772. *The Chemical Action of Ionising Radiations on Simple Aliphatic Alcohols. Part I. Irradiation of Ethanol in the Liquid and in the Solid State and in the Presence of Solutes.*

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The radiation chemistry (^{60}Co γ-rays and 200 kv X-rays) of ethanol has been studied, particularly as a function of temperature and of the concentration of some selected solutes (oxygen, chloroacetic acid, glycollic acid, acetic acid, 2-chloroethanol) with the object of elucidating the primary radiolytic mechanism. It is suggested that ethanol is, to a large extent, ionised into positive and negative " polarons " which may then react:

$$(CH_3{\cdot}CH_2{\cdot}OH)^+ \longrightarrow CH_3{\cdot}CH{\cdot}OH + H^+$$
$$(CH_3{\cdot}CH_2{\cdot}OH)^- \longrightarrow CH_3{\cdot}CH_2{\cdot}O^- + H$$
$$(CH_3{\cdot}CH_2{\cdot}OH)^- + H^+ \longrightarrow CH_3{\cdot}CH_2{\cdot}OH + H$$
$$CH_3{\cdot}CH_2{\cdot}O^- + H^+ \longrightarrow CH_3{\cdot}CH_2{\cdot}OH$$

In the presence of solutes with good electron-accepting properties, such as oxygen and chlorinated organic compounds, the negative polarons can react directly with them:

$$(CH_3{\cdot}CH_2{\cdot}OH)^- + O_2 \longrightarrow CH_3{\cdot}CH_2{\cdot}OH + O_2^-$$
$$(CH_3{\cdot}CH_2{\cdot}OH)^- + RCl \longrightarrow CH_3{\cdot}CH_2{\cdot}OH + R + Cl^-$$

This mechanism is similar to that proposed for aqueous systems.

McDONELL and NEWTON [1] studied the effect of the bombardment by 28 Mev helium ions on deaerated liquid alcohols. The major products were aldehydes, glycols, and ketones,

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[1] McDonell and Newton, *J. Amer. Chem. Soc.*, 1954, **76**, 4651; Newton and McDonell, *ibid.*, 1956, **78**, 4554.

depending on the nature of the alcohol. Hydrogen was the main gaseous product, with smaller amounts of carbon monoxide and methane and traces of lower hydrocarbons. The yields of the products resulting from the action of ^{60}Co γ-ray on deaerated liquid methanol were determined by McDonell and Gordon,[2] Meshitsuka and Burton,[3] and Adams and Baxendale.[4]

The reaction mechanisms were inadequately defined and we therefore investigated the two simple alcohols, methanol and ethanol, using relatively low doses of radiation, at different temperatures for the liquid and the frozen state; the effect of selected solutes was also investigated.

RESULTS

Deaerated Systems.—Irradiations were carried out in Pyrex glass vessels, cleaned and dried as described below. Irradiation of pure ethanol with ^{60}Co γ-radiation or with X-rays (200 kv) in the absence of oxygen gave acetaldehyde and butane-2,3-diol as the only detectable products, with hydrogen as the major gaseous component. Small amounts of methane and carbon monoxide and traces of ethane, ethylene, and acetylene were also found. The dependence of the yields on the dose of γ-radiation for liquid ethanol at 20° is shown in Fig. 1: the yields of acetaldehyde, butane-2,3-diol, and hydrogen were linear functions of dose up to a total of 8×10^{16} ev ml.$^{-1}$. A similar linear dependence was obtained in all cases at low doses both for γ- and for X-irradiations.

Table 1 gives the initial yields (G-values: molecules/100 ev) of the products for X- and γ-radiolysis of deaerated ethanol in the liquid (20°) and the frozen state (−196°; liquid nitrogen) as derived from the linear parts of the yield–dose plots, from at least four runs. The yields obtained on γ-irradiation of frozen ethanol are within 10—15% of those at room temperature, except for butane-2,3-diol, the yield of which was appreciably less at the low temperature. With X-radiation the overall yields are greater but they are considerably reduced in the frozen state.

TABLE 1. *Initial yields* (G-*values*) *of products of irradiation of deaerated ethanol with* ^{60}Co *γ-rays* ($1{\cdot}60 \times 10^{15}$ ev ml.$^{-1}$ min.$^{-1}$) *and* X-*rays* (200 kv) ($1{\cdot}34 \times 10^{16}$ ev ml.$^{-1}$ min.$^{-1}$)

Products	γ-Rays 20°	γ-Rays −196°	X-Rays −196°
Acetaldehyde	3·14 ± 0·1	3·60 ± 0·2	3·52 ± 0·1
Butane-2,3-diol	1·67 ± 0·2	0·95 ± 0·2	2·58 ± 0·2
H_2	4·87 ± 0·2	4·50 ± 0·3 *	5·96 ± 0·2
CH_4	0·58	0·45	0·22
CO	0·26	0·20	0·11

Traces of C_2H_2, C_2H_4, and C_2H_6 in all experiments.

* Johnsen (*J. Phys. Chem.*, 1959, **63**, 2088) obtained $G(H_2)$ 4·78 from γ-irradiation of air-free ethanol at −196°.

In the Presence of Oxygen.—In irradiations of ethanol in the presence of air or oxygen (1 atm.) no appreciable amounts of the diol could be detected: G(diol) $\sim$ 0·3. The products found were acetaldehyde, hydrogen peroxide, small amounts of hydrogen, and traces of the lower hydrocarbons. No organic hydroperoxides or peroxides were found ($G \sim 0{\cdot}1$). Fig. 2 shows the dependence of the yields of acetaldehyde and hydrogen peroxide on radiation dose for the γ-irradiation of air-saturated and oxygen-saturated liquid ethanol at 20°. The yields of acetaldehyde and hydrogen peroxide, even at the smallest dose, are higher in air-saturated than in oxygen-saturated liquid ethanol; the same difference was observed in the X-ray experiments.

The initial yields (G-values) of the products obtained in irradiations of ethanol with γ- and X-rays in the presence of air and oxygen and in the liquid and frozen state are given in Table 2. The yields were within ±10% the same for both γ- and X-rays (cf. Table 1). Irradiation of frozen ethanol (−196°) in the presence of air or oxygen (1 atm.) gave the same products as were found for the liquid state, but the yields were lower in the former cases. The difference

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[2] McDonell and Gordon, *J. Chem. Phys.*, 1955, **23**, 208.
[3] Meshitsuka and Burton, *Radiation Res.*, 1958, **8**, 285.
[4] Adams and Baxendale, *J. Amer. Chem. Soc.*, 1958, **80**, 4215.

TABLE 2. *Initial yields* (G-*values*) *of the products obtained on irradiation of pure ethanol in the presence of air and oxygen* (1 atm.) *with* ^{60}Co γ-*rays and* 200 kv X-*rays* (*doses as* Table 1).

	γ-Rays At 20°		X-Rays At 20°		At −196°	
Products	Air-satd.	O_2-satd.	Air-satd.	O_2-satd.	Air-satd.	O_2-satd.
Acetaldehyde	6·40	4·5	6·10	4·10	2·81	2·82
H_2O_2	4·62	3·2	4·10	2·33	2·97	2·94
H_2	1·73	1·41	2·03	1·54	1·46	1·41

Traces of CO, CH_4, C_2H_2, C_2H_4, C_2H_6 were found in all experiments.

in the yields between oxygen-saturated and air-saturated ethanol was negligible at the low temperature.

Effects of Solutes.—The solutes used in deaerated ethanol were chloroacetic acid, glycolic acid, acetic acid, and 2-chloroethanol, whose radiation-chemical behaviour in aqueous solution has been studied recently.[5] Table 3 shows the dependence of the yields of hydrogen,

FIG. 1. *Dependence of products on time of irradiation* (^{60}Co γ-*rays*) *of pure deaerated ethanol at* 20° *at dose rate* 1·6 × 10^{15} ev ml.$^{-1}$ min.$^{-1}$. □, H_2. △, Me·CHO. ○, $(HO{\cdot}CHMe{\cdot})_2$.

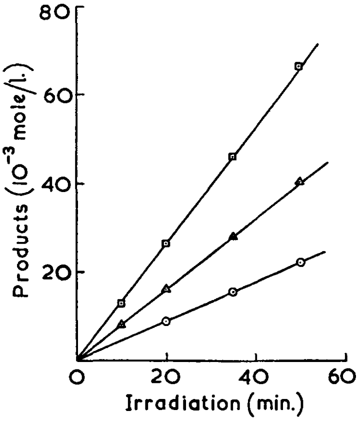

FIG. 2. *Dependence of products on time of irradiation* (^{60}Co γ-*rays*) *of air- and oxygen* (1 atm.)-*saturated ethanol at* 20° *at dose rate* 1·6 × 10^{15} ev ml.$^{-1}$ min.$^{-1}$. Me·CHO: ○ air, ● O_2. H_2O_2: □ air, ■ O_2.

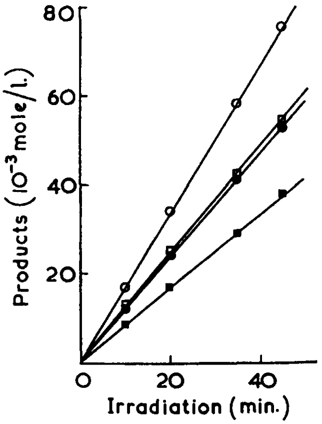

TABLE 3. *Initial yields* (G-*values*) *of* H_2, CH_4, *and* CO *obtained from* Co^{60} γ-*irradiation* (1·60 × 10^{15} ev ml.$^{-1}$ min.$^{-1}$) *of deaerated ethanol in the presence of various organic solutes.*

Solute (mole/l.)	Yields (*G*)			Solute (mole/l.)	Yields (*G*)		
$CH_2Cl{\cdot}CO_2H$	H_2	CH_4	CO	$CH_2Cl{\cdot}CH_2{\cdot}OH$	H_2	CH_4	CO
10^{-4}	3·53	0·54	0·21	10^{-4}	3·5	0·53	0·23
10^{-2}	3·43	0·49	0·21	10^{-3}	3·49	0·51	0·20
10^{-1}	3·27	0·41	0·18	10^{-2}	3·50	0·52	0·15
1·0	2·43	0·26	0·15	1·0	2·61	0·44	0·10
8·0	0·68	0·19	0·11	5·0	1·80	0·28	0·03
$HO{\cdot}CH_2{\cdot}CO_2H$				AcOH			
10^{-5}	3·96	0·54	0·25	10^{-4}	4·75	0·53	0·19
10^{-4}	3·53	0·51	0·25	10^{-2}	4·77	0·49	0·16
10^{-3}	3·43	0·47	0·35	10^{-1}	4·43	0·49	0·15
10^{-2}	3·43	0·48	0·20	1·0	3·28	1·02	0·13
10^{-1}	3·19	0·48	0·13	5·0	1·78	1·34	0·25
1·0	2·61	0·25	0·07				
4·0	1·34	0·27	0·37				

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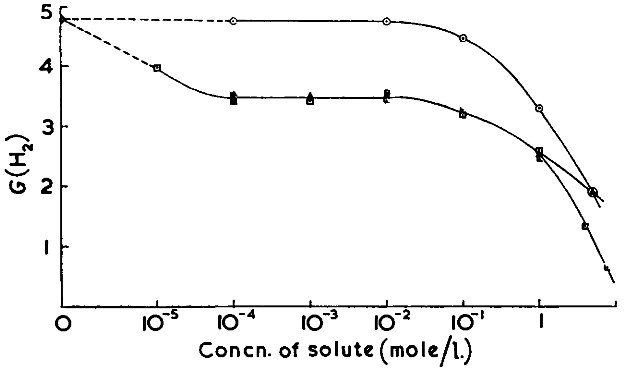
[5] Hayon and Weiss, Proc. Internat. Conf. Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. XXIX, p. 80; *J.*, 1960, 1591.

methane, and carbon monoxide on the concentration of the solutes. Carbon dioxide was also formed (except in the case of 2-chloroethanol) but was not determined quantitatively since a liquid-nitrogen trap was used to condense any ethanol vapour. It will be seen that the yields of several products decrease with increasing solute concentration.

Fig. 3 shows a plot of the yields of hydrogen (G-values) against concentration of the different solutes in ethanol. The results indicate that the decrease in the hydrogen yield with increasing solute concentration (from 10^{-5} to 1·0M) is almost the same for chloroacetic acid, glycollic acid, and 2-chloroethanol, amounting to a decrease of about 33% in 10^{-1}M and about 48% in the M-solutions. On the other hand, the effect of acetic acid as a solute was much smaller; in 10^{-1}M-acetic acid the yield of hydrogen decreased by only 7·7%, with 30% decrease in M-solution.

Yields of acetaldehyde for different concentrations of monochloroacetic acid and of acetic acid increased from G(aldehyde) 3·1 in 10^{-2}M- to ~7·2 in 1·0M-chloroacetic acid, and from ~3·1 to 4·5 for acetic acid over the same concentration range. In the chloroacetic acid solutions, the yields of chloride also increased with increasing solute concentration, particularly in solutions above 10^{-1}M.

FIG. 3. *Initial yields of hydrogen* (G-*values*) *obtained on irradiation* (^{60}Co *γ-rays*) *of pure deaerated ethanol in the presence of acetic acid* (⊙), *glycollic acid* (⊡), *chloroacetic acid* (⌞), *and* 2-*chloroethanol* (▲). *Dose rate* 1·6 × 10^{15} ev ml.$^{-1}$ min.$^{-1}$.



DISCUSSION

Table 4 shows the yields of the products obtained in different laboratories on irradiation of deaerated liquid ethanol. It is very likely that the differences in these values are due to the difference in the purity of the ethanol used.

TABLE 4. *Yields* (G-*values*) *obtained by different authors in the irradiation of pure liquid ethanol.*

Radiation	$G(H_2)$	$G(CH_4)$	G(CO)	G(aldehyde)	G(glycol)	Ref.
28 Mev He ions	3·46	0·43	0·11	2·1	1·05	1
800 kv Electrons ...	6·0	0·20	0·30	1·0	—	*a*
^{60}Co γ-Rays	4·35	0·60	—	—	—	*b*
,, ...	3·66	—	—	—	—	*c*
,, ...	4·87	0·58	0·26	1·67	1·67	*d*

(*a*) Bach, Proc. Internat. Conf. Peaceful Uses of Atomic Energy, Geneva, 1955, Vol. VII, p. 538; Bach and Sorokin, Symp. Radiation Chem. Acad. Sci., U.S.S.R., 1955, Vol. I, p. 135. (*b*) Adams, Baxendale, and Sedgwick, *J. Phys. Chem.*, 1959, **63**, 854. (*c*) Burr, jun., *J. Amer. Chem. Soc.*, 1957, **79**, 751; *J. Phys. Chem.*, 1957, **61**, 1477. (*d*) Present work.

The effect of ionising radiations on simple aliphatic alcohols is presumed to be removal of a hydrogen atom from the α-carbon atom since deaerated alcohols give 1,2- rather than 1,3-glycols. In addition to the formation of 1,2-glycols one has to account also for that of acetaldehyde, hydrogen, methane, and carbon monoxide. Since no glycols were formed in the irradiation of ethanol in the presence of oxygen, one must conclude that the glycol is formed by a radical-dimerisation process:

$$CH_3{\cdot}CH_2{\cdot}OH \rightsquigarrow CH_3{\cdot}CH(OH){\cdot} + H \quad . \; . \; . \; . \; . \; . \; . \; . \quad (A)$$

$$2CH_3{\cdot}CH(OH){\cdot} \longrightarrow CH_3{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_3 \quad . \; . \; . \; . \; . \quad (1)$$

Reaction (A) describes the overall primary process in the absorption of the radiation energy.

It has been suggested[7] that ionising irradiation of polar liquid radiations leads in general to the primary formation of negative and positive polarons. Hayon and Weiss[5] interpreted their results for aqueous systems on this basis and it has been discussed from a theoretical viewpoint.[7]

However, the positive and negative polarons in ethanol, $(CH_3{\cdot}CH_2{\cdot}OH)^+$ and $(CH_3{\cdot}CH_2{\cdot}OH)^-$, may be more subject to self-decomposition than those in water, in view of the lower polarity of the solvent and of their more complex structure, and they may dissociate to some extent, *e.g.*:

$$(CH_3{\cdot}CH_2{\cdot}OH)^+ \longrightarrow CH_3{\cdot}CH(OH){\cdot} + H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$(CH_3{\cdot}CH_2{\cdot}OH)^- \longrightarrow CH_3{\cdot}CH_2{\cdot}O^- + H \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$CH_3{\cdot}CH_2{\cdot}O^- + H^+ \longrightarrow CH_3{\cdot}CH_2{\cdot}OH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

although the experimental results suggest that $(CH_3{\cdot}CH_2{\cdot}OH)^-$ will react normally preferentially with protons, thus:

$$(CH_3{\cdot}CH_2{\cdot}OH)^- + H^+ \longrightarrow H + CH_3{\cdot}CH_2{\cdot}OH \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

One cannot at present eliminate the possibility of a small contribution from excited ethanol molecules which may give radicals:

$$CH_3{\cdot}CH_2{\cdot}OH^* \longrightarrow CH_3{\cdot}CH(OH){\cdot} + H \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

or molecular products:

$$CH_3{\cdot}CH_2{\cdot}OH^* \longrightarrow CH_3{\cdot}CHO + H_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

Burr[8] found that the percentage of deuterium in the hydrogen obtained on γ-irradiation of $CH_3{\cdot}CD_2{\cdot}OH$ or $CH_3{\cdot}CH_2{\cdot}OD$ was about 40%, whereas it was only about 4% in the irradiation of $CD_3{\cdot}CH_2{\cdot}OH$, which supports the mechanism postulated above.

Conclusive evidence of an ionic mechanism for the primary process in the irradiation of alcohols is not yet available, although the results obtained from the irradiation of deaerated solutions of ethanol with solutes of different electron affinity seem to provide some support for the above mechanism. Table **3** and Fig. **3** show that the decrease in the yield of hydrogen with increasing solute concentration in the solute concentration range from 10^{-5} to 1·0M is almost the same for chloroacetic acid, glycollic acid, and 2-chloroethanol, whereas the behaviour of acetic acid is rather different.

It is suggested that in the presence of, *e.g.*, chloroacetic acid (and similarly with the other solutes which can act as strong electron-acceptors) the negative polarons are captured by the solute to give Cl^- and $\cdot CH_2{\cdot}CO_2H$ radicals:

$$(CH_3{\cdot}CH_2{\cdot}OH)^- + Cl{\cdot}CH_2{\cdot}CO_2H \longrightarrow Cl^- + {\cdot}CH_2{\cdot}CO_2H + CH_3{\cdot}CH_2{\cdot}OH \quad . \; . \; . \; . \quad (8)$$

In acetic acid, however, the yield of hydrogen in $>10^{-1}$M-solutions also decreases with

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[6] Lea, " Actions of Radiations on Living Cells," Cambridge University Press, London, 1946; Weiss, *Ann. Rev. Phys. Chem.*, 1953, **4**, 143; Platzman, *Radiation Res.*, 1955, **2**, 1.

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

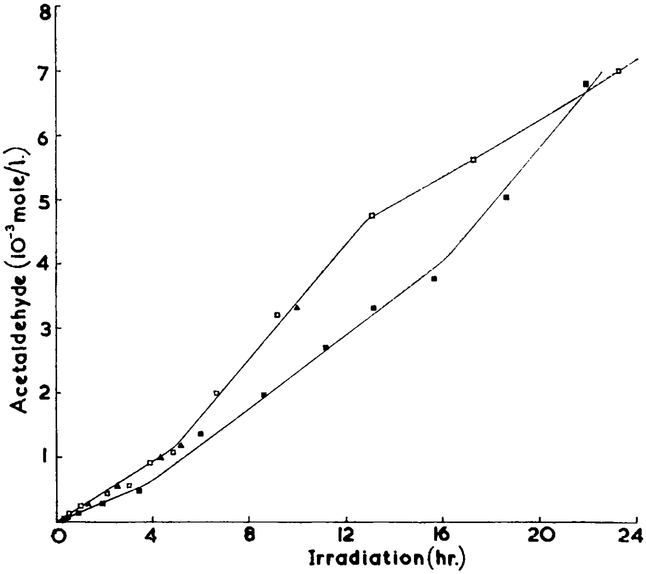
[8] Burr, jun., footnote (*c*), Table 4.

further increase in acetic acid concentration, seeming to indicate that at these higher concentrations acetic acid can react with the polarons to give different products, *viz.*:

$$CH_3{\cdot}CO_2H + (CH_3{\cdot}CH_2{\cdot}OH)^- \longrightarrow \begin{cases} CH_3{\cdot}CO{\cdot} + OH^- + CH_3{\cdot}CH_2{\cdot}OH & (9a) \\ CH_3{\cdot}C{\cdot}O{\cdot}O^- + H + CH_3{\cdot}CH_2{\cdot}OH & (9b) \\ CH_3{\cdot}CO^- + {\cdot}OH + CH_3{\cdot}CH_2{\cdot}OH & (9c) \end{cases}$$

In support of this, it was found that irradiation of M-acetic acid in ethanol leads to increased yields of aldehyde and the formation of biacetyl $(CH_3{\cdot}CO)_2$ (detected by paper chromatography of the 2,4-dinitrophenylhydrazone). No biacetyl was formed in $<10^{-1}$M-acetic acid. Similarly, on γ-irradiation of pure deaerated 2-chloroethanol the yields were reduced to $G(H_2)$ 0·75 and $G(Cl^-)$ 4·0, the sum of the two being approximately equal to the hydrogen yield ($G \sim 4{\cdot}86$) obtained on the irradiation of pure deaerated ethanol (Table 1).

FIG. 4. *Dependence of the formation of acetaldehyde on time of irradiation* (^{60}Co γ-*rays*) *of ethanol in air-saturated* (□) *and oxygen* (1 atm.)-*saturated solutions* (■) *and in irradiations by* X-*rays* (200 kv) *in air-saturated solutions* (▲).



In the absence of added solutes, the $CH_3{\cdot}CH(OH){\cdot}$ radicals formed react to give acetaldehyde and butane-2,3-diol and the hydrogen atoms normally dehydrogenate an ethanol molecule on the α-carbon atom:

$$H + CH_3{\cdot}CH_2{\cdot}OH \longrightarrow H_2 + CH_3{\cdot}CH(OH){\cdot} \quad . \; . \; . \; . \; . \; . \; . \quad (10)$$

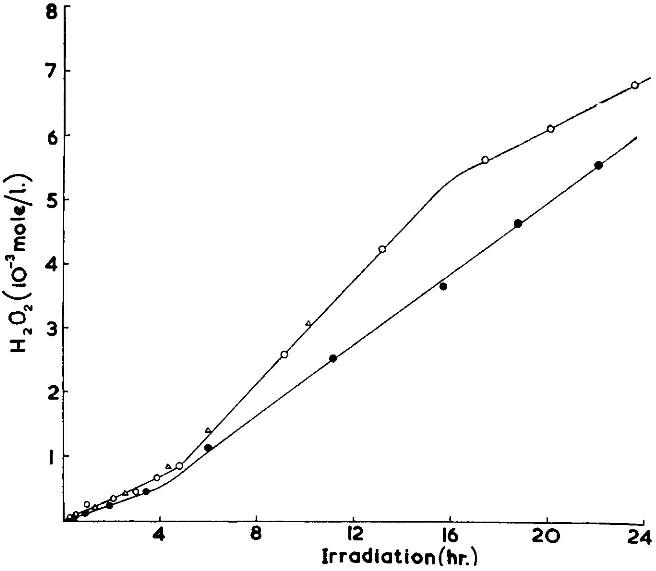
Irradiation of ethanol in the presence of oxygen gives $G(H_2) \sim 1{\cdot}73$ for an air-saturated solution and $G(H_2) \sim 1{\cdot}41$ for an oxygen-saturated solution (Table 2). This indicates that there is competition between ethanol and oxygen for hydrogen atoms, *i.e.* reaction (10) competing with:

$$H + O_2 \longrightarrow HO_2{\cdot} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

It is interesting that $\{G(CH_3{\cdot}CHO) - G(H_2)\} = G(H_2O_2)$ for both air-saturated and oxygen-saturated liquid ethanol (Table 2). This means that the yield of aldehyde formed by the radical processes is equal to the yield of hydrogen peroxide. This, however, does not allow a decision whether the hydrogen formed in oxygenated solutions is produced by a radical process (eqn. 10) or by molecular decomposition of excited molecules (eqn. 7).

On X- and γ-irradiation of liquid ethanol in the presence of oxygen (Fig. 2, Table 2) the initial yields of acetaldehyde and hydrogen peroxide are lower in oxygen (1 atm.) than in air-saturated solutions. This difference can be explained if one assumes that some other oxidation product is also formed. The formation of this product, thought [9] to be acetic acid, was found to depend on the actual concentration of oxygen in the solution, since the yields of acetaldehyde and hydrogen peroxide increased on prolonged irradiation, after the oxygen has been partly used up. Fig. 4 shows the dependence of the yield of acetaldehyde on radiation dose in the γ-ray irradiation of ethanol, in the presence of air and oxygen (1 atm.); Fig. 5 shows the corresponding yields of hydrogen peroxide. From Figs. 4 and 5 it can be seen that for air-saturated ethanol the yields go through a maximum with increasing radiation dose. However, in oxygen-saturated ethanol, the yields of these two products increase with increasing dose. Almost identical yields were obtained on irradiation with *X*-rays (200 kv) although the dose rate here was approximately 10 times greater than of the γ-rays (Figs. 4 and 5).

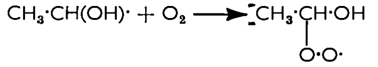
FIG. 5. *Formation of hydrogen peroxide on irradiation* (^{60}Co γ-*rays*) (1·6 × 10^{15} ev ml.$^{-1}$ min.$^{-1}$) *of ethanol in air-saturated* (○) *and oxygen-saturated* (●) *solutions and from irradiation* (X-*rays*, 200 kv) *of air-saturated solutions* (△) (1·34 × 10^{16} ev ml.$^{-1}$ min.$^{-1}$).



The following scheme of reactions is suggested to account for the yields of the products in irradiations of ethanol in the presence of oxygen: the negative polaron $(CH_3{\cdot}CH_2{\cdot}OH)^-$ may either give hydrogen atoms [reaction (5)] or react with oxygen:

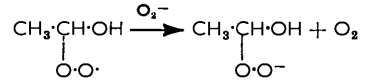
$$(CH_3{\cdot}CH_2{\cdot}OH)^- + O_2 \longrightarrow O_2^- + (CH_3{\cdot}CH_2{\cdot}OH) \quad \ldots\ldots\ldots \quad (12)$$

The formation of acetic acid could occur by dehydration of a hydroperoxide formed:



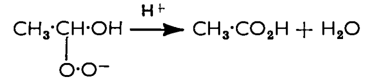
$$CH_3{\cdot}CH(OH){\cdot} + O_2 \longrightarrow CH_3{\cdot}\underset{O{\cdot}O{\cdot}}{\underset{|}{C}}H{\cdot}OH \quad \ldots\ldots\ldots \quad (13)$$

(13)



$$CH_3{\cdot}\underset{O{\cdot}O{\cdot}}{\underset{|}{C}}H{\cdot}OH \xrightarrow{O_2^-} CH_3{\cdot}\underset{O{\cdot}O^-}{\underset{|}{C}}H{\cdot}OH + O_2 \quad \ldots\ldots\ldots \quad (14)$$

(14)



$$CH_3{\cdot}\underset{O{\cdot}O^-}{\underset{|}{C}}H{\cdot}OH \xrightarrow{H^+} CH_3{\cdot}CO_2H + H_2O \quad \ldots\ldots\ldots \quad (15)$$

(15)

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[9] Bach, ref. (*a*), Table 4.

The sequence of reactions (13—15) and (12) also accounts for the effect of the oxygen concentration upon the yields of acetaldehyde and hydrogen peroxide.

In the presence of air or oxygen the yields obtained on irradiation of ethanol were of the same order for both *X*- and γ-radiation (Table 2).

EXPERIMENTAL

Irradiation Technique.—The *X*-ray source was a Victor Maximar *X*-ray therapy set, stripped of all filters and operating at 200 kv and 15 mA. For the irradiations with γ-rays a 500-c ^{60}Co-source was used, the irradiation arrangements being similar to those described by Ghormley and Hochanadel.[10]

The rate of energy absorption in the various irradiation positions was calculated from the measured rate of a ferrous sulphate dosimeter, in a similar irradiation vessel containing an air-saturated solution of 10^{-3}M-ferrous sulphate in 0·8N-sulphuric acid. The concentration of Fe^{III} was determined by a S.P. 500 " Unicam " spectrophotometer at 304 mμ. The extinction coefficient in 0·8N-sulphuric acid was taken as $\varepsilon = 2220$ at 25°, and the yield of ferrous oxidation as $G(\text{Fe}^{III}) = 15{\cdot}5$ molecules per 100 ev of energy absorbed by the solution.

Cormack and Johns [11] and Spiers [12] suggested that the average value of the energy of the electron produced from 200 kv *X*-ray therapy sets is of the order of 60 kv. Under such conditions, the Compton and photoelectric effect for energy loss in water would be of about equal importance. The real electronic absorption coefficient of ethanol relative to 0·8N-sulphuric acid was calculated to be 0·67. This value is based on the assumption that the energy flux of the photon beam is the same for both, and that one may take the ratio of the absorption coefficients for the two liquids. For ^{60}Co γ-radiation the ratio of the densities (0·78) of ethanol to 0·8N-sulphuric acid was taken.

Absolute " AnalaR " ethanol (40 or 25 ml.) was contained in Pyrex irradiation vessels that had been washed with sulphuric–nitric acid, rinsed many times with triply distilled water, followed by alcohol, placed in an oven at ~100°, and rinsed again with ethanol. Addition of 1% of water did not change the yield of hydrogen obtained on irradiation with γ-rays.

For the irradiations of frozen alcohols, round-bottomed cylindrical Pyrex vessels were placed inside Dewar vessels containing liquid nitrogen.

Evacuation of the solutions to 10^{-3} mm. Hg (measured by a Pirani guage) was effected with a three-stage mercury-diffusion pump backed by a two-stage oil-pump. For experiments in the presence of oxygen, gas (British Oxygen " Medical " grade) was bubbled through the solution for about 45 min., after which the vessels were closed. Correction for loss of alcohol was made.

Gas Analysis.—The gas formed on irradiation of deaerated ethanol was pumped from the vessels by means of a Töpler pump, through a trap containing liquid nitrogen. The volume of gas was measured on a semimicro-burette, then collected in a gas-sampling vessel. Analyses were carried out by mass-spectrometry (we are obliged to Mr. P. Kelly for this work).

In the irradiation of air-saturated and oxygen-saturated ethanol, where it was necessary to measure small quantities of hydrogen, in the presence of relatively large amounts of nitrogen and oxygen, the gas from the irradiation vessels was passed through a charcoal trap kept at liquid-nitrogen temperature. Almost all the oxygen and most of the nitrogen were removed in this way. The charcoal used (B.D.H. Ltd.) was activated by evacuation at ~300°. Experiments with known amounts of hydrogen showed a loss of ±4% on passage of the gas over a charcoal trap at −196°.

Determination of Acetaldehyde.—This was based on Friedman and Haugen's method using 2,4-dinitrophenylhydrazine, in the modified form reported by Johnson and Scholes.[13]

Determination of Butane-2,3-diol.—Butane-2,3-diol was determined by the liberation of acetaldehyde on treatment with periodate. Potassium periodate (0·5 g.) and concentrated sulphuric acid (2 ml.) were added to a 50 ml. aliquot part. The acetaldehyde formed was steam-distilled *in vacuo* at 40° and the distillate collected in a 0·25% w/v solution (20 ml.) of 2,4-dinitrophenylhydrazine in 30% w/v perchloric acid (kept at 2°), as used in the acetaldehyde determination. An accuracy of up to ±10% was obtained with standard glycol solutions.

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[11] Cormack and Johns, *Brit. J. Radiol.*, 1952, **25**, 369.

[12] Spiers, *Discuss. Faraday Soc.*, 1952, **12**, 13.

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

Determination of Hydrogen Peroxide.—The method adopted for the determination of hydrogen peroxide was essentially Eisenberg's.[14]

No hydroperoxides were formed on irradiation of ethanol in the presence of oxygen, as shown by the iodide method of Hochanadel.[15]

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