TABLE VIII

HIGH TEMPERATURE ENTROPIES AND FREE ENERGY FUNCTIONS

	Y_2O_3		La_2O_3		Nd_2O_3	
Temp., °K.	$S°$, cal. mole^{-1} deg.$^{-1}$	$-(F° - H_0^0)/T$, cal. mole^{-1} deg.$^{-1}$	$S°$, cal. mole^{-1} deg.$^{-1}$	$-(F^0 - H_0^0)/T$, cal. mole^{-1} deg.$^{-1}$	$S°$, cal. mole^{-1} deg.$^{-1}$	$-(F^0 - H_0^0)/T$, cal. mole^{-1} deg.$^{-1}$
298.16	23.69	10.31	30.58	14.74	36.92	20.21
500	37.98	18.75	45.02	24.39	51.44	30.16
1000	59.04	34.15	66.08	40.49	73.80	46.94
1500	72.18	44.76	79.22	51.33	88.26	58.44
2000	82.00	52.89	89.04	59.58	98.86	67.28
2500	89.97	59.52	97.01	66.28	107.08	74 45

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RADIOLYSIS OF METHANOL AND METHANOLIC SOLUTIONS BY Co^{60} γ-RAYS AND 1.95 × 10^6 VOLT VAN DE GRAAFF ELECTRONS[1]

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Yields of hydrogen, formaldehyde, ethylene glycol (determined by means of an improved procedure), methane and carbon monoxide per 100 e.v. of absorbed radiation obtained on irradiation of methanol are compared with values reported in the literature. The several sets of data are not in good agreement with each other. Initial study of the effects of several solutes suggests a variety of modes of intervention in the radiolytic process.

The radiolysis of methanol and methanolic solutions has been the subject of an increasing number of investigations.[3] Two recent reports[4,5] dealing with the action of Co^{60} γ-rays on pure dry methanol and on a variety of solutions in this solvent include extensive discussions of the mechanisms of the radiolytic processes. These two reports are not in good agreement with each other or with earlier work[3c] with respect to the *G*-yields of the principal products[3b] of radiolysis of pure methanol, H_2, CH_4, CO, CH_2O and $HOCH_2CH_2OH$, nor as to the effect of small amounts of water. Although the work described below does not provide a basis for mechanistic interpretation, it presents additional extensive data on the radiolysis of pure methanol. These data are not in complete accord with any one of the previously published reports.

The results of a preliminary survey of the yields of the five principal products obtained on radiolysis of solutions containing a wide variety of solutes are also reported and discussed.

Experimental

Methanol.—Mallinckrodt AR anhydrous grade material was employed. This was generally subjected to rectification by means of a 50 theoretical plate glass-helix packed column protected from atmospheric moisture; the first third of the distillate routinely was discarded. (The methanol employed in half of the Van de Graaff runs was not rectified. No systematic difference in results distinguished these runs from the other experiments.) Eastman 99.9% "Grignard Grade" magnesium (1 to 2 g./100 ml. methanol) was added and the flask containing the methanol then was attached *via* a ₸ joint to a manifold used in drying and degassing the methanol and filling the radiation cells. After dissolution of the magnesium was complete, the methanolic $Mg(OCH_3)_2$ was refluxed for a minimum of three hours. Tubes containing silica gel and "Ascarite" protected the solution so long as H_2 was venting. Degassing was next accomplished by alternately pumping with a diffusion pump while the methanol was frozen in liquid nitrogen and permitting the methanol to warm to room temperature under autogenous pressure. A minimum of three such cycles was always employed. Each aliquot of dry degassed methanol was distilled at autogenous pressure through a trapping system into a radiation cell (chilled to −80°) which was attached to the manifold *via* a ₸ joint. The cell then was sealed off at a constriction. Sample sizes were determined by weight. The density of methanol was taken as 0.790 in calculations.

Solutes and Preparation of Solutions.—Magnesium methoxide solution was prepared by distilling dry degassed methanol onto magnesium metal (Eastman "Grignard Grade") maintained at −80°. Dissolution of the metal did not appear to begin until the solvent warmed to room temperature. Hydrogen evolved into an isolated portion of the manifold and was removed rigorously by a degassing procedure like that described above. Water and heptaldehyde (Eastman "White Label") were introduced into cells equipped with stopcocks and were separately degassed in the usual way before the solvent was distilled in. Cells containing samples of benzoquinone (Eastman "Practical," recrystallized from ligroin and then sublimed) and maleic anhydride (Pfanstiehl, "Pure") were also equipped with stopcocks and were subjected to prolonged pumping while maintained at −80° before distilling in the solvent. Cells containing lithium chloride (Baker "Analyzed"), pyrogallol (Eastman "White Label"), anthracene (Eastman "Fluorescent Grade"), sulfuric acid (concd. B. and A., C.P.), $FeCl_3 \cdot 6H_2O$ (B. and A. "Reagent" grade) and boric oxide (B. and A. "purified grade") were subjected to prolonged pumping at room temperature. A trace of the anthracene and a substantial fraction of the ferric chloride (estimated as 10–20% of added solute) did not dissolve even after prolonged shaking at

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[1] Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] Visiting Chemist at the Brookhaven National Laboratory, 1957–1958. Department of Chemistry, Boston University, Boston, Mass.

[3] (a) W. J. Skraba, J. C. Burr, Jr., and D. N. Hess, *J. Chem. Phys.*, **21**, 1296 (1953); (b) W. R. McDonell and A. S. Newton, *J. Am. Chem. Soc.*, **76**, 4651 (1954); (c) W. R. McDonell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955); (d) W. R. McDonell, *ibid.*, **23**, 208 (1955); (e) G. Meshitsuka, K. Ouchi, K. Hirota and G. Kusumoto, *J. Chem. Soc. Japan*, **78**, 129 (1957).

[4] G. Meshitsuka and M. Burton, *Radiation Research*, **8**, 285 (1958).

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

room temperature. Methyl borate solution was prepared by dissolving the boric oxide in methanol which was distilled onto it in the usual way.

Radiation Cells.—Cells for irradiation in the Co^{60} source were fabricated of Pyrex glass. Each was provided with a breakoff seal and a side-arm equipped with a ₮ joint for attachment to the charging manifold. The sizes of the cells were adapted to the amount of methanol required to give convenient yields of gaseous products, namely, 12 to 70 ml. Free volume varied from 10 to 50% of cell volume.

The Van de Graaff cells, which also were made of Pyrex, were provided with glass-clad iron propellers for magnetic stirring, 0.01″ thick windows, breakoff seals and ₮ joint equipped side-arms.[6] Each cell was charged with about 30 ml. of methanol. Both types of cells were cleaned by a sequence that included soaking in a hot "acid bath" (concd. H_2SO_4 and HNO_3 at above 110°), rinsing with water, soaking in aqueous ammonia, and final thorough rinsing with water. All the cells were oven dried and, immediately before being filled, subjected to prolonged pumping at about 10^{-6} mm. The cells for γ-ray irradiation were thoroughly flamed while being pumped but the Van de Graaff cells were too delicate to permit this treatment.

Irradiations.—The cobalt source has been described in detail.[7] The dose rate was in the vicinity of 1.8×10^{16} e.v. $ml.^{-1}$ $min.^{-1}$. The temperature in the source was maintained at 20–25°.

The Van de Graaff electron accelerator was a High Voltage Engineering model capable of delivering 2×10^6 volts. The electron beam was operated at 1.95×10^6 volts and 0.7×10^{-7} to 1.5×10^{-7} ampere, corresponding to dose rates in the range 1.7×10^{18} to 3.7×10^{18} e.v. $ml.^{-1}$ $min.^{-1}$. Irradiations took place at ambient temperature without detectable warming. During irradiation cell contents were stirred at 1000 r.p.m. by a motor-driven external magnet.

Dosimetry.—The intensity of the cobalt source had been established previously by H. A. Schwarz by means of the acid $FeSO_4$ dosimeter. The dose rate in methanol was calculated by multiplying the rate in 0.8 *N* aqueous H_2SO_4 by the factor $0.790 \times (18.02/32.04)/1.021 \times (10/18)$, thus correcting for the difference in electron density in the two media.

Determination of dose for irradiations by Van de Graaff electrons presented an unexpected difficulty. *G*-values calculated from the total doses indicated by the current integrator were erratic and in poor agreement with the value for γ-ray irradiation; discrepancies ranged as high as 29%. These dose values have accordingly been discarded. Because of the constancy of G_{H_2} for γ-ray irradiation over the dose range of the Van de Graaff experiments, hydrogen production has been used as an internal dosimeter for the latter, using $G_{H_2} = 4.57$. This procedure assumes that the 100 to 200-fold greater dose *rate* characteristic of the Van de Graaff experiments does not alter this value. In any case, this dosimetry permits a comparison of *relative* yields of products to be made conveniently. This matter is discussed further in connection with the data.

Analysis of Gaseous Products.—After irradiation, each cell was sealed to a vacuum line provided with the equipment necessary for collecting and analyzing the gaseous products. The methanol was cooled to −80°, the breakoff tip was smashed with a glass-clad magnetic hammer and the gaseous products Toepler pumped through a trap immersed in liquid nitrogen into a McLeod bulb. In almost all the runs involving irradiation of pure methanol with γ-rays, and in half the Van de Graaff runs, the methanol was next subjected to bulb-to-bulb distillation after which Toepler pumping was repeated. In other runs bulb-to-bulb distillation was replaced by warming the methanol to room temperature and agitating it. No significant differences were observed between the results of these two procedures. The latter procedure was used for analysis of almost all runs involving solutes. After total gas yield had been measured in the McLeod bulb an aliquot was transferred to a Saunders–Taylor type manometric microcombustion apparatus[8] where H_2 was determined by combustion at 295° over CuO for 5 minutes and absorption of resulting water on $MgClO_4$, CO by absorption on "Ascarite" of the CO_2 produced in this combustion, and CH_4 by subsequent combustion over CuO at 510° for 20 minutes and absorption of water and CO_2 as before. The CuO-packed furnace usually was pumped for 1–18 hours at 190–260° before an analysis (or set of duplicate analyses) was carried out. Analysis of a few sets of duplicate aliquots indicated a precision of 0.2%, or better, in the determination of H_2. The precision of the CH_4 and CO analysis was, on a similar basis, 1 to 5% of the value determined. The reliability of the CO and CH_4 analyses is not properly indicated by this degree of precision, however. The excessive scatter is indicated by the data of Fig. 1. In view of this scatter and the fact that these analyses were not tested against known mixtures during the course of these experiments, analytical results for CO and CH_4 must be treated with caution. This uncertainty does not appear to apply to the analyses for hydrogen which composed more than 90% of the gaseous product.

Residual gas was assumed to be nitrogen. It normally constituted 0.5%, or less, of the gas.

Analysis for Formaldehyde and Ethylene Glycol.—After removal of gaseous products and, in some cases, sealing off a bulb containing a sample for determination of water (*vide infra*), air was admitted to the cell and the contents transferred to a glass stoppered volumetric flask which had been subjected to a cleaning procedure like that employed with the cells.

Formaldehyde was determined with chromotropic acid according to the procedure of Bricker and Johnson.[9] Matheson, Coleman and Bell "practical' grade chromotropic acid was purified by filtering a 10% aqueous solution. Such filtered solutions were stored in glass stoppered flasks for no more than 24 hours before use. A calibration curve was established with solutions prepared by dilution of formalin (General Chemical Co. "Reagent Grade") which had been analyzed shortly before use[10] by oxidation with alkaline H_2O_2.[11] Both methanolic and aqueous calibration solutions were employed. Aliquots of methanol and of water, respectively, were used as blanks. Data for these solutions were in good agreement. Beer's law was obeyed up to concentrations around 65 γ of CH_2O/ml. (O.D. = 0.65), with negative deviation of the optical density at higher concentrations. The method was used only for solutions in the range of adherence to Beer's law. In this range, molecules of CH_2O per ml. = $2.025 \times 10^{18} \times$ optical density. All analyses were carried out in duplicate, usually on 1-ml. aliquots of irradiated methanol. For doses smaller than 8×10^{18} e.v. $ml.^{-1}$, 2-ml. aliquots were also analyzed. For doses greater than 7×10^{19} e.v. $ml.^{-1}$, 1-ml. aliquots of suitably diluted solutions were employed. The average of the mean deviations of all duplicate analyses for irradiated pure methanol was 0.003 optical density units per ml. This corresponds to an uncertainty of about ±10% for the smallest dose and of less than ±4% for all doses greater than 7×10^{18} e.v. $ml.^{-1}$.

Ethylene glycol was determined by an adaptation of the method of Critchfield and Johnson[12] which employs the chromotropic acid method to estimate formaldehyde produced from glycol by the action of periodate. It was established in the present work, however, that periodate converts methanol into formaldehyde at a rate which is significant compared to its rate of attack on ethylene glycol when the ratio of concentrations, (MeOH)/(glycol), is in the range encountered in this work (roughly 1.7×10^3 to 3×10^5). It was necessary, therefore, to devise a procedure for the essentially quantitative removal of methanol before introducing periodate. Formaldehyde was simultaneously completely removed. Thus the determinations of glycol and formaldehyde reported here are completely independent of each other. The procedure described below was validated by showing that over a 50-fold concentration range standard solutions of ethylene glycol in water and in methanol yield the same results. These solutions were prepared from Eastman "White Label" ethylene glycol which was analyzed[10] by oxidation with periodic acid,[13] reduction of ex-

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[6] These cells were adapted from the design of Saldick and Allen, *J. Chem. Phys.*, **22**, 438 (1954).

[7] H. A. Schwarz and A. O. Allen, *Nucleonics*, **12**, 58 (1954).

[8] *Cf.*, R. H. Schuler and C. T. Chmiel, *J. Am. Chem. Soc.*, **75**, 3792 (1953).

[9] C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 400 (1945). Aliquots of irradiated methanol were analyzed directly without removing methanol.

[10] Analysis performed by J. K. Rowley.

[11] "Scott's Standard Methods of Chemical Analysis," D. Van Nostrand, Inc., 5th Ed., New York, N. Y., 1939, p. 2149.

[12] F. E. Critchfield and J. B. Johnson, *Anal. Chem.*, **29**, 797 (1957).

cess periodate with iodide and titration of iodine with arsenite.

The glycol analysis yields solutions of the chromotropic acid–formaldehyde derivative which obey Beer's law up to glycol concentrations equivalent to 90 γ of formaldehyde per ml. The ratio, O.D.:concn. of equivalent formaldehyde, determined from this calibration line is 6% smaller than the corresponding ratio determined from the formaldehyde calibration line. Apparently this small fraction of the ethylene glycol is oxidized to products other than formaldehyde. Thus $1.072 \times 10^{18} \times$ O.D. = molecules of glycol per ml. All analyses were run at least in duplicate. Sample sizes (or dilutions) were chosen so as to provide convenient quantities of glycol. The average of the mean deviations for all replicate analyses of irradiated pure methanol was 0.010 optical density units per ml. corresponding to an uncertainty of ±5% or less at doses above 7×10^{18} e.v. ml.$^{-1}$ and increasing to about 20% for the lowest dose employed. A description of the procedure is given.

Procedure for Determination of Ethylene Glycol.—To each of a series of 12-ml. graduated centrifuge tubes sealed to 14/20 female ₸ joints is added an aliquot of unknown, an Alundum boiling chip and a small drop of concentrated hydrochloric acid.[14] A complete male 14/20 ₸ joint is inserted and the "distillation unit" immersed in a boiling-water bath and heated almost to dryness. On cooling, the condensed vapors in the unit should yield a residual volume of 0.2 to 0.25 ml. The unit is rinsed down with 0.25 ml. of water with a hypodermic syringe and the contents made up to 1.2 ml. with benzene. Heating in the boiling water-bath is resumed until no more benzene distils out of the unit, the walls are washed down with 0.25 ml. of H_2O and, after drainage is complete, the male joint is removed. The tube is returned to the water-bath to complete removal of the benzene. The tube then is allowed to cool and drain and an excess of solid $NaHCO_3$ is added, followed by 0.1 ml. of 0.2 *F* HIO_4. The walls of the tube are rinsed with 0.25 ml. of H_2O and 25 minutes (at room temperature) is then permitted for reaction before adding 0.5 ml. of 1.0 *F* Na_2SO_3 to consume excess periodate. The resulting solution then is subjected to the usual conditions for determination of formaldehyde with chromotropic acid. Finally, a rapid stream of nitrogen is passed through the diluted developed dye solution for 40 minutes before adjusting its volume precisely.

All optical densities were determined at 570 γ with a model DU Beckman spectrophotometer using 10 mm. Corex cells and correcting for absorption by the cells. All optical densities were measured against blanks obtained by subjecting aliquots of methanol to the corresponding analytical procedure. In most cases, the methanol used as a blank had been subjected to the same purification sequence as the irradiated methanol.

In order to test the effects of solutes on the determination of glycol and formaldehyde, solutions, each of which was approximately 0.01 *F* in one of the solutes as well as of fixed concentration in formaldehyde and ethylene glycol (*ca.* 1×10^{-3} and 5×10^{-4} *F*, respectively), were analyzed. It was found that $MgSO_4$ (model for $Mg(OCH_3)_2$), maleic anhydride, LiCl and $FeCl_3 \cdot 6H_2O$ do not interfere significantly with the aldehyde determination whereas benzoquinone, anthracene, pyrogallol and heptaldehyde do. The situation is the same with respect to analysis for ethylene glycol except that heptaldehyde does not interfere.

Determination of Water, Borate and Hydroperoxide.—Determinations of water[10] content were carried out with the objective of establishing the efficacy of the drying procedure and of estimating the value of G_{H_2O}. Analyses were by an amperometric version of the Karl Fischer method. In order to exclude atmospheric moisture, aliquots of methanol, before or after irradiation, were transferred by distillation on the vacuum line or by direct pouring within the sealed cell, respectively, into thin walled bulbs which were attached by ₸ joints to the appropriate cell or line. The necks of the bulbs were sealed off with the methanol held at −80°. The bulbs were broken under the surface of excess Karl Fischer reagent in a vessel closed to the atmosphere and the resulting current change related to the amount of water *via* a calibration curve. The results were too erratic to provide useful information on radiation yields of water. The analyses demonstrated, however, that, prior to irradiation, the methanol contained less than 0.001% of water.

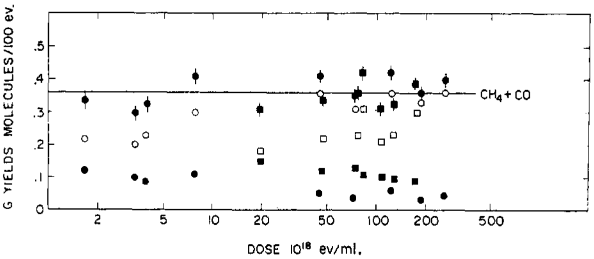

Fig. 1.—Yields of CO and CH_4 for irradiation of pure methanol: ●, ○ and ◐ represent G_{CO}, G_{CH_4} and the sum thereof, $G\Sigma$, respectively, for a given irradiation with γ-rays; ■, □ and ▮|▮ represent the same quantities for a given irradiation with 1.95×10^6 volt electrons. The horizontal line represents the average value of G_Σ.

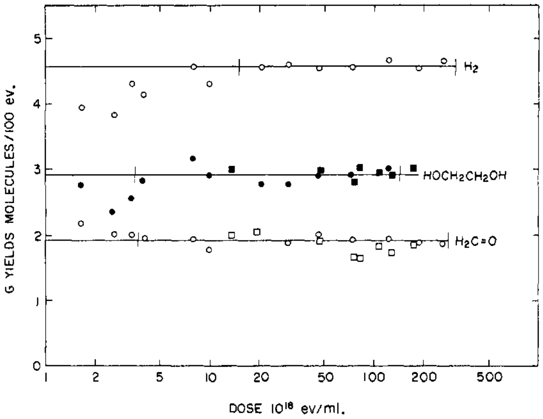

Fig. 2.—Yields of major products from irradiation of pure methanol: ○ and ● data for γ-rays; □ and ■ data for 1.95 $\times 10^6$ volt Van de Graaff electrons. Horizontal lines are average values of yields obtained with γ-rays over the dose ranges indicated by vertical lines.

Information that methyl borate may influence the photolysis of methanol[15] instigated the determination of boron in samples of methanol which had been stored in a Pyrex flask for seven weeks as well as an experiment in which a methanolic solution of methyl borate was irradiated. No dissolved boron was detected upon analysis[10] by a procedure[16] capable of detecting 6×10^{16} atoms of boron per ml. (4×10^{-4} mole %).

Analysis for H_2O_2 plus CH_3OOH was carried out by a procedure[17] capable of detecting as little as 2.5×10^{16} molecules of peroxide per ml. None was detected in aliquots of solutions which had absorbed doses of 7.84×10^{18} e.v. ml.$^{-1}$ of γ-rays or 1.94×10^{19} and 10.7×10^{19} e.v. ml.$^{-1}$ of Van de Graaff electrons.

Stopcock Grease.—All stopcocks and ₸ joints employed in this work were lubricated with Spectro Vac Type II grease.

Data

Hydrogen, Ethylene Glycol and Formaldehyde Yields from Pure Methanol.

—Yields per 100 e.v. are plotted as a function of total dose in Fig. 2 for hydrogen, ethylene glycol and formaldehyde. G_{H_2} for γ-irradiation is constant for total doses in the range from 2×10^{19} e.v. ml.$^{-1}$ (6.5×10^{-3} % reaction) to 2.6×10^{20} e.v. ml.$^{-1}$ (8.8×10^{-2} % reaction). The apparent diminution in G_{H_2} at lower dose (down to 4.7×10^{-4} % reaction) seems

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(13) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, New York, N. Y., 1957 p. 490.

(14) The acid is necessary to catalyze the formation of methylal which azeotropes with methanol. Formaldehyde may not be completely removed in the absence of acid.

(15) Private communication from A. O. Allen.

(16) W. T. Dible, E. T. Truog and K. C. Berger, *Anal. Chem.*, **26**, 418 (1954).

(17) *Cf.*, C. J. Hochanadel, THIS JOURNAL, **56**, 587 (1952).

TABLE I

YIELDS OF MAJOR PRODUCTS FROM IRRADIATION OF METHANOL WITH Co^{60} GAMMA-RAYS AND 1.95×10^6 VOLT ELECTRONS

		G, molecules/100 e.v.			
Product	Radiation	This report[a]	Ref. 3c	Ref. 4	Ref. 5
H_2	γ-Ray	4.57 ± 0.08[b]	4.0[f]	5.39[h]	4.1[j]
H_2	Van de Graaff	(4.57)[c]			
$HOCH_2CH_2OH$	γ-Ray	2.91 ± 0.11[d]	3.0[g]	3.63[i]	3.1[k]
$HOCH_2CH_2OH$	Van de Graaff	$2.96 \pm .09$[c]			
$H_2C{=}O$	γ-Ray	$1.91 \pm .06$[c]	1.3[g]	1.84[i]	2.05[l]
$H_2C{=}O$	Van de Graaff	$1.84 \pm .12$[c]			

[a] Calculated by averaging data of Fig. 1 over indicated dose ranges. Uncertainties are standard deviations. Van de Graaff yields normalized to $G_{H_2} = 4.57$; *cf.* "Experimental." [b] 20.5 to 262 × 10^{18} e.v. ml.$^{-1}$. [c] 13.7 to 174 × 10^{18} e.v. ml.$^{-1}$. [d] 3.92 to 122.3 × 10^{18} e.v. ml.$^{-1}$. [e] 3.92 to 262 × 10^{18} e.v. ml.$^{-1}$. [f] 3.6 to 14.4 × 10^{18} e.v. ml.$^{-1}$. [g] 346 to 1728 × 10^{18} e.v. ml.$^{-1}$. [h] 4 to 400 × 10^{18} e.v. ml.$^{-1}$. [i] 400 × 10^{18} e.v. ml.$^{-1}$. [j] 1.6 to 8.8 × 10^{18} e.v. ml.$^{-1}$. [k] Extrapolated to zero dose from data over the range 5.5 to 20 × 10^{18} e.v. ml.$^{-1}$. For dose of 12 to 20 × 10^{18} e.v. ml.$^{-1}$. $G_{glycol} = 3.3$. [l] 6 to 16 × 10^{18} e.v. ml.$^{-1}$.

to be paralleled in the data of Adams and Baxendale[5] although these workers treated their data as indicating that G_{H_2} is independent of dose. Hydrogen yields observed in this low dose range are very nearly the same as those reported by Adams and Baxendale for virtually the same range. Caution must be exercised with respect to this apparent dose dependence of G_{H_2}. It should be noted, however, that, aided by variation in the amount of methanol irradiated, the precision of the analysis for H_2 does not depend significantly on the dose per ml. Average values of the essentially constant G-yields obtained in the higher dose region are presented in Table I along with published results of other workers. Neither the plateau value of G_{H_2} (4.57) nor the values characteristic of lower doses agree with that reported by Meshitsuka and Burton (5.39). Moreover the data of the latter workers do not indicate any dependence of G_{H_2} on dose at low dose values. McDonell and Gordon[3c] report a value of G_{H_2}, in substantial agreement with that reported by Adams and Baxendale. This is based on data for a range of total dose values similar to that employed by the latter workers. However, McDonell and Gordon did not report any variation of G_{H_2} with total dose in this range.[18]

The present data indicate that G_{glycol} is essentially constant to somewhat lower dose levels than is G_{H_2}. There is a suggestion of diminution in yield at the low end of the dose range but this is the least reliable portion of the data. The data of Adams and Baxendale are sufficiently suggestive of a similar dose dependence to lead these workers to treat the trend as real. The value of G_{glycol} found by these workers for doses of about 1–2 × 10^{19} e.v. ml.$^{-1}$ is about 13% higher than the plateau value of Fig. 1. Meshitsuka and Burton report an even higher value of G_{glycol} for a sample about 0.25% of which had been radiolyzed.

The present and two[4,5] of the older values of G_{CH_2O} are in reasonable accord and no dose dependence of this specific yield is apparent in any of the data. The significance of the low value of G_{CH_2O} reported by McDonell and Gordon is complicated by uncertainty as to the concentration of water in their methanol and the effect of any which may have been present (*vide infra*).

The values of G_{glycol} and G_{CH_2O} calculated from the data for Van de Graaff irradiations by using hydrogen yield as a measure of dose are in good accord with the corresponding yields from γ-irradiation as determined in this work. This tends to support the "dosimetry" employed but does not prove its validity. The data establish unequivocally, however, that *relative yields* of hydrogen, ethylene glycol and formaldehyde are the same for the two types of irradiation in spite of the hundredfold difference in dose rates.

CH_4 and CO Yields from Pure Methanol.—The scatter of G_{CO} and G_{CH_4} apparent in Fig. 1 prevents the detailed analysis of these quantities. It is clear, however, that the analytical difficulty lies in determination of the separate quantities; their sum, G_Σ, is much more constant. The average value of G_Σ is 0.36 with a standard deviation of 0.04. This can be taken as representing an upper limit for both G_{CO} and G_{CH_4}. There is no apparent trend in G_Σ with dose. Thus, a limited comparison of G_{CH_4} (and G_{CO}) with the results of other workers is possible.

There is very poor agreement among different workers as to G_{CH_4}. Thus, Adams and Baxendale report a slight negative dependence on dose of G_{CH_4} and a value, extrapolated to zero dose, of 1.23. Meshitsuka and Burton report the opposite sign of dose dependence and, ascribing this dependence to incomplete collection of methane in low dose runs, report a value of G_{CH_4} based on data of highest dose (400 × 10^{18} e.v. ml.$^{-1}$), namely, 0.54. Adams and Baxendale find G_{CO} to be 0.15 and independent of dose (up to about 2 × 10^{19} e.v. ml.$^{-1}$). Meshitsuka and Burton report G_{CO} as 0.11 over this dose range but observe a much lower value at 4 × 10^{20} e.v. ml.$^{-1}$. These two groups of workers analyzed gaseous products mass spectrometrically. McDonell and Gordon, who used a Saunders–Taylor type of manometric combustion analysis, report $G_{CH_4} = 0.24$ and $G_{CO} = 0.16$ for total doses of 3.6 to 14.4 × 10^{18} e.v. ml.$^{-1}$. The values of G_Σ are, respectively, 1.38 (A and B), 0.65 (M and B), 0.40 (M and G). The discrepancies are, at present, without explanation.

Peroxide Yields from Pure Methanol.—No peroxide was detected by the analytical procedure employed. This indicates that ($G_{H_2O_2} + G_{CH_3OOH}$) is less than 0.003.

Material Balance in Radiolysis Products from Pure Methanol.—In order to estimate material balance in the plateau region for hydrogen from

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(18) These workers did not dry or otherwise purify the methanol they employed.

the data for γ-irradiations only, averaged values for G_{CO} and G_{CH_4} in this region have been arbitrarily employed; these are 0.045 and 0.34, respectively. Hence $G_{Red} = G_{H_2} + G_{CH_4} = 4.91$ and $G_{Ox} = G_{glycol} + G_{CH_2O} + 2G_{CO} = 4.91$. The precise agreement is entirely fortuitous. Any choice of G_{CO} and G_{CH_4} reasonably related to the data of Fig. 2 yields a good material balance, however. A certain degree of caution in accepting a good material balance as substantiating its individual components is suggested by the fact that Adams and Baxendale provide an excellent balance (5.33/5.30) based on a quite different distribution of terms.

Yields from Solutions in Methanol.—Data are summarized in Table II. It is seen, in agreement with the report of Meshitsuka and Burton and contrary to that of Adams and Baxendale, that G_{H_2} is substantially reduced in the presence of water. G_{CH_2O} is affected similarly. McDonell and Gordon[3c,18] agree with the present result in finding no effect of water on G_{glycol}. Their finding that G_{CH_2O} varies inversely with water concentration is qualitatively, but not quantitatively, in accord with the present observation. The four other solutes for which information was secured all have the opposite effect on G_{CH_2O}. The results with methanol which had been degassed but not otherwise purified[19] are similar to those obtained in the presence of water.

TABLE II

YIELDS OF PRODUCTS FROM RADIOLYSIS OF METHANOLIC SOLUTIONS BY Co^{60} γ-RAYS[a]

Solute	Concn., mole l.$^{-1}$	G_{H_2}	G_{CH_4}	G_{CO}	G_{CH_2O}	$G_{C_2H_6O_2}$
Unknown[b]	...	3.44	0.25	0.11	1.06	3.00
H_2O	0.48[c]	3.61	.23	.09	1.29	3.00
$Mg(OCH_3)_2$	.0087	4.09	.28	.04	3.33	0.87
LiCl	.021	3.80	.27	.05	2.24	2.52
H_2SO_4	.0094	4.94	.25	.10	2.37	3.62
$FeCl_3 \cdot 6H_2O$[d]	< .0114	2.15	.13	.14	7.13	0.5
Quinone[e]	.0087	2.47	.12	.11	..	..
Heptaldehyde	.0104	3.86	.27	.10	..	2.29
Pyrogallol	.0088	4.09	.22	.09	..	..
Anthracene	.0082	2.60	.21	.10	..	..
Maleic anhydride[f]	.0081	3.57	.24	.11	2.35	0.94
Methyl borate[g]	.51	4.43	..	..	..	..

[a] Total doses were in the range 2.126×10^{19} to 2.412×10^{19} e.v. ml.$^{-1}$. [b] An aliquot from a bottle of Mallinckrodt AR methanol was degassed but was neither dried nor rectified before irradiaton. [c] 1.1% by weight. [d] This sample was contaminated with air equivalent to 2.32×10^{17} molecules of O_2 per ml. of methanol. [e] This sample was contaminated with air equivalent to 7.13×10^{17} molecules of O_2 per ml. of methanol. [f] This sample was contaminated with air equivalent to 2.25×10^{17} molecules of O_2 per ml. of methanol. [g] Values of $G_{CH_4} = 0.18$ and $G_{CO} = 0.04$ have been discarded because the CuO furnace was pumped at 600° before this analysis.

The results with benzoquinone and $FeCl_3 \cdot 6H_2O$ are similar but not identical to those reported by Adams and Baxendale. In view of the fact that a fivefold greater dose was used in the present work and of the presence of a small amount of oxygen in the samples, the differences do not merit discussion. To the extent that comparisons may be made in spite of differences in dose and concentration, sulfuric acid influences the radiolysis of almost dry methanol (~0.002 M in water added in the form of concentrated H_2SO_4) in a fashion qualitatively similar to the effect of sulfuric acid on methanol containing 3% of water.[5] It is the only substance tested which increases the yield of either hydrogen or glycol.

Discussion

These results emphasize that accurate information concerning the radiolysis of "pure" methanol is not easily obtained. Resolution of substantial discrepancies in the reported values of G_{CH_4} and G_{H_2} is needed. The several values for G_{glycol} are not in good agreement. There appears to be no agreement as to the effect of small amounts of water. Whether G_{H_2} and G_{glycol} do, in fact, diminish at very low dose remains to be substantiated. There are no data on G_{H_2O} for radiolysis by γ-rays. Under these circumstances chemical interpretation of the data for "pure" methanol is not justified.

It does not, of course, follow that equal difficulty is to be anticipated in securing reliable information for solutions containing efficient radical scavengers as solutes.[5] The behavior of aqueous systems suggests that such solutions should be more tractable.

Table II summarizes very limited data for solutions of well known radical scavengers (*e.g.*, $FeCl_3$ and benzoquinone) and also of solutes that may perhaps intervene in other ways in the radiolytic process.

Methyl borate appears to have a negligible effect on the hydrogen yield (and probably on the yields of CH_4 and CO as well). This datum, taken in conjunction with the failure to detect borate in methanol which had been in prolonged contact with Pyrex glass appears to eliminate methyl borate as a complicating factor in the radiolysis of liquid methanol. However, extensive evidence that borate does accumulate in anhydrous methanol upon exposure to Pyrex has been reported[20] along with observations concerning the profound influence of methyl borate on the photolysis of methanol in the gas phase. Since the latter is related to more efficient absorption of light by methyl borate, there is not necessarily any conflict between the data on photolysis and radiolysis. The disagreement as to attack of methanol on Pyrex is substantial and without explanation, however.

The effect of $Mg(OCH_3)_2$ is similar in a qualitative way to that observed with $FeCl_3 \cdot 6H_2O$. However, in the latter case two molecules of formaldehyde appear for each molecule of glycol that disappears whereas with $Mg(OCH_3)_2$ less than one molecule of formaldehyde (about 0.7) appears for each glycol molecule lost. An oxidation of CH_2OH radicals to $CH_2O + H^+$ such as that which has been suggested[5] to explain the action of Fe(III) clearly does not apply here. The result with $Mg(OCH_3)_2$ suggests promotion of a disproportionation process: "$2 \cdot CH_2OH$"$\rightarrow$ $CH_2O + CH_3OH$ (where no distinction is made between $\cdot CH_2OH$ and $CH_3O\cdot$). Lacking, as yet,

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[19] This material was subjected to bulb-to-bulb distillation in the course of charging the radiation cell; some purification may have been effected thereby.

[20] R. P. Porter, THIS JOURNAL, **61**, 1260 (1957).

a knowledge of whether Mg(II) ion or methoxide anion (or possibly both) is the active species, more detailed speculation is not justified. Lithium chloride, at twice the concentration, but, if we assume complete dissociation, half the ionic strength has a smaller but analogous effect: somewhat less than one molecule of formaldehyde appears for each molecule of ethylene glycol lost. Whatever the mechanism by which these solutes intervene, it seems highly improbable that it involves oxidation of radicals.

If it is assumed that the value of G_{H_2} found for "pure" methanol in this work can be used for purposes of estimating solute effects, then both electrolytes (a base and a neutral salt) reduce hydrogen formation. Since it is not known as yet whether ionic strength or stoichiometric concentration is the proper measure of concentration, the data do not tell which is more effective. In view of the uncertainty in the determinations of G_{CO} and G_{CH_4} it can only be concluded that no drastic changes in these values are brought about by LiCl or $Mg(OCH_3)_2$ as G_Σ falls in the range of values found for "pure" methanol. Finally, the material balance is good only with $Mg(OCH_3)_2$ as a solute. There appears to be an undetected reduction product formed in the presence of LiCl. These initial results with solutions of "non-oxidizing" electrolytes are suggestive and extensive work in this area is planned.

Heptaldehyde (0.010 *M*) was employed as a conveniently handled model of formaldehyde. Hydrogen and glycol yields are diminished about equally by this solute while G_Σ is not affected. Since irradiation with a dose sufficient to produce 0.020 *M* formaldehyde yielded normal "plateau" values of G_{H_2} and G_{glycol} it appears that heptaldehyde is not a good model for formaldehyde.

Pyrogallol, a very effective scavenger for peroxy radicals, has a relatively small effect on G_{H_2}. Anthracene, which has a high "methyl affinity,"[21a] (although only 1/20th as large as that of benzoquinone[21b]) has about the same effect on G_{H_2} as does benzoquinone and probably is acting as a radical scavenger. Information of G_{CH_2O} and G_{glycol} in the presence of anthracene and quinone would be of great value in determining whether or not they operate by similar mechanisms, but this is, as yet, not available. Neither anthracene nor pyrogallol alters G_Σ sufficiently to treat the effect as real.

Maleic anhydride reduces glycol formation drastically with only a small increase in formaldehyde formation: only about 0.2 molecule of aldehyde appears per glycol molecule lost. The material balance remains fairly good, however. Perhaps some of the glycol is suppressed *via* formation of a product (or products) of addition of H· and $\cdot CH_2OH$ or a precursor thereof to the olefinic link. Information on the fate of maleic anhydride would be useful in formulating a specific mechanistic hypothesis to account for its action. With maleic anhydride as solute, G_Σ is, again, unaffected. Only the radical scavengers benzoquinone and $FeCl_3 \cdot 6H_2O$ affect G_{CH_4} (or G_Σ) so substantially that, in spite of the analytical uncertainty, the effect can be accepted as real. A much larger diminution of G_{CH_4} by oxidizing scavengers has been reported and interpreted by Adams and Baxendale.[5]

In the presence of water or of sulfuric acid material balance appears to be poor: oxidation products appear to be in about 15 to 20% excess over reduction products. This observation is not in accord with the results which Adams and Baxendale report[5] for 97% methanol containing 0.05 *M* H_2SO_4, where they obtain fairly good material balance.

The evidence that the ratio G_{glycol}/G_{CH_2O} is influenced in a variety of ways by different solutes for which this information is available suggests that there are several modes of intervention by solutes and that this quantity may be a valuable guide to their mechanisms of action. It is hoped that analytical procedures can be developed to provide this information for other solutes.

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(21) (a) M. Levy and M. Szwarc, *J. Am. Chem. Soc.*, **77**, 1949 (1955); (b) A. Rembaum and M. Szwarc, *ibid.*, **77**, 4468 (1955).