773. *The Chemical Action of Ionising Radiations on Simple Aliphatic Alcohols. Part II.*[1] *Irradiation of Methanol in the Absence and in the Presence of Oxygen in the Solid and in the Liquid State.*

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The chemical action of ionising radiations (^{60}Co γ-rays and 200 kv X-rays) on methanol has been investigated in the presence and in the absence of oxygen, at 20° and at −196°. The reaction mechanism described is essentially similar to that proposed for ethanol (Part I), the radiation-induced reactive intermediates being formed by the dissociation of the primarily formed polarons $(CH_3{\cdot}OH)^-$ and $(CH_3{\cdot}OH)^+$.

THE radiation chemistry of pure liquid methanol has been the subject of several recent investigations. McDonell and Newton[2] studied the action of 28 Mev helium ions, and McDonell and Gordon[3] the effect of ^{60}Co γ-radiation. Meshitsuka and Burton[4] dealt with the γ-irradiation of methanol in the presence of iodine, and Adams and Baxendale[5] with the same system in the presence of ferric salts and benzoquinone. The effect of γ-irradiation on different methanolic solutions was also briefly reported by Lichtin.[6] Radiolysis of liquid methanol in the absence of oxygen was found to yield formaldehyde, ethylene glycol, and hydrogen as the main products with minor amounts of methane and carbon monoxide and traces of ethane and ethylene. The present work was carried out with the object of comparing the initial yields obtained in the irradiation of methanol with ^{60}Co γ-rays and X-rays (200 kv), *in vacuo* and in air- and oxygen-saturated solutions in the liquid and the frozen state.

TABLE 1. *Initial yields* (G-*values*) *of the products obtained on radiolysis of pure deaerated methanol in the liquid* (20°) *and in the solid state* (−196°) *with* ^{60}Co *γ-rays* ($1{\cdot}60 \times 10^{15}$ ev ml.$^{-1}$ min.$^{-1}$) *and* X-*rays* (200 kv) ($1{\cdot}43 \times 10^{16}$ ev ml.$^{-1}$ min.$^{-1}$).

	CH_2O	$(CH_2{\cdot}OH)_2$	H_2	CH_4	CO
γ-Rays: 20°	1·41	2·43	4·1	0·39	0·13
X-Rays: −196°	0	3·31	3·84	0·51	0·25

RESULTS

Deaerated Systems.—Irradiations were carried out in Pyrex glass vessels, cleaned and dried as described in Part I.[1] The yields of hydrogen, formaldehyde, and ethylene glycol formed by

[1] Part I, preceding paper.
[2] McDonell and Newton, *J. Amer. Chem. Soc.*, 1954, **76**, 4651.
[3] McDonell and Gordon, *J. Chem. Phys.*, 1955, **23**, 208.
[4] Meshitsuka and Burton, *Radiation Res.*, 1958, **8**, 285.
[5] Adams and Baxendale, *J. Amer. Chem. Soc.*, 1958, **80**, 4215.
[6] Lichtin, *J. Phys. Chem.*, 1959, **63**, 1449.

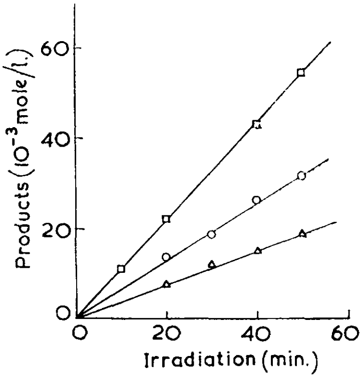
the ^{60}Co γ-irradiation of deaerated liquid methanol as a function of dose are shown in Fig. 1; similar linear relations were obtained in all cases at lower doses with both X- and γ-rays.

Table 1 gives the initial yields (G-values) of the products from irradiations (X- and γ-rays) of deaerated methanol in the liquid (20°) and the frozen state (−196°). At −196°, with either X- and γ-rays, no formaldehyde was found and the yield of ethylene glycol was appreciably increased, whereas irradiation of frozen ethanol gave both acetaldehyde and butane-2,3-diol.[1]

In the Presence of Oxygen.—In the irradiation of air-saturated and oxygen-saturated (1 atm.)

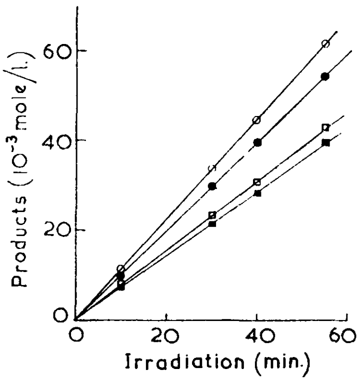
FIG. 1. *Dependence of the products on the time of irradiation* (^{60}Co *γ-rays*) *of pure deaerated methanol at* 20° *at constant dose rate* 1·6 × 10^{15} ev ml.$^{-1}$ min.$^{-1}$.

□, H_2. ○, $(HO\cdot CH_2\cdot)_2$. △, CH_2O.



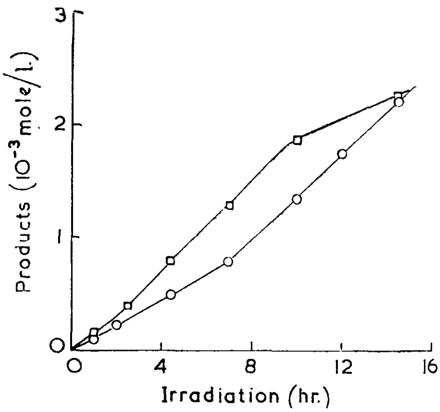
liquid methanol, the products found were formaldehyde and hydrogen peroxide, with smaller amounts of hydrogen: no ethylene glycol could be detected. Fig. 2 shows the dependence of the yields of formaldehyde and hydrogen peroxide on radiation dose for air and oxygen-saturated liquid methanol. As from ethanol, the initial yields of oxidation products are higher in air-saturated solutions both for X- and for γ-rays (Table 2).

FIG. 2. *Dependence of the formation of formaldehyde and hydrogen peroxide on time of irradiation* (^{60}Co *γ-rays*) *of pure methanol at* 20° *at constant dose rate* 1·6 × 10^{15} ev ml.$^{-1}$ min.$^{-1}$.



CH_2O: ○ air, ● O_2. H_2O_2: □ air, ■ O_2.

FIG. 3. *Dependence of the products on the time of irradiation* (^{60}Co *γ-rays*) *of methanol in the presence of air at constant dose rate* 1·6 × 10^{15} ev ml.$^{-1}$ min.$^{-1}$.



□ CH_2O. ○ H_2O_2.

In the irradiation of frozen methanol at −196° in the presence of oxygen, no formaldehyde was detected whereas ethylene glycol was found. This is somewhat surprising and may be partly due to the relatively low solubility of oxygen in methanol at −196°.

As from ethanol, the yields obtained by the irradiation of air-free liquid methanol with γ-rays are appreciably lower than those obtained with X-rays, while the yields in the presence of oxygen are about the same for both X- and γ-rays (Table 2).

TABLE 2. *Initial yields* (G-*values*) *of the products of radiolysis of methanol in the presence of air and oxygen* (1 atm.) *in the liquid* (20°) *and in the frozen state* (−196°). (γ-*Rays*: 1·60 × 10^{15} ev ml.$^{-1}$ min.$^{-1}$. X-*Rays*: 1·43 × 10^{16} ev ml.$^{-1}$ min.$^{-1}$.)

	γ-Irradiation		*X*-Irradiation			
	At 20°		At 20°		At −196°	
Products	Air-satd.	O_2-satd.	Air-satd.	O_2-satd.	Air-satd.	O_2-satd.
CH_2O	4·28	3·78	4·15	3·67	—	—
$(\cdot CH_2\cdot OH)_2$	—	—	—	—	2·65	2·53
H_2O_2	2·89	2·69	3·08	2·94	2·38	2·14
H_2	1·41	1·28	2·10	1·50	1·76	1·50

TABLE 3. *Comparison of the yields obtained in the radiolysis of methanol.*

Radiation	$G(H_2)$	$G(CH_4)$	G(CO)	$G(CH_2O)$	G(glycol)	Ref.
28 Mev He ions	3·46	0·36	0·23	1·67	1·75	2
^{60}Co γ-Rays ...	4·0	0·24	0·16	1·3	3·0	3
,, ...	5·39	0·54	0·11	1·84	3·64	4
,, ...	4·1	1·23	0·15	2·05	3·1	5
,, ...	4·53	—	—	1·9	2·9	6 *
,, ...	4·1	0·39	0·13	1·41	2·43	Present work

* 2 Mev Van de Graaf electrons gave essentially the same products.

DISCUSSION

Table 3 shows the yields of products obtained in various laboratories on radiolysis of methanol. The large discrepancies are probably due partly to the different analytical methods employed and, perhaps more importantly, to the quality and purity of the methanol used.

The primary processes in the absorption of ionising radiation by methanol are presumably similar to that given for ethanol. Some results reported by Meshitsuka *et al.*[7] for the γ-irradiation of liquid $CH_3\cdot OD$ showed that the deuterium content in the hydrogen gas was about 38%. This supports the suggestion that the radiolysis of methanol may involve dissociation of primarily formed polarons:

$$(CH_3\cdot OH)^+ \longrightarrow \cdot CH_2\cdot OH + H^+ \quad (1)$$

$$(CH_3\cdot OH)^- \longrightarrow CH_3\cdot O^- + H \quad (2)$$

$$(CH_3\cdot OH)^- + H^+ \longrightarrow H + CH_3\cdot OH \quad (3)$$

$$CH_3\cdot O^- + H^+ \longrightarrow CH_3\cdot OH \quad (4)$$

In the absence of added solutes the $\cdot CH_2\cdot OH$ radicals can recombine or disproportionate, to give ethylene glycol or formaldehyde, respectively:

$$2\ \cdot CH_2\cdot OH \longrightarrow (\cdot CH_2\cdot OH)_2 \quad (5)$$

$$\cdot CH_2\cdot OH + \cdot CH_2\cdot OH \longrightarrow CH_2O + CH_3\cdot OH \quad (6)$$

However, it was shown that in the photolysis of methanol vapour [8] formation of formaldehyde requires a relatively high activation energy and can compete with that of ethylene glycol only at temperatures above 400°. For this reason, Phibbs and Darwent [8] proposed the reaction

$$\cdot CH_2\cdot OH \longrightarrow CH_2O + H \quad (7)$$

[7] Meshitsuka, Ouchi, Hirota, and Kusumoto, *J. Chem. Soc. Japan*, 1957, **78**, 129.
[8] Phibbs and Darwent, *J. Chem. Phys.*, 1950, **18**, 495.

to account for the formation of formaldehyde under these conditions. Reactions (1)—(5) would also explain the radiation chemistry of liquid methanol, in particular the fact that ethylene glycol is formed instead of formaldehyde on γ-irradiation at $-196°$ of frozen methanol.

On irradiation of liquid methanol, as of ethanol, the initial yields of formaldehyde and hydrogen peroxide are lower in oxygen- than in air-saturated solution for both X- and γ-rays (see Table 2), perhaps because some other oxidation product is formed to a greater extent in oxygen. This further product, presumably formic acid, was shown to be dependent on the concentration of molecular oxygen present in the solution. Fig. 3 shows the dose-dependence of the yield of formaldehyde and hydrogen peroxide in the γ-ray irradiation of air-saturated liquid methanol. At the higher radiation doses the yield of formaldehyde starts to increase; at this stage, the formation of formic acid is reduced, owing to a lower oxygen concentration in the solution.

The following reactions are suggested to account for the products formed in the irradiation of (liquid) methanol in the presence of oxygen:

$$(CH_3\cdot OH)^- + O_2 \longrightarrow O_2^- + CH_3\cdot OH \quad \ldots \quad (8)$$

$$H + O_2 \longrightarrow HO_2\cdot \quad \ldots \quad (9)$$

$$\cdot CH_2\cdot OH + HO_2\cdot \longrightarrow CH_2O + H_2O_2 \quad \ldots \quad (10)$$

Formation of molecular hydrogen may also proceed to some extent by dehydrogenation of the methanol by hydrogen atoms, particularly at lower oxygen concentrations, as discussed in Part I. The formation of formic acid could occur again through the hydro-peroxy-radical, *viz.*:

$$\cdot CH_2\cdot OH + O_2 \longrightarrow \begin{array}{l} CH_2\cdot OH \\ | \\ O\cdot O\cdot \end{array} \quad \ldots \quad (11)$$

$$\begin{array}{l} CH_2\cdot OH \\ | \\ O\cdot O\cdot \end{array} + O_2^- \longrightarrow \begin{array}{l} CH_2\cdot OH \\ | \\ O\cdot O\cdot^- \end{array} + O_2 \quad \ldots \quad (12)$$

$$\begin{array}{l} CH_2\cdot OH \\ | \\ O\cdot O^- \end{array} \xrightarrow{H^+} H\cdot CO_2H + H_2O \quad \ldots \quad (13)$$

The decrease in the yields of formaldehyde and hydrogen peroxide with increasing oxygen concentration could be explained if reaction (12) occurred in preference to reaction (10).

In the irradiation of air- and oxygen-saturated methanol at $-196°$, ethylene glycol, hydrogen peroxide, and hydrogen were the only products found (no formaldehyde). This is in keeping with the assumption that reaction (7) has a relatively high activation energy.

Experimental.—The techniques used were those described in Part I.[1]

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