258. *Chemical Action of Ionising Radiations in Solution. Part XX.* Action of X-Rays* (200 kv) *on Ethanol in Aqueous Solution.*

By G. G. Jayson, G. Scholes, and J. Weiss.

The action of *X*-rays (200 kv) on ethanol in aqueous solution in the presence of oxygen gave only acetaldehyde; in deaerated solutions, butane-2 : 3-diol was also produced. Quantitative studies have been carried out under various experimental conditions and the effects of pH and concentration of the solute have been examined.

A mechanism for the radiation chemistry of aqueous-ethanol solutions in the presence and in the absence of oxygen has been proposed. The detailed study of this system has led to some new aspects regarding the modes of formation of hydrogen peroxide from OH radicals in aqueous systems.

In deaerated ethanol solutions, a feature of interest is the importance of the dehydrogenation of ethanol by hydrogen atoms : $CH_3{\cdot}CH_2{\cdot}OH + H \longrightarrow CH_3{\cdot}CH(OH) + H_2$.

The chemical effects of ionising radiations in dilute aqueous solutions are due, primarily, to the net process,[1] $H_2O \rightsquigarrow H + OH$, and, with hard *X*-rays, to a smaller extent,[2] to $2H_2O \longrightarrow H_2 + H_2O_2$. The study of aqueous systems of organic compounds [3] may yield more information about the primary processes since in inorganic systems the same product is often formed by different routes. This became increasingly apparent in our studies of aqueous ethanol, the results of which are now presented.

Irradiation with *X*-rays [4] or ^{60}Co γ-rays [5] of aqueous ethanol leads to acetaldehyde, the yield of which is greater when dissolved oxygen is present. Some effects of γ-rays on aqueous methyl alcohol have been briefly reported by McDonell; [6] in deaerated solutions, formaldehyde and ethylene glycol have been found.

Results

Experiments in the Presence of Oxygen.—In ethanol solutions irradiated in the presence of molecular oxygen, acetaldehyde was the only detectable oxidation product; tests for acetic acid, butane-2 : 3-diol, ethylene glycol, glycolaldehyde, ethyl hydroperoxide, diethyl peroxide, peracetic acid, and ethyl acetate were negative.

The dependence of the yields of acetaldehyde and of hydrogen peroxide on radiation dose was investigated. $3{\cdot}4 \times 10^{-2}$M-Ethanol (100 ml.; pH 1·2), saturated with oxygen (1 atm.), was irradiated at 18—20° with *X*-rays in Pyrex glass vessels similar to those previously described.[7] Up to total doses of about 5×10^{-6} ev/*N* per ml., the yields of acetaldehyde and hydrogen peroxide were linear functions of dose and were $G(H_2O_2) = 4{\cdot}15$ and G(acetaldehyde) = 2·6 (G = molecules/100 ev).

With air-equilibrated ethanol solutions at pH ~1, it is known that, after a certain dose, a change ("break") in the rate of hydrogen peroxide formation occurs, owing presumably to the exhaustion of the dissolved molecular oxygen in the solution. With these ethanol solutions, although the air "break-point" was very marked, no satisfactory reproducibility could be obtained in this particular region; as the exact position of the break-point is controlled by the amount of dissolved oxygen and this in turn depends on the temperature, it seemed likely that the absence of efficient temperature control was the responsible factor. This was confirmed by the following experiments in which a constant-temperature irradiation vessel was used, water from a thermostat being passed around an outside jacket both before and during the irradiation. The experiments were then fully reproducible. Fig. 1 shows the yield–dose plot from irradiations of air-equilibrated ethanol solutions ($3{\cdot}4 \times 10^{-2}$M; pH 1·2) at 25°; similar measurements

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* Part XIX, *J.*, 1957, 301.

[1] Weiss, *Nature*, 1944, **153**, 748; *Brit. J. Radiol.*, Suppl. 1, 1947, 56.

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

[3] Cf. Johnson, Scholes, and Weiss, *Nature*, 1956, **177**, 883.

[4] Jayson, Ph.D. Thesis, Durham, 1954.

[5] Swallow, *Biochem. J.*, 1953, **54**, 253.

[6] McDonell, *J. Chem. Phys.*, 1955, **23**, 208.

[7] Farmer, Stein, and Weiss, *J.*, 1949, 3241.

have also been carried out at 15° and 33°.[4] Included in these Figures are some acetaldehyde and peroxide yields from the irradiation of oxygen-saturated solutions at the same temperature. It can be seen that, at a given temperature, the initial yields of acetaldehyde and hydrogen peroxide are the same in air and in oxygen-saturated solutions. However, in the air-equilibrated systems, the peroxide yields begin to fall off before the break-point is reached. This fall-off is more marked at the lower temperatures and accounts for the fact that the maximum quantities of peroxide produced (2·45, 2·74, and 2·92 × 10^{-7} moles/ml. at 15°, 25°, and 33° respectively) increase with increasing temperature whereas, of course, the amounts of dissolved oxygen decrease.

FIG. 1. *Irradiation of aqueous solutions of ethanol* (3·4 × 10^{-2}M, pH 1·2) *with* X-*rays* (200 kv). (Temp. 25°.)

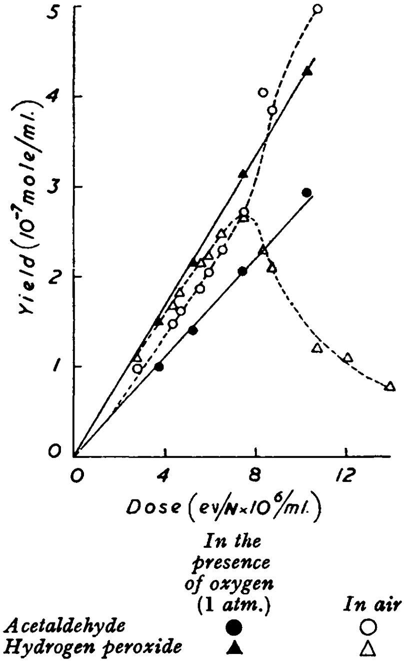
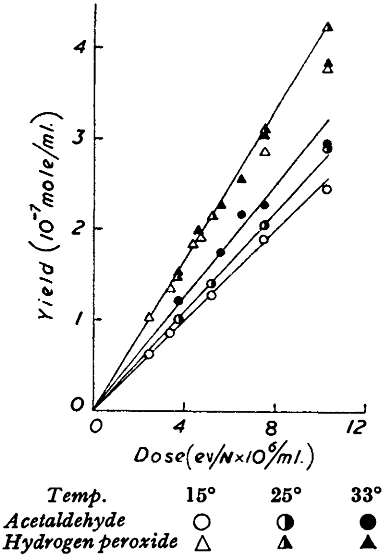


FIG. 2. *Irradiation of aqueous solutions of ethanol* (3·4 × 10^{-2}M, pH 1·2) *with* X-*rays* (200 kv) *in the presence of oxygen* (1 *atm.*).



Decomposition of hydrogen peroxide after the break-point can be attributed to, *e.g.*, the reaction, $H_2O_2 + H \longrightarrow H_2O + OH$. As long as any dissolved molecular oxygen is present, the H atoms can be removed, to a greater or lesser extent, by the process $H + O_2 \longrightarrow HO_2$. The differences between the hydrogen peroxide yields in air and in oxygen, before the break-points, can be the result of competition between molecular oxygen and hydrogen peroxide for the available hydrogen atoms; the greater disparity between the values in air and oxygen at the lower temperatures may, perhaps, be associated with a lower rate of diffusion of oxygen into local regions of oxygen depletion.

Since reduction of a peroxide molecule leads to formation of an OH radical this can lead to increased attack on the ethanol and hence to increased yields of acetaldehyde. It can be seen (Fig. 1; and similarly from the curves obtained at 15° and 33°) that in air, after the break points, the decrease in the hydrogen peroxide is accompanied by an increased formation of acetaldehyde. From these results it can be shown that the *G* values for peroxide decay and for acetaldehyde formation, at the maximum, are both approximately 7.

These general conclusions were substantiated by experiments in which the conditions prevailing immediately after the break-point were simulated. Ethanol solutions (3·4 × 10^{-2}M; pH 1·2) containing added hydrogen peroxide, in amounts expected in the air-equilibrated solutions at the break-point, were evacuated and irradiated with *X*-rays: Table 1 shows some of the results. Peroxide rapidly decayed with simultaneous formation of acetaldehyde, the *G* values for these processes approximating to those observed in air-saturated solutions after the break. It should be pointed out that from these observations alone it is not possible to decide between the mechanism outlined above and a corresponding one in which the rôle of the hydrogen atom is taken by the alcohol radicals formed by reaction (1).

TABLE 1. *Irradiation with* X-*rays* (200 kv) *of evacuated ethanol solutions* ($3{\cdot}4 \times 10^{-2}$M, pH 1·2) *containing added hydrogen peroxide* ($2{\cdot}6 \times 10^{-7}$ *mole/ml.*).

Dose (ev/*N* × 10^6/ml.)	1·68	3·15	6·30
H_2O_2 decomposed * (*G*)	7·35	5·90	4·09
CH_3·CHO formed (*G*)	7·75	4·95	5·06

* Allowance is made here for the formation of hydrogen peroxide (*G* = 0·6) due to the process $2H_2O \longrightarrow H_2 + H_2O_2$.

It was important to establish whether or not all the available oxygen in the air-saturated solutions was eventually reduced to hydrogen peroxide or if some of its was incorporated in other products. For this purpose it was necessary to establish the exact position of the break-point. This lies on the downward slope of the peroxide decay curves (cf. Fig. 1) and is approximated by the dose at which maximum peroxide decay takes place; thus at 15°, 25°, and 33° the break-points may be taken as occurring after doses of 10·0, 8·2, and 8·0 × 10^{-6} ev/*N* per ml. respectively. If no decomposition had occurred before the break-points, the maximum yields of peroxide expected here would have been identical with those in solutions saturated with oxygen, *viz.*, 3·80, 3·42, and 3·34 × 10^{-7} mole/ml. at the respective temperatures. The amounts of oxygen present in solutions saturated with air at 15°, 25°, and 33° are 3·13, 2·60, and 2·26 × 10^{-7} mole/ml. respectively. It is evident that, in addition to the hydrogen peroxide obtained from this molecular oxygen, there is some excess of hydrogen peroxide corresponding to $G \simeq 1{\cdot}2$.

FIG. 3. pH-*Dependence of the* initial *yields of acetaldehyde* (●) *and of hydrogen peroxide* (▲) *on irradiation of aqueous solutions of ethanol* ($3{\cdot}4 \times 10^{-2}$M) *with* X-*rays* (200 kv) *in the presence of oxygen* (1 *atm.*).

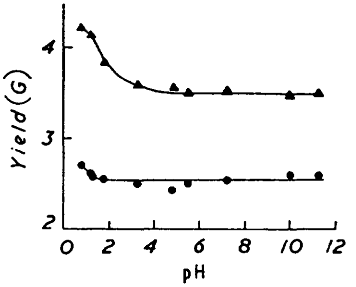
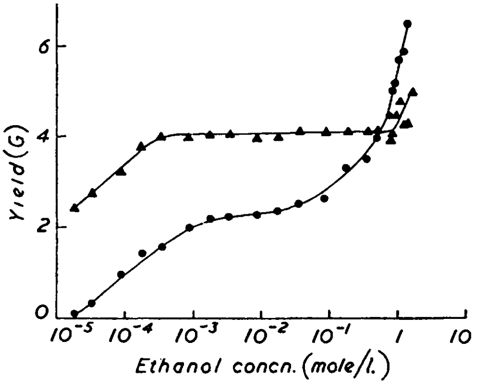


FIG. 4. *Dependence of yield on concentration of ethanol in aqueous solutions irradiated with* X-*rays* (200 kv) *in the presence of oxygen* (1 *atm.*). (pH = 1·2. *Temp.* = 20°. *Total dose* = 3·15 × 10^{-6} ev/*N per ml.*)



● *Acetaldehyde.* ▲ *Hydrogen peroxide.*

Plots of the peroxide and aldehyde yields from oxygen-saturated solutions ($3{\cdot}4 \times 10^{-2}$M-ethanol; pH 1·2) irradiated at 15°, 25°, and 33° are given in Fig. 2 which shows that, whereas the yield of peroxide is practically independent of temperature over the range studied, at $G(H_2O_2)$ = 4·15, the formation of aldehyde increases with increasing temperature: at 15°, 25°, and 33°, *G*(aldehyde) equals 2·5, 2·75, and 3·1 respectively. Although the extent of this temperature dependence would not be very marked over the normal working range (18—20°), all subsequent experiments were conducted at controlled temperatures.

It may be pointed out that the initial *G* values of the reaction products were independent of the dose-rate over the range 0·9—2·7 × 10^{-7} ev/*N* per ml. per min. and were not influenced by the presence of the water-jacket around the irradiation vessel.

The dependence on pH of the yields of acetaldehyde and hydrogen peroxide in oxygen-saturated ethanol solutions ($\sim 10^{-2}$M) were studied over the pH range ~1—11. From a series of yield–dose plots, the influence of pH on the initial yields could be examined. The results (Fig. 3) show that, under these conditions, *G*(acetaldehyde) is relatively constant (= 2·55) over the greater part of the pH range, except in the more strongly acid solutions where there is a slight increase. Over a wide range above pH ~4, $G(H_2O_2)$ = 3·5, but below this pH, it increases up to G ~4·2 at pH ~0·8. Since the additional absorption of X-rays in these solutions amounts only to about 1%, it is apparent that increase in the hydrogen-ion concentration has a definite effect on the formation of hydrogen peroxide at this solute concentration.

FIG. 5. *Dependence of yield on concentration of ethanol in aqueous solutions irradiated with* X-*rays* (200 kv) *in the presence of oxygen* (1 *atm.*). (pH = 5·4. *Temp.* = 20°. *Total dose* = $3·15 \times 10^{-6}$ ev/*N per ml.*)

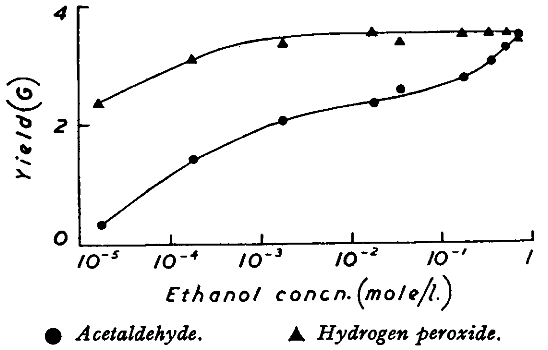
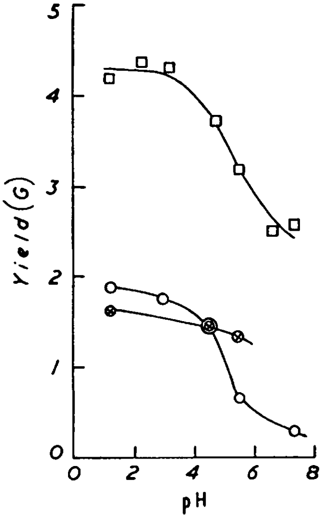


FIG. 6. pH-*Dependence of the initial yields of acetaldehyde* (○), *of hydrogen* (□), *and of butane*-2 : 3-*diol* (⊕) (*total dose* = $3·15 \times 10^{-6}$ev/*N per ml.*), *on irradiation of aqueous solutions of ethanol* ($3·4 \times 10^{-2}$M) *with* X-*rays* (200 kv) in vacuo.



The dependence of the yields of acetaldehyde and hydrogen peroxide on the concentration of ethanol in solutions irradiated in the presence of oxygen at pH 1·2 and at pH 5·4 is shown in Figs. 4 and 5. A low dose (~3×10^{-6} ev/N per ml.) was used in order to avoid the possibility of secondary processes, and this was found to be sufficient to determine the initial yields in solutions down to 10^{-4}M-ethanol. The following facts emerge from these experiments :

(*a*) Over the whole concentration range studied the yields of acetaldehyde never become independent of the solute concentration. The relative increase in the oxidation yields is greatest in the lower region, that is, up to 10^{-3}M. However, at higher concentrations of ethanol, the yield continues to increase, and, in this system, can eventually attain values which are considerably greater than the maximum that could arise from the hydroxyl radicals resulting solely from the decomposition of water. Over the concentration range considered here, " direct effects," *i.e.*, changes due to the direct absorption of the radiation energy by the solute, cannot amount to more than about 10% even at the highest concentrations employed.

(*b*) The initial yield of hydrogen peroxide, in contrast to that of acetaldehyde, is more or less independent of solute concentration over a relatively wide range (~10^{-3}M to ~1M). Above about M-ethanol, $G(H_2O_2)$ again increases. It is noteworthy that the yield of hydrogen peroxide becomes practically independent of the ethanol concentration when the latter exceeds about 10^{-3}M, *i.e.*, the concentration at which the rate of increase of the yield of acetaldehyde changes markedly.

(*c*) The effect of pH on the yields of aldehyde is more pronounced in the more concentrated ethanol solutions. Between 10^{-4}M and 10^{-1}M, the acetaldehyde yield is more or less the same at pH 1·2 as at pH 5·5. However, in acid solutions, at concentrations above 10^{-1}M, G(acetaldehyde) becomes increasingly greater than the corresponding value at pH 5·5. Using ^{60}Co γ-rays, Swallow [5] has also reported a concentration-dependence of the yields of acetaldehyde. In some preliminary experiments with ^{60}Co γ-radiation,[8] we have shown that

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[8] Collyns, Scholes, and Weiss, unpublished experiments.

the dependence of the yields of aldehyde and of hydrogen peroxide on ethanol concentration is essentially similar to that observed with *X*-rays. In addition, the yields of these products (at pH 5·5) are very nearly the same for 200 kv *X*-rays and γ-radiation.

Experiments in the Absence of Oxygen.—Determination of the yield–dose plots for the formation of acetaldehyde, hydrogen, and hydrogen peroxide in 10^{-2}M-ethanol solutions irradiated in the absence of oxygen at pH 1·2 and pH 5·5 shows that at both these pH's the yields of acetaldehyde and of hydrogen are proportional to the dose.[4] In acid solutions, hydrogen peroxide appears to be formed initially in a yield corresponding to $G \simeq 0{\cdot}6$. Under neutral conditions, however, practically no hydrogen peroxide could be detected, owing presumably to the efficient secondary decomposition of this substance.

The variation of the initial yields of aldehyde and hydrogen with pH over the pH range 1—7 is given in Fig. 6. The yields of both these products fall off markedly with increasing pH.

In ethanol solutions, irradiated in the absence of oxygen, butane-2 : 3-diol was also formed. The presence of this diol was established by oxidation by periodic acid. Included in Fig. 6 are some values for the yields of butane-2 : 3-diol (dose = $3{\cdot}15 \times 10^{-6}$ ev/*N* per ml.) in solutions irradiated at various pH's; in contrast to the other radiation products, production of butane-2 : 3-diol is not greatly influenced by pH.

TABLE 2. *Dependence of the yield on concentration of ethanol in solutions irradiated with* X-*rays* (200 kv) *in vacuo.* (pH = 1·2. *Total dose* = $4{\cdot}29 \times 10^{-6}$ ev/*N per ml.*).

Ethanol concn. (mole/l.)	$3{\cdot}4 \times 10^{-2}$	$1{\cdot}7 \times 10^{-3}$	$1{\cdot}7 \times 10^{-4}$
Yield of acetaldehyde (*G*)	1·90	1·40	0·70
Yield of butane-2 : 3-diol (*G*)	1·65	1·15	0·08

The effect of solute concentration on the yields of aldehyde and butane-2 : 3-diol in solutions irradiated *in vacuo* at pH 1·2 is shown in Table 2. Here, also, the yields increase with increasing solute concentration. The yields of the diol fall off rather more rapidly with decreasing ethanol concentration than do those of acetaldehyde.

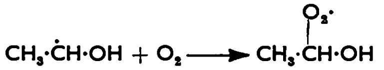
DISCUSSION

It is generally assumed that dehydrogenation of ethanol by OH radicals takes place at the α-carbon atom, according to :

$$CH_3{\cdot}CH_2{\cdot}OH + OH \longrightarrow CH_3{\cdot}\dot{C}H(OH) + H_2O \quad . \; . \; . \; . \; . \; . \quad (1)$$

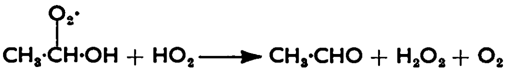
In the present work, the observation that butane-2 : 3-diol can be produced by irradiation supports this view. The nature of the radiation products from aqueous ethanol suggests, in fact, that dehydrogenation at the α-position is the only significant chemical primary process which occurs in this system.

In the presence of molecular oxygen, the process $H_2O \rightsquigarrow H + OH$ can be followed by process $H + O_2 \longrightarrow HO_2{\cdot}$, and process (1) by :

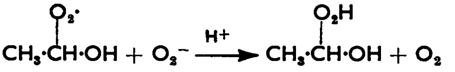
 (2)

$$CH_3{\cdot}\dot{C}H{\cdot}OH + O_2 \longrightarrow CH_3{\cdot}\overset{O_2\cdot}{\overset{|}{C}}H{\cdot}OH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Hence, under these conditions, we are dealing predominantly with reactions involving peroxy-radicals, and, in the light of the experimental results, the following possibilities may be considered :

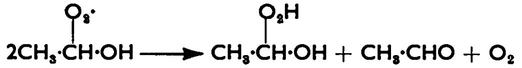
 (3)

$$CH_3{\cdot}\overset{O_2\cdot}{\overset{|}{C}}H{\cdot}OH + HO_2 \longrightarrow CH_3{\cdot}CHO + H_2O_2 + O_2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

 (4)

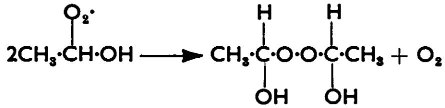
$$CH_3{\cdot}\overset{O_2\cdot}{\overset{|}{C}}H{\cdot}OH + O_2^- \xrightarrow{H^+} CH_3{\cdot}\overset{O_2H}{\overset{|}{C}}H{\cdot}OH + O_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$HO_2 \rightleftharpoons H^+ + O_2^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

 (6a)

$$2CH_3{\cdot}\overset{O_2\cdot}{\overset{|}{C}}H{\cdot}OH \longrightarrow CH_3{\cdot}\overset{O_2H}{\overset{|}{C}}H{\cdot}OH + CH_3{\cdot}CHO + O_2 \quad . \; . \; . \; . \; . \quad (6a)$$

or



$$2CH_3\cdot\overset{O_2\cdot}{C}H\cdot OH \longrightarrow CH_3\cdot\underset{OH}{\overset{H}{C}}\cdot O\cdot O\cdot\underset{OH}{\overset{H}{C}}\cdot CH_3 + O_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6b)$$

$$2HO_2 \longrightarrow H_2O_2 + O_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

Interactions between organic peroxy-radicals to form acetic acid, or to form alkoxy-radicals which may then dismutate, can be eliminated since no acetic acid was detectable and, from the results, it follows that no oxygen is used by processes other than those leading to hydrogen peroxide.

Rieche[9] found that in aqueous systems, 1-hydroxyethyl hydroperoxide tends to go over into the di-1-hydroxyethyl peroxide. Kooijman and Ghijsen[10] confirmed this and found that, under these conditions, formation of the peroxide is favoured by a factor of about ten. If, therefore, the hydroperoxide is a product of irradiation it should be converted to a large extent into the peroxide. From some experiments with aqueous solutions of 1-hydroxyethyl hydroperoxide prepared by Rieche's method[9] we have concluded that, if the organic hydroperoxide and peroxide are present at all in the irradiated ethanol solutions, they would be determined as hydrogen peroxide and acetaldehyde by the analytical methods used; from the experimental results, therefore, we are unable to distinguish between reaction (3) on the one hand and reactions (4) and/or (6) on the other.

Wieland and Wingler[11] have studied the behaviour of bishydroxymethyl peroxide in aqueous solution and found that, with titanium sulphate, the yellow colour was formed only after slight warming. This appeared to provide an opportunity for testing whether any organic peroxide was present in irradiated methanol solutions. An aqueous solution of methanol (10^{-2}M) was saturated with oxygen and irradiated with a total dose of $5{\cdot}4 \times 10^{-6}$ ev/N per ml. Two aliquot parts were then treated with the titanium reagent, and one of these was warmed. Identical optical densities were observed, presumably indicating the absence of bishydroxymethyl peroxide. If one assumes that the mechanisms of the radiation-induced oxidation of methanol and of ethanol are similar, one may conclude that acetaldehyde is probably formed from ethanol according to reaction (3). However, for a given number of HO_2 and RO_2 radicals, the overall stoicheiometry in terms of hydrogen peroxide and acetaldehyde is the same whether these radicals react according to reaction (3) or according to reactions (4) and/or (6) and (7).

One of the most important quantitative observations in the presence of oxygen is that the yields of hydrogen peroxide are almost independent of ethanol concentration over a wide range (cf. Figs. 4 and 5) and can maintain a relatively high value down to concentrations at which the yields of acetaldehyde are rather low, *i.e.*, when presumably not all of the available OH radicals are reacting with the solute. These findings are incompatible with a mechanism consisting of the primary actions on water followed by the sequence of reactions $H + O_2 \longrightarrow HO_2$, (1), (2), (3), and (7). The additional amounts of hydrogen peroxide which are required to satisfy the observed stoicheiometry, particularly at the lower ethanol concentrations, can only be accounted for if we assume that a certain amount of this substance is formed more or less directly from OH radicals. It has often been suggested that there is a direct recombination of OH radicals to give hydrogen peroxide. However, as has been pointed out,[12] there is strong evidence against such a reaction in the gaseous state, where, according to Bonhoeffer and Pearson,[13] the interaction proceeds according to $2OH \longrightarrow H_2O + O$. A possible explanation of the predominance of this reaction may be that a relatively high activation energy is necessary for the recombination of OH radicals owing to dipolar repulsion.[12] However, in the

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[9] Rieche, *Ber.*, 1931, **64**, 2328.

[10] Kooijman and Ghijsen, *Rec. Trav. chim.*, 1947, **66**, 205.

[11] Wieland and Wingler, *Annalen*, 1923, **431**, 301.

[12] Weiss, *Trans. Faraday Soc.*, 1940, **36**, 856.

[13] Bonhoeffer and Pearson, *Z. phys. Chem.*, 1931, *B*, **14**, 1.

presence of certain other molecular species, and particularly in solutions, the situation might be different and recombinative formation of hydrogen peroxide may be catalysed by various molecules or ions. It appears, therefore, that in solutions one has to include a process in which hydrogen peroxide is formed from OH radicals. This may occur predominantly within the tracks or clusters produced by the radiation. It may be necessary, therefore, to differentiate between OH radicals capable of entering into such a process and those which diffuse into the bulk of the solution or which are formed outside the tracks—hereafter called " readily available OH radicals "—*i.e.*, they can react more readily with the solute than the OH radicals in the densely populated clusters.

Increase in the solute concentration will gradually suppress the reaction :

$$HO_2 + OH \longrightarrow H_2O + O_2 \qquad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (8)$$

On this basis, it would seem that, at ethanol concentrations above about 10^{-3}M, when the hydrogen peroxide yields begin to flatten out (cf. Figs. 4 and 5), most of these " readily available OH radicals," have been used up by the solute. Thereafter, increasing the solute concentration increases the extent of reaction with the solute [eqn. (1)] compared to the recombination to give hydrogen peroxide. According to the experimental results, the number of such " readily available OH radicals " corresponds to a value of $G = 2$, *i.e.*, corresponding to the yield of acetaldehyde at the point where the curve for the yield of hydrogen peroxide flattens out.

The dependence of the yield of acetaldehyde on temperature (Fig. 2) could be accounted for on the basis of reaction (1) and interaction of OH radicals to form hydrogen peroxide by OH recombination. Increase of reaction (1) at the expense of the latter process would result if rise in temperature influenced (i) the rate of diffusion of the OH radicals from the tracks or (ii) the relative rates of reaction (1) and of the recombination process. In either case, the yield of hydrogen peroxide could remain practically unaltered, as observed experimentally. In terms of activation energies, the observed temperature coefficient could be interpreted as a difference of the order of 0·5—1 kcal. mole^{-1}, a value which would be compatible with each of the above alternatives.

Also of interest is the observation that, at the break-points in aerated solutions, the yields of hydrogen peroxide are slightly higher than would be expected from the amounts of dissolved oxygen present. It may be assumed that the reaction $2H_2O \longrightarrow H_2 + H_2O_2$ would contribute to the yield of hydrogen peroxide to the extent of $G \sim 0{\cdot}6$, this being the value of $G(H_2)$ found for 200 kv *X*-rays. The remaining difference, $G = 1{\cdot}2 - 0{\cdot}6 = 0{\cdot}6$, would be explained if some hydrogen peroxide is also formed by a recombination process from OH radicals.

Another point to consider is the higher yield of peroxide in acid solutions (cf. Fig. 3). The increase between pH 4 and pH 1 amounts to $G \simeq 0{\cdot}6$. This may be regarded as a greater net decomposition of water under acid conditions and can be expressed in terms of an additional overall process :

$$2H_2O \longrightarrow 2H + H_2O_2 \qquad . \ . \ . \ . \ . \ . \ . \ . \quad (A)$$

which is similar to that known as the " E reaction." [14] Process (A) differs from the " E reaction " in that it must be assumed that the decomposition of water which, in acid solution, leads to hydrogen peroxide according to process (A), does not occur at all in neutral solution; in the case of the " E reaction " it is assumed that the decomposition of water leading to peroxide in acid solution leads, in neutral solution, to OH radicals.

From the point of view of a unified mechanism, it is preferable to regard process A as also resulting primarily from decomposition of water into H and OH; if there is an increased opportunity for interactions of the OH radicals to form hydrogen peroxide, the

$$H + OH \longrightarrow H_2O \qquad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (9)$$

back-reactions (8) and (9) will be inhibited and this will manifest itself in an increased net decomposition of the water. In acid solutions, process A could be mediated by hydrogen

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[14] Allen, *Radiation Res.*, 1954, **1**, 85; Hart, *J. Amer. Chem. Soc.*, 1954, **76**, 4198.

ions, inasmuch as the H_2O^+ ion, which is related to the OH radical by the equilibrium,[15]

$$H_2O^+ \rightleftharpoons OH + H^+ \qquad (10)$$

could react according to :

$$H_2O^+ + OH \longrightarrow H_3O_2^+ \qquad (11)$$

$$H_3O_2^+ \rightleftharpoons H_2O_2 + H^+ \qquad (12)$$

and thus lead to the formation of hydrogen peroxide.

The OH radicals which are utilised in this way may not become available to the solute until relatively high concentrations of the latter are reached; this may explain, at least in part, the greater yields of aldehyde in acid solutions when the concentration of ethanol exceeds about 10^{-1}M. A G value of 0·6 being taken for the reaction $2H_2O \longrightarrow H_2 + H_2O_2$, then at pH ~1 it would follow that $G(OH) = G(H) = 3{\cdot}55$, and at pH >4, $G(OH) = G(H) = 2{\cdot}90$. We thus obtain a more or less complete picture of the processes in ethanol solutions up to between 10^{-2} and 10^{-1}M. At higher concentrations, however, processes other than those involving OH radicals begin to take place. Among these we must consider :

(*a*) Reactions of the solute with hydrogen atoms when the concentration of the former is sufficiently high to compete with oxygen in the process $H + O_2 \longrightarrow HO_2\cdot$. In this case, dehydrogenation of ethanol by hydrogen atoms,

$$CH_3{\cdot}CH_2{\cdot}OH + H \longrightarrow CH_3{\cdot}\dot{C}H{\cdot}OH + H_2 \qquad (13)$$

will increase the yield of aldehyde but not influence that of hydrogen peroxide since both the H atoms and the organic radicals ($CH_3{\cdot}\dot{C}H{\cdot}OH$) lead to equivalent amounts of hydrogen peroxide *via* reactions $H + O_2 \longrightarrow HO_2\cdot$ plus (3) and (6) + (7) respectively.

(*b*) Electronic excitation of the ethanol molecules by the slow electrons produced by the ionising radiations.[16]

(*c*) Chemical changes due to the direct absorption of the radiation by the ethanol. Such a process could result in an increased yield of hydrogen peroxide as well as of acetaldehyde.

In solutions irradiated in the absence of oxygen we can account for the general qualitative and quantitative features if, in addition to reactions (1) and (13), we have the following processes :

$$\left.\begin{aligned} 2CH_3{\cdot}\dot{C}H{\cdot}OH &\longrightarrow CH_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_3 \\ CH_3{\cdot}\dot{C}H{\cdot}OH + OH &\longrightarrow CH_3{\cdot}CHO + H_2O \\ CH_3{\cdot}\dot{C}H{\cdot}OH + H &\longrightarrow CH_3{\cdot}CH_2{\cdot}OH \end{aligned}\right\} \qquad (14)$$

$$\left.\begin{aligned} H + H^+ &\rightleftharpoons H_2^+ \\ CH_3{\cdot}CH_2{\cdot}OH + H_2^+ &\longrightarrow CH_3{\cdot}\dot{C}H{\cdot}OH + H_2 + H^+ \\ CH_3{\cdot}\dot{C}H{\cdot}OH + H_2^+ &\longrightarrow CH_3{\cdot}CHO + H_2 + H^+ \\ H_2^+ + H &\longrightarrow H_2 + H^+ \\ 2H &\longrightarrow H_2 \end{aligned}\right\} \qquad (15)$$

Reactions involving the H_2^+ radical-ion, formed as shown above, will be more predominant at low pH; in this way, we can account for a pH-dependence of all the yields (cf. Fig. 6).

It may be pointed out that if, under vacuum conditions, reaction (16) occurred, this would also lead to higher yields of hydrogen. However, some studies of the effects of *X*-rays on deaerated solutions of ethanol containing methylene-blue[17] strongly suggest that this reaction does not take place and that the alcohol is dehydrogenated by hydrogen atoms as shown above. In these circumstances, we have also excluded the ordinary dismutation process between two $CH_3{\cdot}\dot{C}H{\cdot}OH$ radicals (leading to acetaldehyde and alcohol).

$$CH_3{\cdot}CH_2{\cdot}OH + CH_3{\cdot}\dot{C}H{\cdot}OH \longrightarrow HO{\cdot}CHMe{\cdot}CHMe{\cdot}OH + H \qquad (16)$$

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[15] Weiss, *Experientia*, 1956, **12**, 280.

[16] Weiss, *Nature*, 1954, **174**, 78; *J. Chim. phys.*, 1955, **52**, 40.

[17] Hayon, Scholes, and Weiss, *J.*, 1957, 301.

In the irradiations of the more strongly acid solutions *in vacuo*, the yields of molecular hydrogen correspond to a radical yield of $G(\mathrm{H}) = 3{\cdot}6$, in good agreement with the value derived from the corresponding experiments in the presence of oxygen.

In the absence of oxygen, there appears to be no evidence for any hydrogen peroxide formation from OH radicals; it is, therefore, suggestive that such a process may be catalysed by molecular oxygen.

It is known that many free radicals show a great tendency to combine with molecular oxygen. It would, therefore, be reasonable to assume that this may happen also in the case of OH radicals [18] possibly according to the equilibrium process, *viz.*,

$$\mathrm{OH} + \mathrm{O_2} \rightleftharpoons \mathrm{HO_3} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (17)$$

and the $\mathrm{HO_3}$ could then react according to:

$$\mathrm{HO_3} + \mathrm{OH} \longrightarrow \mathrm{H_2O_2} + \mathrm{O_2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

thus leading to hydrogen peroxide. Some support for the assumption of $\mathrm{HO_3}$ comes from the existence of the corresponding metal compounds ($\mathrm{Me^IO_3}$) which have been investigated by various authors.[19]

Both reactions (10)—(12), and (17) and (18), would provide a mechanism for the interaction of OH radicals to give hydrogen peroxide which would be free from the objections discussed above. As an alternative to the above suggestions for the additional yields of hydrogen peroxide in certain conditions, it is not impossible that in these conditions a back-reaction between hydrogen peroxide (or one of its precursors) and hydrogen atoms may be inhibited.

The adoption of these suggestions regarding the mechanisms of the above processes must rest on a more detailed study of the initial yields of hydrogen peroxide *in vacuo* and perhaps also on a rather more precise determination of the yields of butane-2 : 3-diol under various conditions.

In solutions irradiated *in vacuo*, interaction between OH radicals by reaction (10) could still result in oxidation of ethanol by means of the oxygen atoms, *viz.*,

$$\mathrm{CH_3{\cdot}CH_2{\cdot}OH} + \mathrm{O} \longrightarrow \mathrm{CH_3{\cdot}\dot{C}H{\cdot}OH} + \mathrm{OH}$$

followed by reaction (14). However, the formation of acetaldehyde in this way is already covered by reactions (1) and (14) of our suggested mechanism for evacuated solutions.

EXPERIMENTAL

Irradiations.—The solutions were irradiated with *X*-rays (200 kv, 15 mA) as previously described.[7] Dose rates were determined by the ferrous sulphate dosimeter, $G(\mathrm{Fe^{3+}})$ being taken [20] as 15·5, and, in these experiments, were of the order of $0{\cdot}9$—$2{\cdot}7 \times 10^{-7}$ ev/*N* per ml. per min.

The Pyrex vessel for irradiation at constant temperature is shown in Fig. 7. Water from a large constant-temperature reservoir was pumped through the outer jacket (*A*) both before and throughout the irradiation. By measurements of the oxygen contents of the aerated ethanol solutions at different temperatures, by Winkler's method,[21] it was found that equilibrium between the gas phase and the solution was established sufficiently rapidly by this procedure.

Solutions were prepared in triply distilled water, ordinary distilled water being redistilled in an all-glass still from alkaline permanganate and then from phosphoric acid. The final distillate had a pH between 5·3 and 5·6. Where it was necessary to adjust the pH of the solutions, sulphuric acid was used for pH $<4{\cdot}0$, Sørensen buffer ($\mathrm{KH_2PO_4}$–$\mathrm{Na_2HPO_4}$) for pH 4·5—pH 7·5, and sodium hydroxide for pH $>10{\cdot}0$. "AnalaR" ethanol was used without further purification. Other materials were, when possible, of "AnalaR" grade.

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[18] Stein, *J. Chim. phys.*, 1955, **52**, 634.

[19] Kasarnowsky, Nikolskii, and Abletsova, *Doklady Akad. Nauk S.S.S.R.*, 1949, **64**, 960; Whale and Kleinberg, *J. Amer. Chem. Soc.*, 1951, **73**, 79.

[20] Farmer, Rigg, and Weiss, *J.*, 1955, 582.

[21] Winkler, *Ber.*, 1888, **21**, 2843.

A strict procedure was adhered to when cleaning the irradiation vessels. After being washed with "Teepol" the vessel was rinsed several times, washed with cleaning mixture (either sulphuric acid–nitric acid or ethanol–nitric acid), and rinsed with triply distilled water.

Irradiations were carried out in the presence of air or of oxygen (1 atm.), the solution being saturated by passage of oxygen for about 15 min. For experiments in the absence of oxygen, the evacuation was carried out as follows: the solution was pumped out by means of a two-stage "Hyvac" oil-pump, shaken for a few minutes, and next morning, evacuated with a mercury-diffusion pump. The amounts of dissolved oxygen in the solutions were then less than $0{\cdot}5 \times 10^{-9}$ mole/ml.

Detection and Determination of Acetaldehyde.—The aldehyde was isolated from the irradiated solutions as its 2 : 4-dinitrophenylhydrazone, identified by paper-chromatography, the solvent being light petroleum–methanol.[22] This 2 : 4-dinitrophenylhydrazone was determined by Johnson and Scholes's method.[23] Barker and Summerson's method [24] could not be used in the irradiated solutions owing to interference by ethanol and hydrogen peroxide.

Determination of Hydrogen Peroxide.—This was estimated with titanium sulphate;[25] no interference was observed by acetaldehyde in the quantities formed in the irradiated solutions. Identical results were obtained by Hochenadel's iodide method.[26]

Determination of Butane-2 : 3-diol.—Experiments with the pure substance showed that it could be readily detected and determined by the formation of acetaldehyde on treatment with periodic acid. The procedure was as follows: to a 100-ml. sample in a distillation apparatus were added, from a dropping funnel, 100 ml. of periodic acid (0·01M-potassium periodate in 0·15M-sulphuric acid) followed by 5 ml. of concentrated sulphuric acid and 15 ml. of distilled water. About 80 ml. of the mixture were then distilled over into a flask (containing about 10 ml. of distilled water) cooled in ice–water. The distillate was then made up to 100 ml., and the acetaldehyde content determined.

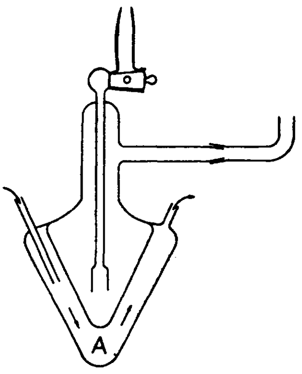

FIG. 7. *Constant-temperature reaction vessel.*

For irradiated solutions, hydrogen peroxide in the presence of alcohol interfered in the determination of butane-2 : 3-diol, giving additional amounts of acetaldehyde equivalent to about 25% of the peroxide present. Correction was made for this by the addition of comparable amounts of hydrogen peroxide to the blank solutions. The butanediol estimations has an estimated accuracy of ±7%.

Gas Analysis.—The gas-analysis apparatus was similar to that described by Stein and Weiss.[27] After irradiation *in vacuo*, the gases were pumped from the vessel, through a liquid-air trap, by means of a semiautomatic Töpler pump, and hydrogen was determined manometrically after combustion in the presence of excess of oxygen.

Tests for the Presence of Other Possible Reaction Products in Solutions irradiated in the Presence of Oxygen.—(a) *Acetic acid.* A suitable method for this substance appeared to be that of Hutchens and Kass.[28] Since the lower limit of this method is about 2×10^{-6} moles/ml., it was necessary to concentrate the irradiated solutions before applying the test. This was carried out as follows:

To eliminate acetaldehyde (which might be oxidised to acetic acid by hydrogen peroxide) 20 ml. of a solution of 2 : 4-dinitrophenylhydrazine (0·25% w/v in 30% perchloric acid) were added to 100 ml. of the irradiated solution (10^{-2}M-ethanol, total dose $= 3 \times 10^{-6}$ ev/*N* per ml.). The bulk of the solution was then distilled *in vacuo* into strong alkali. The distillate was taken to dryness, the residue acidified with phosphoric acid, and the solution distilled into a few ml. of strong alkali. This process was repeated once more and the final distillate (~3 ml.) was tested with the lanthanum nitrate reagent. A negative result was obtained, even after

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[22] Meigh, *Nature*, 1952, **170**, 579.
[23] Johnson and Scholes, *Analyst*, 1954, **79**, 217.
[24] Barker and Summerson, *J. Biol. Chem.*, 1941, **138**, 535.
[25] Eisenberg, *Ind. Eng. Chem. Analyt.*, 1943, **15**, 327.
[26] Hochenadel, *J. Phys. Chem.*, 1952, **56**, 587.
[27] Stein and Weiss, *J.*, 1949, **3245**.
[28] Hutchens and Kass, *J. Biol. Chem.*, 1949, **177**, 571.

combining the products of three irradiations, and it was therefore concluded that, if acetic acid was formed at all, the G value must be less than 0·3.

This conclusion was substantiated by measurements of the " titratable acidity " of the blank and irradiated solutions. Small amounts of titratable acid could be detected, but only after relatively high doses. For instance, after a total dose of $8{\cdot}5 \times 10^{-6}$ ev/N per ml., the G values of acetic acid in 3×10^{-2}M- and $6{\cdot}8 \times 10^{-1}$M-ethanol solutions were 0·26 and 0·44 respectively. This strongly suggests that acetic acid is not a primary radiation product but can arise by some secondary oxidation processes.

(b) *Ethylene glycol.* This was tested for by a combination of the methods reported by Tompsett and Smith [29] and by O'Dea and Gibbons.[30] This involved oxidation to formaldehyde with periodic acid, removal of the aldehyde by distillation, and colorimetric determination with chromotropic acid. No glycol could be detected in 10^{-2}M-ethanol solutions which had been irradiated with a total dose of 6×10^{-6} ev/N per ml.

(c) *Glycolaldehyde.* This forms an osazone with 2 : 4-dinitrophenylhydrazine, which gives a strong blue colour on addition of alkali; benzene was used to extract the osazone from the aqueous solution. In spite of the fact that this solvent extracts a relatively large quantity of the unchanged reagent as well as acetaldehyde 2 : 4-dinitrophenylhydrazone, it was possible to detect added osazone in quantities down to about 10^{-8} mole/ml. When the irradiated ethanol solutions (10^{-2}M; total dose = $8{\cdot}5 \times 10^{-6}$ ev/N per ml.) were treated in this way, a negative result was obtained.

(d) *Ethyl hydroperoxide and diethyl peroxide.* Neither of these substances reacts with the titanium reagent. The former, however can oxidise iodide to iodine and ferrous thiocyanate to ferric thiocyanate; [31] the latter can oxidise ferrous thiocyanate but not iodide.

Since identical yields of peroxide were obtained by using these three methods, it was concluded that no ethyl hydroperoxide or diethyl peroxide was formed on irradiation.

(e) *Peracetic acid.* That this compound was not produced was indicated by the absence of any significant amounts of " titratable acid " after irradiation.

(f) *Ethyl acetate.* This can be detected in relatively low quantities (10^{-4}M) by the method developed by Lipmann and Tuttle [32] and adapted by Lieberman : [33] 25 ml. of the irradiated solution were treated with 20 ml. of alkaline hydroxylamine reagent, and the whole set aside for 10 min. The mixture was then acidified with hydrochloric acid, and ferric chloride added. There was no absorption at 540 mμ, a wavelength characteristic of the ferric–acetohydroxamic acid which is formed from ethyl acetate under these conditions.

Experiments with 1-*Hydroxyethyl Hydroperoxide.*—This hydroperoxide was prepared as described by Rieche [9] as follows : 50 ml. of hydrogen peroxide (30% w/v) were extracted three times with 40 ml. of ether, and the combined extracts dried (Na_2SO_4). The ethereal solution contained ~0·1 mole of hydrogen peroxide, and an equimolar quantity of freshly prepared acetaldehyde was added. This mixture was stored for two days in a refrigerator. For analytical purposes the ether was distilled off *in vacuo*, and the 1-hydroxyethyl hydroperoxide weighed.

An aqueous solution containing $0{\cdot}35 \times 10^{-7}$ mole per ml. of the hydroperoxide was made up. The amounts of hydrogen peroxide as determined by titanium sulphate, and of acetaldehyde as found by treatment with 2 : 4-dinitrophenylhydrazine, were 0·34 and $0{\cdot}32 \times 10^{-7}$ mole per ml. respectively. With these analytical methods, therefore, the total hydroperoxide could be accounted for in terms of hydrogen peroxide and acetaldehyde.

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[29] Tompsett and Smith, *Analyst*, 1953, **78**, 209.
[30] O'Dea and Gibbons, *Biochem. J.*, 1953, **55**, 580.
[31] Egerton, Everett, Minkoff, Rudrakanchana, and Salooja, *Analyt. Chim. Acta*, 1954, **10**, 422.
[32] Lipmann and Tuttle, *J. Biol. Chem.*, 1943, **159**, 21.
[33] Lieberman, *Arch. Biochem. Biophys.*, 1954, **51**, 350.