where $g = (k_{20}/k_{17}[\mathrm{M}])(1 + f - f^*)$ and $h = (r_{16}k_{20}/k_{17}[\mathrm{M}])(1 - f - f^*)$. We make the reasonable approximation that f and f^* are independent of t; then integration of the above expression gives (21), where $\xi = ([\mathrm{M}]/r_{16})(1 + f - f^*)/(1 - f - f^*)$, $\eta = (k_{17}[\mathrm{M}]/k_{20} \cdot r_{16})(2f)/(1 - f - f^*)^2$, and $\zeta = (k_{20}/k_{17})(1 - f - f^*)$. The low conversion approximation (22) does not contain f^*. This indicates that, to an approximation correct up to $[\mathrm{H}_2]^2$, the hot radical effect can be neglected. Equa-

tion 22 can also be derived from the eq. 7 of a paper by Cvetanović, Falconer, and Jennings[22] with the approximations that $0li = 0$ and $k_7 = 0$. In this connection, it should be noted that $f = (^1/_2)[k_{18}/(k_{18} + k_{19})]$. Here the numerical factor, $^1/_2$, is necessary, because only one-half of the alkyl radicals undergoing disproportionation reaction finally ends up as olefins.

(22) R. J. Cvetanović, W. E. Falconer, and K. R. Jennings, *J. Chem. Phys.*, **35**, 1225 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BOSTON UNIVERSITY, BOSTON, MASSACHUSETTS]

The Radiolysis of Methanol and Methanolic Solutions. III. The Effect of Oxygen on the Radiolysis of Liquid Methanol by ^{60}Co γ-Rays and by ^{10}B$(n,\alpha)^7$Li Recoils[1,2]

BY SANG UP CHOI AND NORMAN N. LICHTIN

Vapor phase chromatography was used to determine yields of gaseous products. Yields of products per 100 e.v. absorbed obtained by γ-radiolysis *in vacuo* are: H_2, 5.0; CH_4, 0.43; C_2H_6, 0.006; C_2H_4, 0.004; CO, 0.06; CH_2O, 2.2; and $(CH_2OH)_2$, 3.2. Yields per 100 e.v. obtained by recoil radiolysis *in vacuo* are: H_2, 5.5; CH_4, 0.66; C_2H_6, 0.04; C_2H_4, 0.04; CO, 1.0; CH_2O, 3.0; and $(CH_2OH)_2$, 0.87. In the presence of O_2, $G(H_2)$, $G((CH_2OH)_2)$, and $G(CH_4)$ decrease, while $G(CH_2O)$ increases. Products formed in the presence of O_2, but not in its absence, include CO_2, HCO_2H, H_2O_2, and probably CH_3OOH. $G(CO)$ from γ-radiolysis is increased by O_2 but is decreased in the case of recoil radiolysis. Limiting yields of products are obtained at concentrations of O_2 of the order of 1×10^{-3} mole l.$^{-1}$ or less. Important limiting yields per 100 e.v. from γ-radiolysis include: H_2, 1.9; CH_4, 0.18; CO, 0.09; peroxide, 3.1; CH_2O, 8.7; $(CH_2OH)_2$, 0.1; and HCO_2H, ca. 1.5. Important limiting yields per 100 e.v. from recoil radiolysis include: H_2, 2.4; CH_4, 0.6; CO, 0.8; peroxide, 1.5; CH_2O, 3.9; $(CH_2OH)_2$, 0.4; and HCO_2H, ca. 1.0. The γ-radiolysis data are consistent with a mechanism which assumes that only molecular products in unreactive states and free radicals diffuse into bulk solution from the spurs and which does not involve chain autoxidation of methanol. Radical and "molecular" yields relating to the proposed mechanism can be estimated. In contrast, the recoil radiolysis data cannot be explained entirely in terms of free radicals and unreactive molecular products. The data can be rationalized by assuming that metastable, excited methanol molecules also diffuse into bulk solution. The various relevant "molecular" and radical yields can also be estimated for recoil radiolysis.

Introduction

A study of the radiolysis by X-rays and by ^{60}Co γ-rays of methanol saturated with air and with oxygen, respectively, at 1 atm. has been reported.[3] The extent of variation of oxygen concentration is not sufficient in this work to permit other than qualitative interpretation. In the present study, oxygen concentration was varied systematically, and both ^{60}Co γ-rays and ^{10}B-$(n,\alpha)^7$Li recoils were employed in radiolyses.

The unsatisfactory reproducibility of product yields from the γ-radiolysis of "pure" liquid methanol is well known.[4] Although this lack of reproducibility cannot be correlated with the methods of analysis employed, improvement in analytical reliability was sought in the present case through vapor phase chromatographic determination of gaseous products. In addition, further attention was directed toward achieving the complete degassing of radiolyzed methanol, in accord with the experience of Theard and Burton.[5]

Experimental

Materials.—Methanol (Eastman Organic, Spectrograde) was purified as described previously.[4,6] Oxygen (Matheson) was passed through a column of Ascarite and silica gel, followed by a

trap cooled by Dry Ice, before it was introduced into the vacuum line.

Methyl borate (Matheson) employed in recoil radiolysis was rectified on a Todd column. The middle fraction of distillate was further rectified under vacuum after transfer to the vacuum line. The middle third from the second distillation was stored on the vacuum line. Aliquots were transferred by distillation.

Preparation of Oxygenated Solutions.—The amount of oxygen transferred to a cell (containing methanol at Dry Ice temperature) was determined manometrically by difference, with the aid of a calibrated volume. The concentration of oxygen in solution at the temperature of irradiation (taken as 25°) was then calculated from the methanol volume and the known[7,8] solubility.

Irradiation.—Pyrex glass cells used for γ-irradiation were prepared, cleaned, and attached to the vacuum line, and methanol was transferred under vacuum from the storage system to irradiation cells, all as described previously.[4] The irradiation cells were sealed off from the line under vacuum and the amounts of methanol in the cells determined by weighing.[9]

γ-Irradiations were carried out at about 20° in a Schwarz–Allen type ^{60}Co source[10] for 9 to 35 min. Irradiation times as long as 70 min. were employed occasionally to facilitate analyses for minor gaseous products. Dose rates were determined by means of the aerated acid (0.8 N sulfuric acid) ferrous ammonium sulfate (10^{-3} mole/l.) dosimeter.[4] The dose rate to methanol was about 1.8×10^{17} e.v.$^{-1}$ ml.$^{-1}$ min.$^{-1}$. The volume of methanol was 10–20 ml. in most cases. The ratio of the volume of vapor to that of the liquid was about 1:2.

Recoil radiolyses were carried out in the Brookhaven thermal neutron facility.[4] Quartz irradiation cells and procedures employed in filling the cells, and in irradiating and determining doses, were those reported previously.[4] Concentrations of

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission under Contract AT(30-1)2383.

(2) Presented at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964.

(3) E. Hayon and J. J. Weiss, *J. Chem. Soc.*, 3970 (1961).

(4) M. Imamura, S. U. Choi, and N. N. Lichtin, *J. Am. Chem. Soc.*, **85**, 3565 (1963).

(5) L. M. Theard and M. Burton, *J. Phys. Chem.*, **67**, 59 (1963).

(6) The present preparation corresponds to methanol C of ref. 4.

(7) "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 262.

(8) C. B. Kretschmer, J. Nowakowska, and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946).

(9) N. N. Lichtin, *J. Phys. Chem.*, **63**, 1449 (1959).

(10) H. A. Schwarz and A. O. Allen, *Nucleonics*, **12**, 58 (1954).

TABLE I

PRODUCT YIELDS[a] PER 100 E.V. IN THE ABSENCE OF ADDED SOLUTE

Radiation	H_2	CH_4	C_2H_6	CO	CH_2O	$(CH_2OH)_2$	C_2H_4
γ	4.98 ± 0.08[c]	0.43 ± 0.00[c]	0.006 ± 0.000[c]	0.057 ± 0.001[c]	2.20 ± 0.09[d]	3.23 ± 0.10[d]	0.004[e]
Recoil[b]	5.53 ± 0.16[c]	0.66[e]	0.044[e]	1.0[e]	3.04 ± 0.02[c]	0.87 ± 0.07[c]	0.035[c]

[a] Indicated precisions are mean deviations. [b] In the presence of added methyl borate; cf. Experimental. [c] Duplicate experiments. [d] Triplicate experiments. [e] Single experiment.

(MeO)₃B were in the range 0.033–0.123 M. Neutron flux was approximately 3 × 10⁹ cm.⁻¹ sec.⁻¹. Recoil dose rates were in the range (0.57–2.7) × 10⁻¹⁶ e.v. ml.⁻¹ min.⁻¹. Irradiation times varied from 295 to 1136 min. Yields from recoil radiolysis were corrected for radiolysis by the γ-background in the thermal column. The latter accounted for less than 5% of the observed yields.

Analysis of Nonvolatile Products.—Ethylene glycol and formaldehyde were determined by the methods used previously.[4,9]

Peroxide was determined by the method of Hochanadel.[11] We have reported[12] that peroxide yields depend on water concentration and that no peroxide is detectable in dry methanol. It has since been established[13] that the dependence of peroxide yields on water concentration is a post-irradiation effect: water inhibits the decay of methanolic hydrogen peroxide. In the work of this paper, analyses were carried out after γ-irradiation with no more than a few minutes delay. After recoil irradiation, samples were stored at Dry Ice temperature for as long as 28 hr. before analyses for peroxide. The samples were, however, at ambient temperature during the lengthy pile irradiations (5–16 hr.). It was subsequently found[13] that trimethyl borate is an effective inhibitor of decay of peroxide in methanol solution, so that it can be assumed that peroxide decay during irradiation was negligible.

Formic acid was determined by a modification of the method of Grant[14] which was developed by Mrs. L. A. Rosenberg in this laboratory. The procedure involves treatment of 0.5 ml. of irradiated methanol with 0.1 ml. of 0.1 M aqueous NaHCO₃, addition of 0.5 ml. of benzene, evaporation to dryness, addition of a second 0.5-ml. aliquot of benzene, and evaporation to dryness followed by dissolution of the residue, containing HCO₂Na, in 0.5 ml. of water and analysis of the solution essentially as described by Grant.[14] Formaldehyde (the compound which is actually determined in Grant's method) is completely removed in this way. The absence of interference by CH₂O, (CH₂OH)₂, and H₂O₂ was established experimentally. If methyl formate is a product of radiolysis, all or most of it would be lost during the evaporation procedure. The use of NaOH in place of NaHCO₃ led to irreproducible results, presumably due to varying amounts of Cannizzaro reaction.

Analysis of Gaseous Products.—After irradiation, each cell was attached to the gas-collecting portion of the vacuum line by a round-glass joint. A Dry Ice bath was placed around a trap located between the cell and an automatic Toepler pump. The break-off seal of the cell was broken with the aid of a glass-enclosed iron bar and a pair of magnets. The Toepler pump was started and the cell heated with warm water. The pumping procedure was continued until the contents of the cell had distilled into the cold trap, where the methanol remained liquid. It should be noted that the use of gas chromatography for analysis of the gaseous products renders complete removal of methanol from these products unnecessary. In this way, all the gaseous products were removed from the cell and pumped into a gas-collection vessel which was attached to the vacuum line by two ball joints. Upon completion of pumping, the gas-collection vessel was removed from the line and attached to another vacuum line for gas chromatographic analysis in an F & M Model 500 unit, equipped with a Model 1720 dual column detector.

An 8-ft. silica gel column was used for determination of ethylene and a 4-ft. Molecular Sieve 5A column for determination of all other gaseous products. Nitrogen was used as the carrier gas for the hydrogen analysis and helium for all the other gases. Flow rate of the carrier gases was kept at approximately 33 ml./min. The Molecular Sieve column was kept at room temperature until the methane peak was recorded. The column was then maintained at 75° for the carbon monoxide peak. The ethane peak

and the ethylene plus carbon dioxide peak were recorded at 200 and 300°, respectively. The silica gel column was temperature programmed from 50° at a heating rate of 4°/min.

Calibration curves were determined for each gas analyzed by using known amounts of gases and by measuring the corresponding peak heights or areas under the same conditions as those used for irradiated samples. The calibrations were repeated occasionally in order to check any unexpected change in the sensitivity of the determinations.

Data

γ-Radiolysis.—Yields from methanol to which no solute had been added were not investigated extensively in the present work. Because radiolytic yields from pure methanol are not yet unequivocally established, it was, however, necessary to determine these yields under the same conditions and by the same methods employed with oxygenated solutions. These data are presented in Table I.

The fact that $G(CH_4)$ for γ-radiolysis agrees well with the value, 0.44, reported by Theard and Burton[5] can be attributed to the use, in the present case, of a method of collecting gaseous products which provided complete degassing and eliminated the opportunity for entraining methane in trapped solid methanol. Yields of hydrogen, formaldehyde, and ethylene glycol correspond rather well with the values which have been reported most recently[4,5]; $G(CO)$ is, however, significantly lower.[4,5] McDonell and Newton[15] reported $G(C_2H_6)$ = 0.014 from radiolysis of methanol by 28-Mev. cyclotron α-particles. Only one worker[16] has previously identified ethane as a product of the ⁶⁰Co γ-radiolysis of methanol, but his reported yield, 0.14, is in poor agreement with the present value. Ethylene does not appear to have been identified previously as a radiolytic product from methanol. The present values of G(oxidn.) and G(redn.), 5.6 and 5.4, respectively, are in reasonably good balance.

The most important data for oxygenated solutions are presented in Fig. 1. Yields of CO, CO₂, and C₂H₆ from methanol initially 1.5 mM in O₂ and of C₂H₄ from methanol initially 0.38 mM in O₂ are summarized in Table II. $G(CO)$ and $G(CO_2)$ both increase smoothly from their values in deaerated methanol. In addition, the yield of formic acid, a product not formed in the absence of O₂, was found to be 1 molecule/100 e.v. in a single experiment with oxygen at 158.5 mm. (1.63 × 10⁻³ M calculated concentration). In a more extensive set of γ-radiolyses with aerated methanol,[12] $G(HCO_2H)$ was found to be 1.8 ± 0.2. The relatively large discrepancy is probably due to the analytical method.

The data show that oxygen inhibits the formation of H₂, (CH₂OH)₂, and CH₄, has little or no effect on the production of CO, C₂H₆, and C₂H₄, and increases the yield of CH₂O. Oxidation products observed in the presence, but not in the absence of O₂, include CO₂, formic acid, and peroxide. It should be noted that the

(11) C. J. Hochanadel, J. Phys. Chem., **56**, 588 (1952).
(12) N. N. Lichtin, L. A. Rosenberg, and M. Imamura, J. Am. Chem. Soc., **84**, 3587 (1962).
(13) Unpublished work by J. W. Wilson.
(14) W. M. Grant, Anal. Chem., **20**, 267 (1948).
(15) W. R. McDonell and A. S. Newton, J. Am. Chem. Soc., **76**, 4651 (1954).
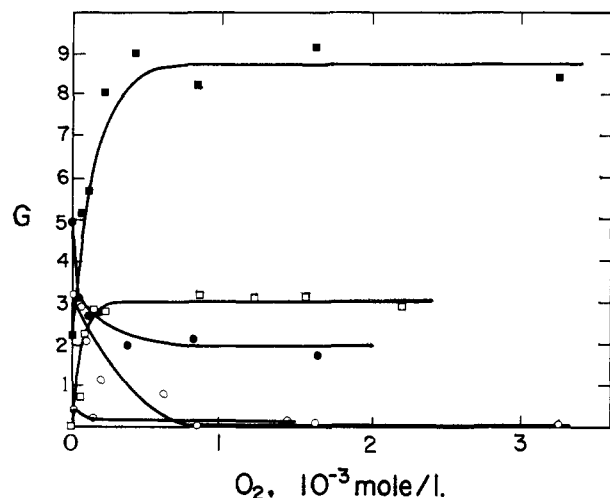(16) R. H. Johnsen, J. Phys. Chem., **65**, 2144 (1961).

Fig. 1.—^{60}Co γ-radiolysis: $G(\text{H}_2)$, ●; $G(\text{C}_2\text{H}_6\text{O}_2)$, O; $G(\text{CH}_2\text{O})$, ■; $G(\text{peroxide})$, □; $G(\text{CH}_4)$, ◒

method[11] used to determine the latter product would not distinguish H_2O_2 from CH_3OOH. Some of the present data can be compared with those which Hayon and Weiss reported[3] for air-saturated solutions in which the concentration of O_2 is[8] about $2 \times 10^{-3}\ M$. These workers reported[17] $G(\text{H}_2) = 1.8$, $G(\text{CH}_2\text{O}) = 4.2$, and $G(\text{H}_2\text{O}_2) = 3.0$ for doses in the range 1.6×10^{16} to 1×10^{17} e.v. ml.$^{-1}$ and presented data which suggest that yields of CH_2O and H_2O_2 may be dose dependent at total doses similar to those employed in this work (typically 1.6×10^{18} e.v. ml.$^{-1}$). In addition, their dose rates were one-hundredth (γ) and one-tenth (X-ray) that employed in the present work (1.8×10^{17} e.v. ml.$^{-1}$ min.$^{-1}$). We have not carried out a systematic investigation of dose or dose-rate effects. However, the agreement of the present values of $G(\text{peroxide})$ and $G(\text{H}_2)$ in solutions, comparable in O_2 concentration with those employed by Hayon and Weiss, with the "initial" values reported by the latter suggest that at least these yields are independent of dose and dose rate. One series of radiolyses of air-saturated methanol which was carried out at a dose rate of 1.07×10^{16} e.v. ml.$^{-1}$ min.$^{-1}$ over the dose range 5.7×10^{17} to 1.9×10^{18} e.v. ml.$^{-1}$ provided[18] yields of CH_2O which were substantially in agreement with the data of Fig. 1. It is assumed, for purposes of interpreting the present data that yields are neither dose nor dose-rate dependent.

Figure 1 shows that, at concentrations of O_2 comparable to those obtained by air saturation, peroxide yields from rigorously dried methanol are in agreement with values previously reported[12] from this laboratory for solutions containing more than 0.5 wt. % of H_2O. The curious effect of water which was reported[12] has been shown[13] to be a post-irradiation phenomenon. Peroxide yields are, in fact, not dependent on water concentration, but it is necessary to avoid or prevent post-irradiation decay of peroxide by carrying out analyses with minimum delay or by adding an inhibitor, e.g., water.

Oxygen consumption was not determined in this work. $G(-\text{O}_2)$ was estimated for the "plateau" region, i.e., at concentrations of O_2 where G-values no

(17) The quoted figures are averages of their data for radiolysis by ^{60}Co γ-rays and by 200 kv. X-rays.
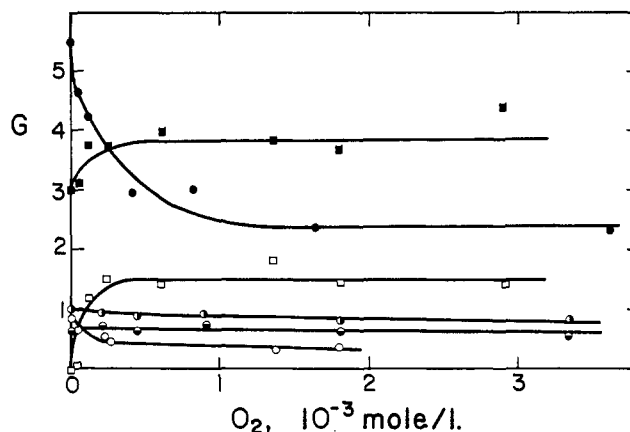(18) Work by L. A. Rosenberg on air-saturated methanol.

Fig. 2.—Recoil radiolysis: $G(\text{H}_2)$, ●; $G(\text{C}_2\text{H}_6\text{O}_2)$, O; $G(\text{peroxide})$, □; $G(\text{CH}_4)$, ◒; $G(\text{CO})$, ◑; $G(\text{CH}_2\text{O})$, ■.

longer depend on (O_2), by means of eq. 1 (where $\Delta G(\text{P}) = G(\text{P})_{\text{plateau}} - G(\text{P})_{vacuo}$) to be 6.4.

$$G(-\text{O}_2) = \frac{1}{2}[\Delta G(\text{CH}_2\text{O}) + \Delta G(\text{CH}_2\text{OH})_2] + G(\text{H}_2\text{O}_2) + \frac{3}{2}G(\text{CO}_2) + G(\text{HCO}_2\text{H}) \quad (1)$$

From this it can be calculated that 65%, or less, of dissolved oxygen was consumed at the beginning of the plateaus for the major products, H_2, CH_2O, $(\text{CH}_2\text{OH})_2$, and peroxide, assuming none transfers from gas to solution phase during radiolysis. For these products, the yield plateaus were followed up to oxygen concentrations such that, at the most, 16% of initial (O_2) was consumed. If equilibrium of oxygen dissolution maintained during radiolysis, these values are 30 and 5%, respectively.

Quantitative interpretation of yield data at oxygen concentrations below the plateau values is excluded because of our inability to separate the results of depletion of oxygen from the effects of competition of O_2 and CH_3-OH for active species. Accordingly, only plateau data are discussed extensively below.

Recoil Radiolysis.—The data of Table I for recoil radiolysis in the absence of O_2 are in good agreement with recently reported[4] values obtained under the same conditions, although ethane and ethylene were not detected in the latter work. $G(\text{oxidn}). = 6.0$ and $G(\text{redn.}) = 6.2$ are in acceptable balance.

The most important data for oxygenated solutions are presented in Fig. 2. Plateau values of $G(\text{C}_2\text{H}_6)$, $G(\text{C}_2\text{H}_4)$, and $G(\text{CO}_2)$ given in Table IV are based on plateaus extending to 3.3, 2.9, and 1.8 mM O_2, respectively. $G(\text{HCO}_2\text{H})$ was found to be 1.0 in a single experiment with $(\text{O}_2) = 1.06 \times 10^{-3}\ M$. The effect of oxygen on recoil radiolysis is superficially similar to its influence on ^{60}Co γ-radiolysis, but there are several interesting differences. The yield of glycol, which is small in the absence of oxygen, is only halved at the plateau, not virtually completely suppressed as it is with γ-radiolysis. The yield of CO is reduced to a small but significant extent while with γ-radiolysis the result, if there is any effect, is a very small increase. $G(\text{CH}_4)$ is reduced relatively much less than it is with γ-radiolysis; the effect may be insignificant. The increases in both $G(\text{CH}_2\text{O})$ and $G(\text{peroxide})$ are considerably smaller than for γ-radiolysis. Only the plateau decreases in $G(\text{H}_2)$ are identical for γ- and recoil radiolyses. However, it is suggested below that this last similarity is

accidental and is *not* due to identical mechanisms of action of O_2.

Application of eq. 1, supplemented by the term ΔG (CO), to plateau yields of CH_2O, $(CH_2OH)_2$, peroxide, CO, and CO_2 and to the single value of $G(HCO_2H)$ gives $G(-O_2) = 2.6$. Thus yield plateaus of H_2, CH_2O, peroxide, CO, and CO_2 were followed up to consumption of 20% or less of the dissolved oxygen. The corresponding values for ethylene glycol and formic acid were 50 and 90%, respectively. Inasmuch as recoil dose rates were of the order of one-tenth γ-dose rates, it is more probable that equilibrium of dissolution of oxygen was maintained in recoil radiolysis. In this event, reductions of (O_2) were about one-third the indicated values.

As in the case of γ-radiolysis, only plateau yields are subject to interpretation below.

Discussion

^{60}Co γ-Radiolysis.—Yields in the plateau region, *i.e.*, at concentrations of oxygen where yields are no longer sensitive to oxygen concentration, and *in vacuo* are compared in Table II. The viewpoint of the inter-

TABLE II

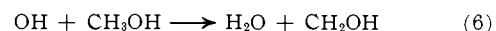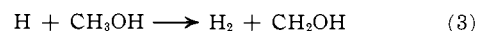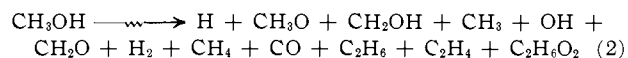YIELDS FROM ^{60}Co γ-RADIOLYSIS IN THE PRESENCE AND ABSENCE OF O_2

Product	$G_{plateau}{}^{a,b}$	G_{vacuo}	Δ^a
H_2	1.9	4.98	−3.1
CH_4	(0.18)	0.43	(−0.25)
C_2H_6	0.006	0.006	0.000
C_2H_4	(0.005)	0.004	(0.001)
Peroxide	3.1	0	3.1
CH_2O	8.7	2.2	6.5
$(CH_2OH)_2$	0.1	3.2	−3.1
CO	(0.09)	0.06	(0.03)
HCO_2H	(∼1.5)	0	(∼1.5)
CO_2	(0.1)	0	(0.1)
−CH_3OH	11.2	9.3	1.9

^{a} Where achievement of a yield plateau was not established experimentally, values are given in parentheses. ^{b} Molecules/100 e.v.

pretations offered in this section is that product yields will be explained entirely in terms of radical reactions as long as the data can reasonably be rationalized in this way. It is also assumed that no significant chain reaction is initiated under the present conditions. This assumption is founded on the evidence of absence of dose-rate dependence which is outlined above. This evidence is convincing for $G(H_2)$ and G(peroxide) over a factor of 100 in dose rate. It is not satisfactory in the case of $G(CH_2O)$. Hayon and Weiss[3] find no variation of $G(CH_2O)$ over a factor of ten in dose rate and similar results have been obtained in this laboratory. However, although the upper end of the range of dose rates employed by Hayon and Weiss overlaps the lower end of our range, Hayon and Weiss report a value of G(CH$_2$O) about one-half that which we have found. The fact that Hayon and Weiss found $G(H_2) = 4.1$ *in vacuo* suggests the possibility[12] that an adventitious solute may have been responsible for their low value of $G(CH_2O)$ in aerated methanol. The fact that ΔG (−CH_3OH) is only 1.9 also tends to support the assumption that there is little or no chain autoxidation of methanol.

The most striking aspects of the data of Table II are the nearly complete inhibition of glycol production and the equality of ΔG(peroxide) and $-\Delta G(H_2)$. The

following reaction scheme rationalizes these and other results. Equation 2 represents the introduction into bulk solution of those species which escape the spurs. Equations 3–7 represent reactions occurring in bulk solution in pure methanol.

$$CH_3OH \xrightarrow{\wedge\wedge\wedge} H + CH_3O + CH_2OH + CH_3 + OH +$$
$$CH_2O + H_2 + CH_4 + CO + C_2H_6 + C_2H_4 + C_2H_6O_2 \quad (2)$$

$$H + CH_3OH \longrightarrow H_2 + CH_2OH \quad (3)$$

$$CH_3O + CH_3OH \longrightarrow CH_3OH + CH_2OH \quad (4)$$

$$CH_3 + CH_3OH \longrightarrow CH_4 + CH_2OH \quad (5)$$

$$OH + CH_3OH \longrightarrow H_2O + CH_2OH \quad (6)$$

$$2CH_2OH \longrightarrow HOCH_2CH_2OH \quad (7)$$

According to eq. 2–7, all radicals are converted rapidly into CH_2OH, and $G_{radicals}$ equals twice the yield of scavengeable glycol, *i.e.*, 6.2, in excellent agreement with the value, 6.3 ± 0.1, which Baxendale and his co-workers[19-21] base on reduction of the oxidizing scavengers, Fe^{+3}, benzoquinone, and duroquinone.

The stage at which oxygen intercepts is clearly indicated for the radicals H and CH_3 since reactions 3 and 5 are both suppressed by a sufficient concentration of O_2 giving (8) and (9) instead. The data are consistent

$$H + O_2 \longrightarrow HOO \quad (8)$$

$$CH_3 + O_2 \longrightarrow CH_3OO \quad (9)$$
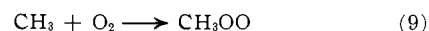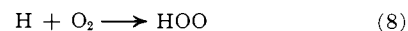
with the assumption that HOO and CH_3OO disappear virtually exclusively *via* reactions 10 and 11. On this

$$HOO + CH_3OH \longrightarrow H_2O_2 + CH_2OH \quad (10)$$

$$CH_3OO + CH_3OH \longrightarrow CH_3OOH + CH_2OH \quad (11)$$
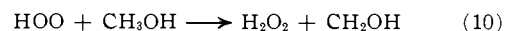
basis, and recognizing that our peroxide analysis did not discriminate between H_2O_2 and CH_3OOH, G(peroxide) should equal $-\Delta G(H_2) - \Delta G(CH_4) = 3.35$. The small discrepancy between this value and the experimental one, 3.1, is very likely due to the slow decay of peroxide which takes place in dry methanol.[13]

There is no direct evidence bearing on the interception of OH and CH_3O since $G(H_2O)$ was not determined, and the data do not discriminate directly between interception of CH_3O and of CH_2OH. The fate of OH is relatively unimportant since it is a minor product. It has been concluded,[5] moreover, from the isotopic composition of hydrogen produced by the radiolysis of various deuterated methanols that CH_3O is an unimportant primary product. The present data are explained most simply if neither OH nor CH_3O is intercepted by O_2 under our plateau conditions since highly exothermic[22] reaction 12 predicts additional peroxide. Thus, it is assumed that reactions 4 and 6 are not inhibited in the presence of O_2.

$$CH_3O + O_2 \longrightarrow HOO + CH_2O \quad (12)$$
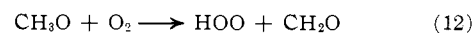
On the basis of the above reasoning, only the fate of the CH_2OH radical remains to be explained. Highly exothermic reaction 13 can be excluded because it also

$$CH_2OH + O_2 \longrightarrow HOO + CH_2O \quad (13)$$

(19) G. E. Adams and J. H. Baxendale, *J. Am. Chem. Soc.*, **80**, 4125 (1958).

(20) G. E. Adams, J. H. Baxendale, and R. D. Sedgwick, *J. Phys. Chem.*, **63**, 854 (1959).

(21) J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4720 (1961).

(22) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Academic Press, New York, N. Y., 1958, p. 270 ff.

<center>TABLE III</center>

<center>RADICAL AND "MOLECULAR" YIELDS FROM THE ^{60}Co γ-RADIOLYSIS OF LIQUID METHANOL</center>

| Species	CH₂O	H₂	CH₄	C₂H₆	C₂H₄	CO	H	CH₃	OH	Σ(radicals)
Yield/100 e.v.	2.2	1.9	0.2	0.006	0.005	0.08	3.1	0.2	0.2	6.2

predicts too large a yield of peroxide. The results can be rationalized, however, by assuming reaction 14 and

$$HOCH_2 + O_2 \longrightarrow HOCH_2OO \qquad (14)$$
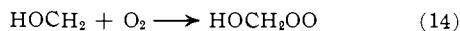
the formation of CH_2O and HCO_2H *via* bimolecular reactions of $HOCH_2OO$. A very difficult problem arises here, however. If the principal or sole fate of HO_2 is reaction 10, then the possible significant occurrence of reaction 15 cannot be ignored. Reactions 14 and 15,

$$HOCH_2OO + CH_3OH \longrightarrow HOCH_2OOH + CH_2OH \quad (15)$$
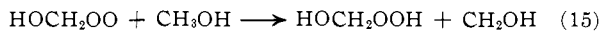
however, constitute chain carrying steps, and the possibility of significant chain reaction appears to be excluded. Apparently $HOCH_2OO$ abstracts hydrogen considerably more slowly than does HOO. Since the steady-state rate at which $HOCH_2OO$ is formed appears to be about twice that at which HOO is formed, and the rate of reaction 16 must be at least ten times that of (15), the rate of (10) must be at least one to two orders

$$2HOCH_2OO \longrightarrow products \qquad (16)$$
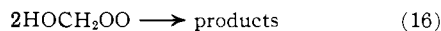
of magnitude greater than that of (15). The reason for such a difference can only be discussed in a speculative fashion. Intramolecular hydrogen bonding between hydroxyl hydrogen and the terminal peroxy oxygen might conceivably diminish the reactivity of $HOCH_2OO$ by enhancing delocalization of the unpaired electron over the two peroxy oxygens, but it seems highly improbable that intramolecular hydrogen bonding could compete with intermolecular bonding with solvent molecules. A small steric effect is possible. The $HOCH_2$ group may render the terminal peroxy oxygen less accessible, particularly, if in the transition state the dihedral angle about the O–O linkage is near 90°,[23] rather than 180°. The conformational constraint in $HOCH_2$-OOH and the transition state preceding it due to dipole repulsion between the two OH groups when they are in or near the eclipsed conformation (assuming no intramolecular hydrogen bonding) may also significantly diminish the rate of (15) relative to that of (10).

The detailing of reaction 16 must be consistent with the observed yields of formaldehyde and formic acid. (It is assumed herein that methyl formate is not a significant product, even though this was not determined experimentally.) Since, as is shown above, all radicals reaching bulk solution can, in the case of pure methanol, be accounted for as ethylene glycol, it can be concluded that all the formaldehyde formed by ^{60}Co γ-radiolysis of pure methanol is "molecular," *i.e.*, formed in the spurs. Thus, it follows that $\Delta G(CH_2O) = 6.5$ plus $\Delta G(HCO_2H) \cong 1.5$ are produced by reaction 16. The entire yield of formic acid and an equal amount of formaldehyde are presumably formed by reaction 17. Equation 18 represents a mechanism for (17) which is analogous to that which has been proposed[24] for the bimo-
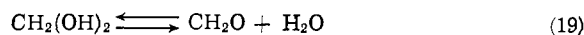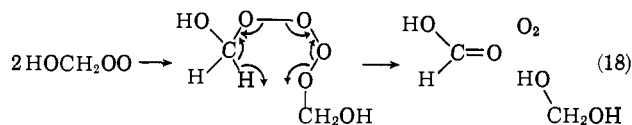
$$2HOCH_2OO \longrightarrow HCO_2H + CH_2O + H_2O + O_2 \quad (17)$$
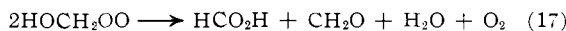
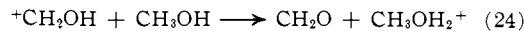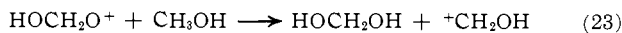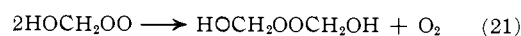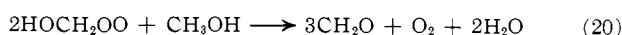lecular reaction of α-phenethylperoxy radicals. The

(23) *Cf.* L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 134.

(24) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

balance of the formaldehyde yield, *i.e.*, approx. 5 molecules/100 e.v. apparently is formed from approximately

$$CH_2(OH)_2 \rightleftharpoons CH_2O + H_2O \qquad (19)$$

three radicals per 100 e.v. Within the precision of the data, this can be rationalized by stoichiometric expression 20 and the speculative mechanism represented by eq. 21–25 and 19. A variant of this scheme can serve

$$2HOCH_2OO + CH_3OH \longrightarrow 3CH_2O + O_2 + 2H_2O \qquad (20)$$

$$2HOCH_2OO \longrightarrow HOCH_2OOCH_2OH + O_2 \qquad (21)$$

$$HOCH_2OOCH_2OH \longrightarrow HOCH_2O^+ + {}^-OCH_2OH \qquad (22)$$

$$HOCH_2O^+ + CH_3OH \longrightarrow HOCH_2OH + {}^+CH_2OH \qquad (23)$$

$${}^+CH_2OH + CH_3OH \longrightarrow CH_2O + CH_3OH_2{}^+ \quad (24)$$

$$HOCH_2O^- + CH_3O^+H_2 \longrightarrow HOCH_2OH + CH_3OH \qquad (25)$$
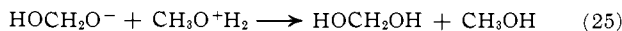
as an alternative to (18). Equation 26 is the most relevant step in this possibility.

$$HOCH_2O^+ + CH_3OH \longrightarrow HCO_2H + CH_3OH_2{}^+ \quad (26)$$
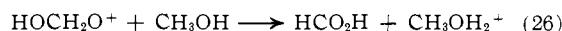
It is assumed that C_2H_4 and C_2H_6 are entirely, or almost so, molecular products. There is an apparent increase in $G(CO)$ in the presence of oxygen but $\Delta G(CO)$ is too small to serve as a limit on interpretive speculation. In the absence of information relating $G(CO_2)$ to total dose, it is not known whether carbon dioxide is formed by attack on other products.

On the whole, the effects of O_2 on the γ-radiolysis of methanol reported herein are consistent with a model which assumes that only radicals and stable molecules escape into bulk solution. The yields of these species which follow from the above treatment are presented in Table III. The fact that no distinction has been made between hydrogen atoms and "solvated electrons" is not meant to imply any judgment concerning the presence of the latter[21,25] in γ-irradiated methanol. Our data simply do not provide any basis for discrimination.

The near identity of G_{CH_2O} and G_{H_2} is striking. The results do not, however, discriminate between unimolecular elimination of H_2 and bimolecular reaction of H + CH₃O or CH₂OH in the spur.

^{10}B$(n,\alpha)^7$Li **Recoil Radiolysis.**—Yields in the plateau region of oxygen concentration and *in vacuo* are compared in Table IV. It is assumed that methyl borate is not involved in the chemical transformations consequent upon radiolysis. This assumption has been verified[4] in the absence of O_2 but not in its presence. The consequences of variation in recoil dose rate were not explored, but the absence of significant chain reaction in recoil radiolysis of oxygenated methanol is also assumed. The small magnitude of $\Delta G(-CH_3OH)$, namely 0.7, tends to support this assumption.

(25) I. A. Taub, M. C. Sauer, Jr., and L. M. Dorfman, *Discussions Faraday Soc.*, **36**, 206 (1963).

TABLE IV

YIELDS FROM $^{10}B(n,\alpha)^7Li$ RECOIL RADIOLYSIS IN THE
PRESENCE AND ABSENCE OF O_2

Product	$G_{plateau}{}^{a,b}$	$G_{vacuo}{}^{a,b}$	Δ^a
H_2	2.4	5.5	−3.1
CH_4	0.6	0.7	−0.1
C_2H_6	0.04	0.04	0.00
C_2H_4	0.03	0.04	−0.01
Peroxide	1.5	0	1.5
CH_2O	3.9	3.0	0.9
$(CH_2OH)_2$	0.4	0.9	−0.5
CO	0.8	1.0	−0.2
HCO_2H	(1)	0	(1)
CO_2	0.03	0	0.03
$-CH_3OH$	7.4	6.7	0.7

^{a} Where achievement of a yield plateau was not established experimentally, values are given in parentheses. ^{b} Molecules/100 e.v.

Attempts to interpret the data for recoil radiolysis on the basis that only free radicals and stable molecular products diffuse into bulk solution appear to encounter

than the rather complicated glycol analysis, $G(H)$ + $G(CH_3)$ is taken to be 1.5 with the individual values 1.4 and 0.1, respectively. It is a corollary of this conclusion that H and CH_3 are the only radicals which escape from the dense ionization track.

From equations 8–11, 14, 17, and 20, together with $G_{plateau}(HCO_2H) = 1$ and the above estimate that G (radical) = 1.5, it follows that the yield of CH_2O arising from oxidation of CH_2OH is 1.8 molecules/100 e.v. Since $\Delta G(CH_2O) = 0.9$, it follows that 0.9 molecule/100 e.v. of the formaldehyde produced in recoil radiolysis of pure methanol is not produced in the presence of oxygen. In addition, $\Delta G(CO) = -0.2$. From the assumption that reactions 27 and 28 are prevented by the quenching

$$CH_3OH^* \longrightarrow CH_2O + H_2 \qquad (27)$$
$$CH_3OH^{**} \text{ (or } CH_3OH^*) \longrightarrow CO + 2H_2 \qquad (28)$$

action of oxygen, it follows that $G(H_2)$ should be reduced by 1.3 units due to this action. The total reduction in $G(H_2)$ from the combined radical scavenging and

TABLE V

YIELDS OF RADICALS, "MOLECULAR" PRODUCTS, AND EXCITED METHANOL FROM THE $^{10}B(n,\alpha)^7Li$ RECOIL RADIOLYSIS OF
LIQUID METHANOL

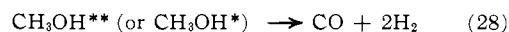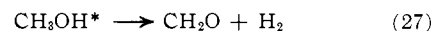| Species	CH_2O	H_2	CH_4	C_2H_6	C_2H_4	CO	$C_2H_6O_2$	H	CH_3	OH	Σ(radicals)	$CH_3OH^* + CH_3OH^{**}$
Yield/100 e.v.	2.1	2.4	0.6	0.04	0.04	0.8	0.4	1.4	0.1	0	1.5	1.3

an insuperable difficulty in the relative magnitudes of $\Delta G(H_2)$ and $\Delta G(C_2H_6O_2)$, respectively, −3.1 and −0.5. If the CH_2OH precursor of scavengeable ethylene glycol were formed solely via reaction 3, $\Delta G(H_2)$ would be −1.0. This appears to be the largest possible depression in $G(H_2)$ which can be explained on the basis of radical scavenging by O_2. Probably the simplest model which can be postulated to account for this result is that a long-lived, possibly triplet, excited state (or states) of methanol escapes from the ionization track and diffuses into bulk solution. It is proposed that in recoil radiolysis molecular oxygen deactivates excited methanol in addition to serving as a radical scavenger.

The assumption that peroxide is formed by reactions 8–11 is reasonably consistent with the above model since $G(peroxide) - 2\Delta G(C_2H_6O_2)$ is only 0.5. This difference can be barely accommodated by the joint uncertainties in the three sets of measurements involved, and it is assumed herein that the difference is negligible.[26] Since $G(peroxide)$ is not based on a difference, and peroxide analyses are more reproducible

(26) A referee has suggested the possibility that $(e_s)_2{}^{-2}$ diffuses from the track and gives H_2 *in vacuo* and H_2O_2 in the presence of oxygen. This mechanism could account for the small apparent excess of $G(peroxide)$ over $2\Delta G(C_2H_6O_2)$ but not for the remaining $\Delta G(H_2) = -1.6$.

quenching action of O_2 is thus calculated to be 2.7. This is sufficiently close to the experimental $\Delta G(H_2) = -3.1$ to lend credence to the proposed mechanism.

It would be interesting but, at this time, premature to speculate further about the nature of CH_3OH^* and CH_3OH^{**}. Their existence and nature are subject to examination by use of other solutes and such work is planned.

Apparently C_2H_6 and C_2H_4 are "molecular" products. The yield of "molecular" ethylene glycol is significantly higher than in γ-radiolysis. Rationalization of the formation of CO_2 in recoil radiolysis of oxygenated methanol is not justified by the limited data.

Table V summarizes the yields of the various radicals, "molecular" products, and excited methanol molecules which escape the ionization tracks on the basis of the proposed model. As should be anticipated, the ratio $\Sigma G_{radicals}/\Sigma G_{\text{"molecular" products}}$ is much higher in the case of low L.E.T. γ-radiolysis (1.4) than for high L.E.T. recoil radiolysis (0.25).