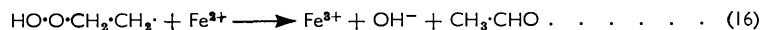
The formation of formaldehyde from ethylene is of interest, since this process is somewhat analogous to the radiation-induced formation of mucondialdehyde from benzene¹⁵ and of formylkynurenin from tryptophan.¹⁶ The opening of a double bond, *i.e.*, $(>\text{C}=\text{C}<) \longrightarrow (>\text{C}=\text{O}) + (\text{O}=\text{C}<)$, appears to be a general reaction under these conditions, and apparently occurs only in the presence of molecular oxygen.

From ethylene solutions irradiated in the presence of ferrous salt, the major product is formaldehyde, with smaller quantities of acetaldehyde. The most probable mode of formation of formaldehyde under these conditions involves reactions (2) and (6) followed by:



Reactions (9) and (10) are analogous to those assumed to explain the effect of certain other organic solutes in increasing the yield of ferrous oxidation.^{17,18} Reaction (11), which involves fission of the C-C bond, is similar to a reaction assumed by Hawkins¹⁹ to explain the formation of dodecane-2:11-dione from 2-ethylcyclopentyl hydroperoxide by reduction with ferrous sulphate solution.

Formation of acetaldehyde under these conditions can be most readily accounted for by reaction (8) followed by:



In order to obtain more information on this point, the products were studied under conditions where OH radicals but not HO_2 radicals are formed. A solution of ethylene-oxygen (3:1 in the gas phase; total pressure 1 atm.; pH = 1.2) containing ferrous sulphate (10^{-3}M) was treated with a solution containing 7×10^{-6} moles of hydrogen peroxide. Analysis of the aldehydes formed, by chromatography of their dinitrophenylhydrazones, showed the presence of formaldehyde but not acetaldehyde. This suggests that the HO_2 radical may be essential for the formation of acetaldehyde in this system.

According to the suggested mechanism, the presence of ethylene should result in an increase in the ferrous oxidation yield equivalent to $2\{G(\text{H}\cdot\text{CHO}) - G(\text{CH}_3\cdot\text{CHO})\}$ above the yield in its absence [*i.e.*, $G(\text{Fe}^{3+}) = 15.5$]. For the measured values of $G(\text{H}\cdot\text{CHO}) = 3.8$ and $G(\text{CH}_3\cdot\text{CHO}) = 1.2$, this would give $G(\text{Fe}^{3+}) = (15.5 + 5.2) = 20.7$, a value somewhat lower than the measured $G(\text{Fe}^{3+}) \sim 23$. This can be easily deduced as follows: In the absence of ethylene one OH produces one Fe^{3+} ; in the presence of ethylene (and oxygen), according to reaction (9)–(15), one OH gives five Fe^{3+} , with the simultaneous

¹⁵ Daniels, Scholes, and Weiss, *J.*, 1956, 832.

¹⁶ Jayson, Scholes, and Weiss, *Biochem. J.*, 1954, 57, 386.

¹⁷ Dewhurst, *Trans. Faraday Soc.*, 1952, 48, 905.

¹⁸ Johnson, Scholes, and Weiss, *J.*, 1953, 3091.

¹⁹ Hawkins, *J.*, 1955, 3463.

formation of 2 H·CHO; thus there is a net increase of 4 Fe³⁺ per OH with the simultaneous formation of 2 H·CHO, *i.e.*, additionally formed 2 Fe³⁺ per 1 H·CHO.

One HO₂ yields 3 Fe³⁺ in the absence of ethylene; in the presence of ethylene, one HO₂ gives [via the intermediate HO·O·CH₂·CH₂ formed according to equation (8) followed by reaction (16)] one Fe³⁺ leading to the formation of one CH₃·CHO. Thus we have a net decrease of 2 Fe³⁺ per CH₃·CHO formed.

EXPERIMENTAL

Preparation of Solutions.—Ordinary distilled water was distilled from alkaline potassium permanganate and then from dilute phosphoric acid. The pH of the pure water was 5.5 and was adjusted to lower pH values by adding sulphuric acid.

Ethylene and oxygen (British Oxygen Co. Ltd.; medical grade) were used directly from the cylinders.

(i) *Irradiations at 1 Atm. Pressure.*—The solutions were prepared and irradiated in cylindrical "Pyrex" glass vessels fitted with a side-arm and a tap. The vessel, containing 50 ml. of water, and the apparatus used for preparing the gas solutions were deaerated by repeated pumping with a 2-stage oil pump and shaking. For experiments in its presence, oxygen gas was then admitted to the required pressure (mercury manometer) and the irradiation vessel filled thereat. The apparatus was then pumped out, and ethylene admitted to a pressure of 1 atm. and the vessel was filled to the required pressure with ethylene. For experiments in the absence of oxygen, before the vessel was filled, the ethylene was condensed in a liquid nitrogen trap and freed from any non-condensable gases by repeated pumping and melting. After the vessels had been filled, the solutions were allowed to become saturated with the gas by standing for at least 12 hr., with occasional shaking.

(ii) *Irradiations at Higher Pressures.*—The irradiations were carried out in a steel "bomb" fitted with a screw cap and two valves (Fig. 1). A "Pyrex" glass vessel containing water was placed inside the "bomb" and the ethylene and oxygen were admitted to the required pressure. Saturation was brought about by shaking for at least 12 hr.

Determination of Ethylene.—A solution of potassium bromide and potassium bromate was added to an aliquot part of the ethylene solution and to an equal volume of water. After acidification with sulphuric acid, the excess of bromine in each solution was determined by adding an excess of a potassium bromide solution and measuring the absorption of the Br₃⁻ ion at 265 mμ. The ethylene concentration was calculated from the difference between the absorptions of the two solutions by use of a calibration curve prepared by measuring the absorption of standard bromine solutions.

Irradiation Arrangements.—We used a 500 Curie ⁶⁰Co γ-ray source of the type described by Ghormley and Hochanadel.²⁰ The dose rate, measured by the ferrous sulphate dosimeter (assuming 15.5 molecules of ferric ion to be formed per 100 ev of energy absorbed), was 1.0 × 10⁻⁷ (ev/N) ml.⁻¹ min.⁻¹.

Identification and Determination of the Products.—(i) Hydrogen peroxide was identified and determined by the titanium sulphate reagent.²¹

(ii) Organic hydroperoxides do not, in general, react with titanium sulphate reagent but oxidise iodide and react with ferrous thiocyanate. Determination of total peroxide in the irradiated solutions by means of potassium iodide²² and by ferrous thiocyanate²³ showed, under certain conditions, the presence of an organic hydroperoxide in addition to hydrogen peroxide. The identity of the hydroperoxide has not been established, the yields always being too low. Its rate of reaction with iodide was measured and found to be practically identical with that of hydrogen peroxide, whereas methyl hydroperoxide and ethyl hydroperoxide (prepared by the methods of Rieche²⁴ and Minkoff,²⁵ respectively) reacted much more slowly under the same conditions.

²⁰ Ghormley and Hochanadel, *Rev. Sci. Instr.*, 1951, **22**, 473.

²¹ Eisenberg, *Ind. Eng. Chem. Anal.*, 1943, **15**, 327.

²² Hochanadel, *J. Phys. Chem.*, 1952, **56**, 587.

²³ Egerton, Everett, Minkoff, Rudrakanchana, and Salooja, *Analyt. Chim. Acta*, 1954, **10**, 422.

²⁴ Rieche and Hitz, *Ber.*, 1929, **62**, 2458.

²⁵ Minkoff, *Proc. Roy. Soc.*, 1954, *A*, **224**, 176.

(iii) Formaldehyde and acetaldehyde were identified as their 2 : 4-dinitrophenylhydrazones, their ethanolic solutions being used for paper chromatography according to Meigh.²⁶

For determination of total aldehyde, Johnson and Scholes's²⁷ method was used. The ratio (formaldehyde/acetaldehyde) was determined by running, on a paper chromatogram, a solution of the dinitrophenylhydrazones of the irradiation products, eluting the developed spots into 5 ml. of ethanol, and comparing the absorption of the solutions at 360 m μ in a Unicam spectrophotometer. The concentrations of acetaldehyde and formaldehyde in the irradiated solutions were calculated from the expressions:

$$[\text{acetaldehyde}] = D/\{RE(\text{H}\cdot\text{CHO}) + E(\text{CH}_3\cdot\text{CHO})\}$$

and $[\text{formaldehyde}] = R[\text{acetaldehyde}]$, where D = total optical density determined by Johnson and Scholes's method, $R = [\text{H}\cdot\text{CHO}]/[\text{Me}\cdot\text{CHO}]$, and $E(\text{H}\cdot\text{CHO})$ and $E(\text{Me}\cdot\text{CHO})$ are the molar extinction coefficients of the formaldehyde and acetaldehyde dinitrophenylhydrazones, respectively, as determined by Johnson and Scholes's method.

(iv) Glycollaldehyde with dinitrophenylhydrazine gives glyoxal dinitrophenylhydrazone which, like other dialdehyde hydrazones, gives a purple-blue colour in strongly alkaline solution. Since this dinitrophenylhydrazone is relatively insoluble in carbon tetrachloride, benzene was used to extract it from the aqueous solution. The irradiated solution was treated with dinitrophenylhydrazine reagent and extracted with benzene; addition of ethanolic sodium hydroxide to the extract gave a blue colour, indicating the presence of either glyoxal or glycollaldehyde in the irradiated solution. The absorption spectrum of the alkaline ethanol-benzene solution was identical with that of glyoxal dinitrophenylhydrazone under the same conditions.

That one of the irradiation products was glycollaldehyde (not glyoxal) was shown by the method of Dechary *et al.*²⁸ This depends upon the formation of a coloured derivative when solutions of this carbonyl compound are treated with 2 : 3-diaminophenazine reagent. Glyoxal reacts in acetic acid solution, but glycollaldehyde only under conditions where conversion into glyoxal can occur, *i.e.*, in concentrated sulphuric acid.

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²⁶ Meigh, *Nature*, 1952, **170**, 577.

²⁷ Johnson and Scholes, *Analyst*, 1954, **77**, 937.

²⁸ Dechary, Kun, and Pitot, *Analyt. Chem.*, 1952, **26**, 449.
