

At very low pressures, it is possible that wall effects could become important. Simple kinetic theory calculations show that for pressures below about 50 μ , collisions with the wall start competing with intermolecular collisions; below 10 μ , wall collisions would predominate. Thus, if wall collisions were important, the plots in Fig. 2 would "flatten out" at low pressure. It is easily seen that this does not occur. Kinetic theory calculations also show that the time required to reach the wall in the absence of intermolecular collisions is about 10^{-5} to 10^{-4} sec. Since wall reactions are unimportant, the lifetime of the excited state at zero pressure must be less than 10^{-5} sec. or k_3 must exceed 10^5 sec. $^{-1}$. The value of k_3 found from the integrated absorption coefficient is 3.1×10^5 sec. $^{-1}$ in agreement with the above.

Equation 7 can be rewritten

$$\log(Q\lambda^{-1} - \alpha) = \log\left(\frac{\alpha k_4}{k_3}\right) + \log(\text{CS}_2) \quad (8)$$

Figure 3 shows log-log plots of $Q\lambda^{-1} - \alpha$ vs. (CS_2) where the values of α used are the intercepts of Fig. 2.

The data fit linear plots of slope unity. The intercepts give $(\alpha k_4/k_3)$, and these are listed in Table II. The values of $\alpha k_3/k_2$ from Fig. 3 are similar to but somewhat different from those in Fig. 2. The values from Fig. 3 are much more accurate because they result from plots covering a pressure range of 10^4 .

The ratio k_4/k_3 is found by dividing the quantity $\alpha k_4/k_3$ obtained from Fig. 3 by α as obtained from Fig. 2. These values are listed in the fifth column of Table II. It is interesting to note that even though α and $\alpha k_4/k_3$ vary by a factor of three for various incident wave lengths, the ratios are constant to within about 20%. The average value of k_4/k_3 is 36 ± 5 mm. $^{-1}$.

Since every collision deactivates, k_4 can be estimated from kinetic theory. Using a reasonable collision diameter of 5 Å., one finds that k_4 becomes 1.0×10^7 (mm.-sec.) $^{-1}$. This gives a value for k_3 of $2.9 \pm 0.4 \times 10^5$ sec. $^{-1}$ in excellent agreement with that of 3.1×10^5 sec. $^{-1}$ found from the integrated absorption coefficient.

Acknowledgment.—The author wishes to thank Mrs. Barbara Peer for assistance with the manuscript.

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The Radiolysis of Methanol and Methanolic Solutions. II. Comparison of Radiolysis by Co^{60} γ -Rays and by $\text{B}^{10}(\text{n},\alpha)\text{Li}^7$ Recoils¹

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RECEIVED JUNE 18, 1963

At recoil dose rates in the vicinity of 4.5×10^{15} e.v. ml. $^{-1}$ min. $^{-1}$ $G(\text{H}_2) = 4.99 \pm 0.36$, $G(\text{CH}_4) = 0.57 \pm 0.14$, $G(\text{CO}) = 1.00 \pm 0.13$, $G(\text{CH}_2\text{O}) = 3.15 \pm 0.38$, $G(\text{C}_2\text{H}_6\text{O}_2) = 0.60 \pm 0.09$, independent of dose over the range $(0.44-10.8) \times 10^{19}$ e.v. ml. $^{-1}$ and of dose rate over the range $(0.33-25) \times 10^{18}$ e.v. ml. $^{-1}$ min. $^{-1}$. All yields are insensitive to added KI up to 0.1 *M*. The effects of change in LET by a factor of 10^3 are rationalized tentatively on the basis that there is little variation in initial relative abundance of primary radical and molecular products but that reactions of higher than first order in primary radicals are of increased importance. Satisfactory reproducibility in the Co^{60} γ -radiolysis of "pure" methanol was not obtained in this work and its achievement remains a problem. Alkali fluorides, chlorides, and bromides all reduce $G(\text{H}_2)$ but have no significant effects on other yields. Alkali iodides also reduce $G(\text{H}_2)$ from Co^{60} γ -radiolysis and, in addition, decrease $G(\text{C}_2\text{H}_6\text{O}_2)$ and increase $G(\text{CH}_2\text{O})$ by equal amounts without significant formation of iodine. This observation can be rationalized by the coupled reduction of CH_3O and oxidation of CH_2OH by I^- and I , respectively, as proposed by Theard and Burton.

Introduction

This paper describes a limited investigation of the effect of variation of LET on the radiolysis of liquid methanol at room temperature. Unfortunately, the results must be interpreted with more than the usual degree of caution because satisfactory reproducibility of yields from the γ -radiolysis of "pure" methanol does not appear to have been achieved as yet. Recently, Baxendale and Mellows² presented evidence indicating that they had obtained reproducible results from "pure" methanol. We have, however, not been able to duplicate their results nor did Theard and Burton.^{3,4}

Recently reported yields from the γ -radiolysis of methanol are presented in Table I along with a few relevant earlier data.⁵⁻¹⁰ That differences among yields cannot be correlated systematically with the methods of

analysis is illustrated for the gaseous products. Values of $G(\text{H}_2)$ appear to fall in three ranges, around 5.4, 4.6-5.0, and 4.0-4.1.^{11,12} Baxendale and Mellows² have concluded that the smallest values arise from adventitious complete scavenging of a reactive precursor of hydrogen, presumed to be the solvated electron. This conclusion is consistent with the fact that either no⁹⁻¹¹ purification procedure or a questionable one¹² was employed where $G(\text{H}_2) = 4.1$ was obtained. Apparently carefully purified methanol has given values falling in the remaining two regions. Values of $G(\text{CH}_4)$ vary over a factor of almost three. Burton and Theard^{3,4} have shown that complete removal of methane from methanol is difficult and, perhaps, the two or three lower values of $G(\text{CH}_4)$ reflect failure to collect this product quantitatively. The highest values of $G(\text{CH}_4)$ are associated with the highest values of $G(\text{H}_2)$, however, suggesting that a chemical factor is involved. Reproducibility of $G(\text{CO})$ should be expected to be poor because of its low value. There appears to be no correlation between values of $G(\text{CO})$ or $G(\text{CH}_2\text{O})$ and those of $G(\text{H}_2)$. $G(\text{CH}_2\text{O})$ is apparently approximately 2.1 and is not highly sensitive to the adventitious impurities common to methanol. If the values of Johnsen⁵ and of Hayon and Weiss⁹ are discarded, values of $G(\text{glycol})$ fall into two groups. Values around $3.0^{4,6-8,11,12}$

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

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TABLE I
 Co^{60} γ -RADIOLYSIS OF "PURE" METHANOL. PRODUCT YIELDS PER 100 E.V. ABSORBED, ACCORDING TO VARIOUS WORKERS

Ref.	H_2	CH_4	CO	CH_3O	$(\text{CH}_2\text{OH})_2$	Method of purification ^a	Method of analysis of H_2 , CH_4 , CO
3	5.39	0.54	0.11	1.84	3.64	B, E, F, G, H	Mass spectral
2	5.40	.80	.15	2.15	3.7	A, D, E, I	Mass spectral
5 ^b	5.66	.57	.45	1.0	2.10	E, F, H	Saunders-Taylor
3 ^{c,d}	4.70 \pm 0.13	0.44 \pm 0.02	0.07 \pm 0.02	1.96 \pm 0.13	2.77 \pm 0.18	E, G, J	Mass spectral
4 ^e	4.99 \pm .03	0.44 \pm 0.02	0.12 \pm 0.02		2.99 \pm .50	D, E, J	Mass spectral
6 ^e	4.57 \pm .08	($\Sigma = 0.36 \pm 0.04$)		1.91 \pm 0.06	2.91 \pm .11	E, G, K	Saunders-Taylor
7 ^{e,f}	4.98 \pm .19	0.28 \pm 0.04	0.09 \pm 0.01	2.14 \pm .13	3.07 \pm .09	E, G, K	Saunders-Taylor
8 ^{e,g}	4.60 \pm .17	.31 \pm 0.05	.15 \pm 0.05	2.41 \pm .28	2.92 \pm .41	C, E, G, L	Saunders-Taylor
9	4.1	.39	.13	1.41	2.43	None ^h	Mass spectral

^a A, refluxed; B, diluted with water and refluxed; C, refluxed with NaBH_4 ; D, refluxed with dinitrophenylhydrazine and H_2SO_4 ; E, rectified; F, dried over CaO ; G, dried over $\text{Mg}(\text{OCH}_3)_2$; H, method of degassing not given; I, degassed by short periods of pumping at room temperature after equilibrating phases with a vibroshaker; J, degassed by refluxing on a vacuum microstill for 4 hr. with periodic pumping off of vapor phase; K, degassed by three or more freeze-pump-thaw-shake cycles; L, degassed by two cycles of pumping at room temp. followed by vac. distillation and then by several freeze-pump-thaw cycles. ^b Reports $G(\text{C}_2\text{H}_6) = 0.14$. This product has not been observed by other workers. ^c Yields are averaged over entire dose range of $(1-30) \times 10^{19}$ e.v. ml.⁻¹ and include 14 measurements of yields of gaseous product and 20 measurements of yields of formaldehyde and glycol, all obtained in Theard's most refined experiments. ^d Uncertainties are mean deviations. ^e Uncertainties are standard deviations of a single measurement. ^f Dose rate ca. 3×10^{17} e.v. ml.⁻¹ min.⁻¹; dose range $(1.75-42) \times 10^{18}$ e.v. ml.⁻¹; yields are averages from 17 experiments. ^g Dose rate ca. 2×10^{17} e.v. ml.⁻¹ min.⁻¹; dose range $(11.6-22.7) \times 10^{18}$ e.v. ml.⁻¹; yields are averages from seven experiments. ^h No details are given but it can be inferred from ref. 10 that the methanol was not purified and that degassing was effected by pumping.

are associated with $G(\text{H}_2) = \text{ca. } 4.1$ and $4.6-5.0$, but $G(\text{glycol}) = 3.7^{2,3}$ is associated with $G(\text{H}_2) = 5.4$ and with high $G(\text{CH}_4)$, again suggesting that a chemical factor is involved.

It is entirely possible that the assumption of Baxendale and Mellows that the purest methanol provides the highest $G(\text{H}_2)$ is correct, but until yields can be reproduced routinely in more than one laboratory all data for "pure" methanol are questionable and interpretations which depend on them can only be tentative.

Experimental

Purification of Methanol.—Methanol which came from different supply houses and which was purified by slightly different procedures was used for the experiments described herein. All batches of methanol were rectified on a Todd column operated at a reflux ratio of 10:1 or higher. Only the middle third was taken in each case. All batches of methanol were dried by refluxing for at least 5 hr. with $\text{Mg}(\text{OCH}_3)_2$, prepared by dissolving 2-3 g. of Mg (Baker "purified" or freshly turned Dow "superpure") in 150 ml. This operation was performed on a high vacuum line with protection by Ascarite and silica gel from atmospheric moisture and CO_2 during evolution of H_2 . All subsequent operations involving degassing and transfer of methanol were performed on the same vacuum line. Different sources, preliminary treatments, and degassing procedures are indicated in the following.

Methanol A was Fisher certified reagent. It was degassed by several freeze-pump-thaw cycles. **Methanol B** was from a different lot of Fisher Certified Reagent. It was degassed by pumping at room temperature, distilling under vacuum, and pumping at Dry Ice temperature twice and then by several chill (-78°)-pump-thaw cycles. **Methanol C** was Eastman Spectrograde. It was treated with NaBH_4 (Metal Hydrides, 2 g./500 ml.) and refluxed for 6-8 hr. before being rectified. The degassing procedure was the same as for methanol B.

Analysis of Methanol.—Gas chromatography on Carbowax 20M in an F&M 500 programmed from 75 to 250° at 4°/min. did not reveal any impurity in methanol B before purification. Its ultraviolet spectrum, however, included absorptions at 233 (w), 237 (w), 248 (s), and 268 (w) μ which coincided with maxima in the spectrum of a solution of benzene in methanol. These peaks were barely discernible in the middle third fraction obtained by rectification on the Todd column. The spectra of liquid Eastman Spectrograde, Matheson Spectroquality, and Baker Analyzed methanols, as provided by the suppliers, consisted only of broad weak absorption at and below 210-220 μ . The intensity of the absorption at 210-220 μ was lowered to some extent by rectification.

The absence of detectable amounts of boron after prolonged storage of methanol in a Pyrex container was reported previously.⁶ It was, however, established in the present work that the method of analysis¹³ previously employed is not reliable when applied to methanolic methyl borate. Apparently, a major portion of the borate is lost during evaporation with the ethanolic

curcumin-oxalic acid solution. It was found that evaporation in the presence of a volume of water equal to that of the aliquot of methanol, in addition to the reagent solution, results in retention of most of the boron. The modified analytical procedure was not investigated extensively, but it was established that, before purification, Eastman Spectrograde methanol contains less than 10^{-4} g.-atom of boron per liter. After treatment with NaBH_4 and rectification, the borate concentration in the middle third of distillate was approx. 10^{-2} M, but after treatment with $\text{Mg}(\text{OCH}_3)_2$ the concentration was again less than 10^{-4} M.

Other Materials.—Metal Hydrides methyl borate was rectified on a 40-cm. column packed with glass helices and the middle fraction was stored under vacuum on the vacuum line. Baker Analyzed $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and KI were used without further purification. All other alkali halides were of Analytical Reagent grade. They, as well as DuPont reagent sulfuric acid and Eastman chromotropic acid, were used without further purification. Water used for Fricke dosimetry was redistilled in Pyrex or subjected to three redistillations, from acidic dichromate, from alkaline permanganate, and without added reagents. Water used as a solute was redistilled in Pyrex.

Radiolysis Cells.—Pyrex glass cells were used for γ -radiolysis. They were cleaned in a hot nitric acid-sulfuric acid bath or in hot chromic acid solution, rinsed with water, soaked in aqueous ammonia, and thoroughly rinsed with distilled water before drying. The cells, of approx. 30-ml. capacity and equipped with ground joints and breakoff seals, were sealed *via* constricted side tubes to the vacuum line. They were pumped for several hours during which time they were periodically baked and sparked with a Tesla coil. Sparking was omitted when salts (*e.g.*, KI, etc.) were present in the cell; 15 to 20 ml. of dried degassed methanol was distilled into each cell after which it was sealed off. For some experiments a weighed amount of degassed methyl borate was also distilled into the irradiation cell on the vacuum line. Concentrations of these solutions were determined by weighing.

Quartz cells of about 50-ml. capacity were used for neutron irradiation. They were cleaned and degassed as described above. They were similar in design to the Pyrex cells except that they were attached to the charging vacuum manifold by means of ground joints. Each cell was filled, as described above, with approx. 30 ml. of methanol and an appropriate amount of methyl borate and was then sealed off.

Irradiations.— γ -Irradiations were carried out in Schwarz-Allen type sources¹⁴ with the circulating water maintained at about 20°. Dose rates to methanol fell in the range 2 to 3×10^{17} e.v. ml.⁻¹ min.⁻¹. Neutron irradiation was carried out in the Brookhaven thermal neutron facility,¹⁵ recently modified so as to provide three flux levels, namely, ca. 5×10^7 , 5×10^8 , and 2.5×10^9 cm.⁻² sec.⁻¹. Two layers of cells were mounted horizontally in a styrofoam block which was bored to accommodate eight tubes. One central position in each layer was occupied by a (quartz) recoil dosimeter (*cf.* below) and one (quartz) γ -dosimeter was located in an outer position of the matrix. Gold foils were attached to the upper and lower surfaces of each cell and dosimeter.

Dosimetry.— γ -Energy absorbed in the cobalt sources and the thermal column were determined by means of the aerated acid (0.8 N sulfuric) ferrous ammonium sulfate (10^{-3} M) dosimeter.

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TABLE II

YIELDS^a FROM RADIOLYSIS OF METHANOL C BY Co⁶⁰ γ - AND B¹⁰(n, α)Li⁷ RECOILS AT DOSES OF $(1.5 \pm 0.9) \times 10^{19}$ E.V. ML.⁻¹

Radiation	Dose rate 10 ¹⁶ e.v. ml. ⁻¹ min. ⁻¹	(Borate), mole l. ⁻¹	G(H ₂) ^f	G(CH ₄) ^f	G(CO) ^f	G(CH ₂ O) ^f	G(C ₂ H ₄ O ₂) ^f	n ^b
Gamma	20	0	4.60 ± 0.17	0.31 ± 0.05	0.15 ± 0.05	2.41 ± 0.28	2.92 ± 0.41	7
Gamma	20	0.08–0.14 ^c	4.81 ± .14	.32 ± .04	0.15 ± .02	2.00 ± .17	1.95 ± .26	7
Recoil ^d	0.033–0.061	.14–.16	5.62 ± .11	.58 ± .13	1.08 ± .06	3.54 ± .29	0.79 ± .12	5
Recoil ^d	0.33–0.55	.07–.16 ^c	4.99 ± .36	.57 ± .14	1.00 ± .13	3.15 ± .38	.60 ± .09	11
Recoil ^d	2.0–2.5	.14–.16	5.47 ± .26	.65 ± .03	1.10 ± .17	3.22 ± .39	.61 ± .15	5
Recoil ^{d,e}	0.45–0.55	.14–.17	5.11 ± .33	.57 ± .05	1.06 ± .13	3.27 ± .18	.49 ± .04	7

^a Indicated uncertainties are standard deviations of a single measurement. ^b Number of experiments. ^c No systematic variation of any yield was apparent over this range of borate concentrations. ^d Indicated doses and yields refer to recoil particles only. All recoil yields are corrected for concurrent γ -radiolysis. Absorbed γ -energy was 3 to 14% of absorbed recoil energy. ^e Average yields from solutions 0.000573, 0.00283, 0.00670, 0.0135, 0.0302, 0.0655, and 0.101 M, respectively, in KI. ^f Molecules/100 e.v.

The molar absorptivity index of Fe³⁺ at 304 m μ was taken¹⁶ as 2170 l. mole⁻¹ cm.⁻¹ at 23° with a temperature coefficient of 0.7% deg.⁻¹ and $G(\text{Fe}^{3+})$ was assumed to be 15.6.¹⁷ Dose rates in methanol were calculated by multiplying dose rates in the dosimeter by 0.783, the ratio of electron densities. It was ascertained that the dose rate was ca. 3.5% higher at the top and bottom of the irradiation compartment of the Schwarz-Allen source at Boston University than at the middle, and the radial inhomogeneity was of similar magnitude. Dose rates employed in calculating γ -radiolysis yields were determined with dosimeters similar in size to the methanol ampoules and placed in the same position as were the ampoules.

Recoil energy absorbed was determined with the aid of aerated acid ferrous ammonium sulfate dosimeters containing 0.05 to 0.1 M boric acid; $G(\text{Fe}^{3+})$ was assumed to be 4.22.¹⁸ Necessary corrections were made for Fe³⁺ arising from γ -radiolysis, amounting typically to 10 to 15% of the total, as determined by boron-free Fricke dosimeters placed in the thermal neutron column as described above. Neutron fluxes were calculated from recoil doses by means of the same procedure which Schuler and Barr used in calculating their value of $G(\text{Fe}^{3+})$ from known neutron fluxes, *i.e.*, by their eq. 3.¹⁸ Their procedure for correcting for self-shielding by boron was also employed. The concentration of Fe³⁺ was determined as indicated above for γ -dosimetry. Neutron fluxes were also determined by absolute counting¹⁹ of Au¹⁹⁸. Although occasional discrepancies as large as 15% were recorded, neutron fluxes determined in the latter fashion differed randomly from the values calculated from Fe³⁺ dosimetry with a mean deviation (over nine comparisons) of 3%. Gold foil dosimetry was employed to detect and correct for differences between neutron fluxes at the chemical dosimeters and at nearby sample ampoules. Dose to an individual sample ampoule was (unless otherwise indicated) calculated by normalizing to the dose at a nearby chemical dosimeter, as determined from Fe³⁺ concentration, by means of gold foil data for the ampoule and the chemical dosimeter. Corrections were made as needed for differences in borate concentration. It was assumed that recoil energy was entirely absorbed within the methanolic solutions.

Analysis of Gaseous Products.—Gaseous products were removed from irradiated methanol at Dry Ice temperature with the aid of an automatic Toeppler pump. In all the experiments involving methanolic methyl borate solutions and in most of the others, after initial removal of gases, two cycles of bulb to bulb distillation, each followed by Toeppler pumping, were carried out. Measurements of gas volumes after each stage, carried out on five γ -radiolyzed samples, gave an average of 98.6% of final gas volume collected after the first distillation and 81.5% after the initial Toeppler. In some experiments, three or more cycles of pumping at -78° followed by warming to room temperature were employed. In every case the gaseous products were passed through a liquid nitrogen trap before being collected. Analyses were by the Saunders-Taylor micromanometric method using CuO containing 1.3% of Fe₂O₃, prepared by the method of Brückner and Schick²⁰ and were validated by analysis of known mixtures. The gaseous products from each of five recoil radiolyses were divided into two portions which were analysed separately. Average percentage mean deviations of the results were: H₂, 0.5; CH₄, 5.1; CO, 0.7.

Analysis of Nonvolatile Products.—Ethylene glycol and formaldehyde were determined by methods which have been described previously.^{8,21} In agreement with Theard,⁴ it was found that iodide interferes somewhat with the chromotropic acid estimation of formaldehyde (which was also employed in glycol

analysis). In early work (γ -radiolysis), correction (about 10%) for the interference was made on the basis of data for solutions containing known amounts of iodide and formaldehyde. In experiments involving methanolic methyl borate, *i.e.*, α -radiolyses and γ -radiolyses to be compared with them, formaldehyde and glycol were separated from KI, without exposure to air, by heating the solution *in vacuo* at 100° and collecting the distillate in liquid nitrogen for 5 to 6 hr., a process which was validated with known solutions.

Data

Because of the unsolved problem of reproducibility of yields from the radiolysis of methanol, effects of variation in LET or of solutes must be evaluated by experiments employing methanol of as nearly identical history as possible. Tables II–VI are arranged in accord with this requirement.

The data of Table II show that ca. 0.1 M borate has a negligible effect on yields of all products from γ -radiolysis except ethylene glycol, the yield of which appears to be reduced significantly. Variations in recoil yields with change in dose rate are random and are best ascribed to the poor reproducibility of the data and the complications of dosimetry. A set of eleven experiments, not detailed here, showed no systematic variation of yields with recoil dose in the range $(0.44\text{--}10.79) \times 10^{19}$ e.v. ml.⁻¹. A similar lack of dependence of yields on total Co⁶⁰ γ -dose was established previously.⁶ The largest difference between yields from γ and recoil radiolysis occurs, as has been reported previously,²¹ in $G(\text{CO})$. This is sevenfold greater for recoil radiolysis. The latter provides about twice as high a yield of methane and one and one half times as much formaldehyde as does γ -radiolysis. Only the yield of ethylene glycol is lower with the more densely ionizing radiation; $G(\text{H}_2)$ differs least of all, *i.e.*, by only about 10%. There is no significant effect of KI on recoil radiolysis.

Table III presents a survey of the effects of alkali halides and water on the radiolysis of methanol. The data of Theard and Burton^{3,4} are included to facilitate comparison. Earlier reports^{6,22} that yields from γ -radiolysis are influenced by small concentrations of water are, in agreement with more recent work,^{2,3} not confirmed by the data of Table III. In agreement with Burton and his co-workers,^{4,22} iodides are found to increase $G(\text{CH}_2\text{O})$ and to decrease $G(\text{glycol})$ and $G(\text{H}_2)$. The other alkali halides appear to influence only the hydrogen yield. Agreement between the present data and those of Theard and Burton is no better than has been obtained for solutions in "pure" methanol.

The effect of iodide on γ -radiolysis of methanol was explored with solutions in methanol B, which was subsequently found spectrophotometrically to be contaminated with traces of benzene (*cf.* Experimental). The results are shown in Tables IV and V. Concentrations of KI from 2.3×10^{-4} to 1.7×10^{-2} M had no significant effect on the (low) yields of H₂ and CH₄ characteristic of methanol B nor on the yield of CO.

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TABLE III

SURVEY OF THE EFFECT OF ALKALI HALIDES AND WATER ON THE γ -RADIOLYSIS OF METHANOL A^a

Solute	Concn., moles l. ⁻¹	Dose, 10 ¹⁹ e.v. ml. ⁻¹	G(H ₂) ^e	G(CH ₄) ^e	G(CO) ^e	G(CH ₂ O) ^e	G(C ₂ H ₆ O ₂) ^e	n ^b
None		0.175-4.21 ^c	4.98 ± 0.19	0.28 ± 0.04	0.09 ± 0.01	2.14 ± 0.13	3.07 ± 0.09	17
H ₂ O	0.13-0.25	1.5-2.1	4.60 ± 0.19	.26 ± 0.04	.07 ± 0.03	2.26 ± 0.16	3.05 ± 0.21	4
H ₂ O	1.2	2.1	4.86	.31	.08	2.49	3.08	1
LiF	0.011	1.5	4.57	.35	.07	2.36	3.32	1
NaF	.015	1.5	4.10 ± 0.02	.34 ± 0.05	.08 ± 0.02	2.29 ± 0.16	3.19 ± 0.11	2
KF·2H ₂ O	.006	1.5	3.88 ± 0.01	.47 ± 0.14	.06 ± 0.01	2.37 ± 0.05	3.33 ± 0.07	2
LiCl	.019	1.5	4.41	.31	.05	2.29	2.49	1
LiCl ^d	.05	3.1	4.48	.44	.14	2.61	1.92	1
NaCl	.020	1.5	4.32 ± 0.06	.34 ± 0.01	.05 ± 0.01	2.44 ± 0.08	3.03 ± 0.09	2
KCl	.014	1.5	4.29	.35	.09	2.16	2.79	1
KCl ^d	.05	3.1	4.47	.45	.14	1.76	2.32	1
NaBr	.007-0.018	1.5	4.50 ± 0.20	.32 ± 0.05	.07 ± 0.01	2.35 ± 0.05	3.20 ± 0.20	2
KBr	.0065	1.5	4.06 ± 0.01	.48 ± 0.09	.08 ± 0.01	2.14 ± 0.05	2.72 ± 0.50	2
KBr ^d	.05	3.1	4.44	.44	.13	1.64	2.96	1
NaI	.011	1.5	4.03	.21	.08	4.03	1.09	1
KI	.031-0.046	1.5	3.92 ± 0.11	.33 ± 0.04	.10 ± 0.01	3.29 ± 0.06	1.06 ± 0.09	2
KI ^d	.04	3	3.8	3.0	0.6	1

^a Indicated uncertainties are standard deviations of a single measurement. ^b The number of experiments. ^c Variation of yields with dose was random. ^d Data of Theard and Burton for solutions in methanol which had not been treated with dinitrophenylhydrazine, chosen in order to compare systems with similar histories; ^e cf. Table I for yields in absence of added solutes. ^f Molecules/100 e.v.

TABLE IV

EFFECT OF KI ON YIELDS OF GASEOUS PRODUCTS FROM γ -RADIOLYSIS OF METHANOL B^a

Concn. of KI, mole l. ⁻¹	G(H ₂) ^e	G(CH ₄) ^{b,e}	G(CO) ^e	G(CH ₂ O) ^e	G(C ₂ H ₆ O ₂) ^e	n ^c
None ^d	4.33 ± 0.15	0.28 ± 0.05	0.14 ± 0.08	2.08 ± 0.33	2.72 ± 0.24	7
0.00023-0.017 ^e	4.21 ± 0.07	0.27 ± 0.03	0.14 ± 0.05	^f	^f	5-8

^a Dose rate, 2.35×10^{17} e.v. ml.⁻¹ min.⁻¹. Uncertainties are standard deviations of single measurements. ^b Gas collection was by means of several chill-pump-warm-up cycles, *i.e.*, without distillation. ^c Number of experiments. ^d Doses were $(1.4-4.4) \times 10^{19}$ e.v. ml.⁻¹. ^e Doses were $(1.3-1.6) \times 10^{19}$ e.v. ml.⁻¹. ^f Dependent on concn. of KI. ^g Molecules/100 e.v.

TABLE V

EFFECT OF KI ON YIELDS OF FORMALDEHYDE AND ETHYLENE GLYCOL FROM γ -RADIOLYSIS OF METHANOL B^a

(KI), mole l. ⁻¹ $\times 10^3$	$\Delta G(\text{CH}_2\text{O})^{b,c}$	$\Delta G(\text{C}_2\text{H}_6\text{O}_2)^{b,c}$	$\Delta G(\text{I}_2)^{b,c}$
0.230	+0.36	-0.53	+0.04
.471	+ .62	- .32	
.803	+ .96	- .42	
1.35	+ .89	- .92	+0.09
1.91	+1.24	- .95	+ .05
4.80	+1.14	-1.11	+ .15
12.9	+1.44	-1.46	+ .06
17.0	+1.87	-1.55	+ .18

^a Results of single experiments; ^b cf. footnotes to Table IV for doses and dose rate. ^c ΔG values are relative to those given in Table IV for iodide-free methanol B. ^d Molecules/100 e.v.

methanol which had not been treated with dinitrophenylhydrazine, these workers found $-\Delta G(\text{glycol}) = 2\Delta G(\text{CH}_2\text{O})$. Their ΔG values for DNP-treated methanol differ less from those of Table V than from their ΔG values for untreated methanol. Apparently the magnitude of the effect of KI is sensitive to the history of the methanol.

Related data are presented in Table VI, where the effect of KI on γ -radiolysis in the presence of borate is presented so that it can be compared with its effect on recoil radiolysis. Inefficient reduction in hydrogen yield is apparent. Methane yields are as high as those obtained by Theard and Burton,^{3,4} who removed gaseous products with the aid of a reflux apparatus; $G(\text{CO})$ is essentially unaffected, while $\Delta G(\text{CH}_2\text{O}) > -\Delta G(\text{C}_2\text{H}_6\text{O}_2)$. The main purpose of the data of Table VI

TABLE VI

EFFECT OF KI ON YIELDS^a FROM γ -RADIOLYSIS OF METHANOL C IN THE PRESENCE OF 0.12 TO 0.15 M BORATE

(KI), mole l. ⁻¹ $\times 10^3$	G(H ₂) ^c	G(CH ₄) ^c	G(CO) ^c	G(CH ₂ O) ^c	G(C ₂ H ₆ O ₂) ^c
None ^b	4.81 ± 0.14	0.32 ± 0.04	0.15 ± 0.05	2.00 ± 0.17	1.95 ± 0.26
1.03	4.79	.39	.18	2.87	1.63
31.3	4.60	.42	.17	4.01	0.57
69.5	4.55	.43	.16	4.52	.34
105	4.05	.43	.19	3.65	.93

^a Dose rate = 1.9×10^{17} e.v. ml.⁻¹ min.⁻¹; total doses 1.9×10^{19} e.v. ml.⁻¹ for experiments in presence of KI. The latter data are from single experiments. ^b From Table II. ^c Molecules/100 e.v.

In agreement with Theard and Burton,^{3,4} iodide is a feeble scavenger of hydrogen precursor as compared to adventitious impurities. Within the reproducibility of this work $\Delta G(\text{CH}_2\text{O}) = -\Delta G(\text{glycol})$ over the entire range. Iodine formation, determined spectrophotometrically *via* the absorption of I₃⁻, can be regarded as negligible and may have been wholly adventitious since determinations were performed after admission of air.

The data of Table V are only in qualitative agreement with those of Theard and Burton.⁴ Thus, for

is to serve as a basis for comparison with the data of Table II which demonstrate the absence of a significant effect of KI on recoil radiolysis.

Discussion

Material Balance.—Values of $G(\text{redn.})$ and $G(\text{oxn.})$ are presented in Table VII. $G(\text{oxn.})$ exceeds $G(\text{redn.})$ for γ -radiolysis of each "pure" methanol, although with methanol A the difference is not significant. Part of the deficiency of reduction products may be due to failure

to collect CH_4 quantitatively. The remainder may be due to scavenging of hydrogen precursor by impurities. γ -Radiolysis in the presence of *ca.* 0.1 *M* methyl borate yields, in contrast, a deficiency of oxidation products due largely to diminution of $G(\text{glycol})$, although $G(\text{redn.})$ is not significantly affected. Borate is thus shown to be a feeble scavenger of glycol precursor.

TABLE VII

MATERIAL BALANCE OF RADIOLYSIS PRODUCTS				
Methanol	Solute	Radiation	$G(\text{redn.})$	$G(\text{oxn.})$
A	None	γ	5.2	5.4
B	None	γ	4.6	5.1
C	None	γ	4.9	5.6
C	$\text{B}(\text{OCH}_3)_3$	γ	5.1	4.3
C	$\text{B}(\text{OCH}_3)_3$	Recoil ^a	6.2	6.5
C	$\text{B}(\text{OCH}_3)_3$	Recoil ^b	5.6	5.8
C	$\text{B}(\text{OCH}_3)_3$, KI	Recoil ^b	5.7	5.9
C	$\text{B}(\text{OCH}_3)_3$	Recoil ^c	6.1	6.0

^a Dose rate = $(0.033-0.061) \times 10^{16}$ e.v. ml.⁻¹ min.⁻¹. ^b Dose rate = $(0.33-0.55) \times 10^{16}$ e.v. ml.⁻¹ min.⁻¹. ^c Dose rate = $(2.0-2.5) \times 10^{16}$ e.v. ml.⁻¹ min.⁻¹.

Material balance from recoil radiolysis is as good as could be expected from the precision of the data. The observed equality of $G(\text{oxn.})$ and $G(\text{redn.})$ could result from a compensation of adventitious scavenging of hydrogen precursor and partial scavenging of a greatly reduced yield of glycol precursor. The more economical assumption is made here, however, that this equality can be ascribed to the lower sensitivity to scavengers which is expected for radiolysis of high LET. This assumption is consistent with the negligible effect of iodide on the recoil radiolysis (*cf.* Table II).

Comparison of Results at High LET with Prior Work.

—The radiolysis of methanol by 26–29 Mev. cyclotron alphas²³ and fission recoils,^{24,25} have been described. The work of Wiebe, *et al.*,²⁴ is not comparable with results reported here. Landsman and Butterfield²⁵ irradiated liquid methanol with uranium fission fragments at 100° and found $G(\text{H}_2) = 9.68$, $G(\text{CH}_4) = 0.88$, $G(\text{CO}) = 2.98$, $G(\text{CH}_2\text{O}) = 3.6$, and $G(\text{C}_2\text{H}_6\text{O}_2) = 0.77$. It is assumed herein that the elevated temperature of their work had only minor consequences.

McDonnell and Newton's experiments²³ involved an LET, ~ 3 e.v./ \AA ,²⁶ one-tenth of that characteristic of the 2.35 Mev. per nuclear event recoils, and one hundred times the LET characteristic of Co^{60} γ 's. Unfortunately, these workers employed doses high enough to decompose 2 to 3% of the substrate and very high dose rates ($\sim 3 \mu\text{a}$. beam current). Their data are therefore probably not completely comparable to the present ones which involved, typically, decomposition of *ca.* 0.01% of the methanol and for which constancy of yield with total dose was established. The purity of the methanol may be more important at this intermediate LET than at higher values. Comparison of their results, $G(\text{H}_2) = 3.46$, $G(\text{CH}_4) = 0.36$, $G(\text{C}_2\text{H}_6) = 0.014$, $G(\text{CO}) = 0.23$, $G(\text{CH}_2\text{O}) = 1.67$, $G(\text{C}_2\text{H}_6\text{O}_2) = 1.75$, $G(\text{H}_2\text{O}) = 0.93$, $G(\text{redn.}) = 3.82$, and $G(\text{oxn.}) = 3.87$, with those reported here suggests that relative yields of products undergo large changes only at LET above that characteristic of McDonnell and Newton's experiment. The variations in yields from γ -radiolysis to 28 Mev. cyclotron α -radiolysis

(23) W. R. McDonnell and A. S. Newton, *J. Am. Chem. Soc.*, **76**, 4651 (1954).

(24) A. K. Wiebe, W. P. Conner, and G. W. Kinzer, *Nucleonics*, **19**, No. 2, 50 (1961).

(25) D. A. Landsman and J. E. Butterfield, AERE-R 3625, 1961; *cf.* *Nucl. Science Abstr.*, **15**, 3033 (1961).

(26) L. H. Gray, "Actions Chimiques et Biologiques des Radiations," M. Haissinsky, Ed., 1^{ère} Series, Masson et Cie., Paris, 1955, p. 1.

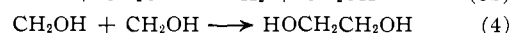
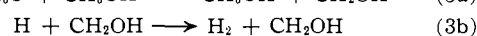
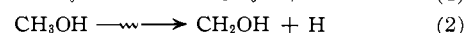
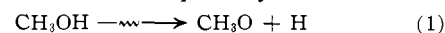
appears, however, to be greater than those observed with paraffins.^{27,28}

The data of the present research and earlier work^{23,25} do not permit conclusions to be drawn concerning the dependence of $G(-\text{CH}_3\text{OH})$ on LET unless it is assumed that H_2 , CH_4 , CO , CH_2O , $\text{C}_2\text{H}_6\text{O}_2$, and H_2O are the only significant products, that $G(\text{CH}_4) + G(\text{CO}) + G(\text{CH}_2\text{O}) + 2G(\text{C}_2\text{H}_6\text{O}_2)$ is a reliable measure of $G(-\text{CH}_3\text{OH})$ from Co^{60} γ -radiolysis in the absence of borate and that the results of both McDonnell and Newton and of Landsman and Butterfield can be compared with the present work. Thus $G(-\text{CH}_3\text{OH})$ is 8.7, 5.7, 5.9, and 9.0 at LET values of 0.03, 3, 30, and 300 e.v./ \AA , respectively. On this basis it appears that, with increasing LET, $G(-\text{CH}_3\text{OH})$ goes through a minimum and then increases at very high LET. If this is, in fact, the behavior of methanol, there is a notable similarity to that of water,²⁹ for which $G(-\text{H}_2\text{O})$ is a minimum with radiation of LET around 4 e.v./ \AA .

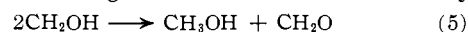
Mechanistic Speculations Based on LET Effects.—

The difference between product yields characteristic of Co^{60} γ -radiolysis and those characteristic of $\text{B}^{10}(\text{n}, \alpha)\text{Li}^7$ radiolysis, hereafter symbolized by $DG(\text{H}_2)$, etc., can be considered conveniently in the light of recent suggestions^{2,4} concerning the mechanism of radiolysis of methanol if it is assumed that primary³⁰ yields of radicals and molecular products do not differ substantially over this range of variation of LET. This assumption can be justified only by its heuristic value.

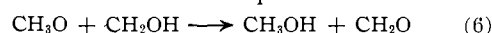
The fact that $DG(\text{C}_2\text{H}_6\text{O}_2)$ is approximately $-2^{1/3}$ ³¹ is consistent with the supposition⁴ that process 1 occurs more frequently than 2 in the ionization track and that the most CH_2OH radical results from 3.³² The higher concentration of primary radicals charac-



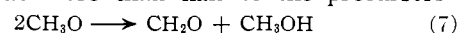
teristic of a cylindrical ionization track would be expected to favor bimolecular reaction of radicals relative to processes of lower order in radical. There is evidence³³ that, in the gas phase, reaction 4 is favored over 5. Thus it appears that glycol yield would not be greatly reduced at high LET if CH_2OH were a major



primary radical. Reaction 6 would compete more favorably with 3a at higher radical concentrations, but a portion, at least, of the increase in $G(\text{CH}_2\text{O})$ can be ascribed to the increased importance of reaction



7,^{4,34,35} so that more than half of the precursors of



secondary formaldehyde would be CH_3O radicals.

(27) A. E. de Vries and A. O. Allen, *J. Phys. Chem.*, **63**, 879 (1959).

(28) H. A. Dewhurst and R. H. Schuler, *J. Am. Chem. Soc.*, **81**, 3210 (1959).

(29) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., Inc., Princeton, N. J., 1961, p. 58.

(30) "Primary" refers here to radicals and molecules formed directly from excited states or ions or by recombination of electrons with ion radicals as distinct from those formed by reaction of radicals with each other or with stable molecules.

(31) $DG(\text{C}_2\text{H}_6\text{O}_2)$ compares the yield of glycol from recoil radiolysis with that from γ -radiolysis in the absence of methyl borate because, as pointed out above, it is assumed that the former process is insensitive to scavenging by borate.

(32) M. Cher, *J. Phys. Chem.*, **67**, 605 (1963).

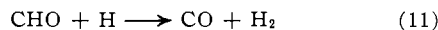
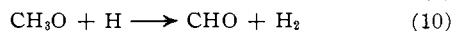
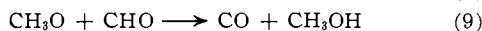
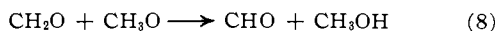
(33) J. B. Farmer and C. A. McDowell, *Trans. Faraday Soc.*, **48**, 624 (1952).

(34) P. Gray, *ibid.*, **52**, 344 (1956).

(35) D. F. Dever and J. G. Calvert, *J. Am. Chem. Soc.*, **84**, 1362 (1962).

The very low sensitivity of $G(\text{C}_2\text{H}_6\text{O}_2)$ from recoil radiolysis to iodide concentration can, however, be interpreted in terms of track recombination of CH_2OH radicals and indicates that some primary CH_2OH is formed. On this basis $G_{\text{CH}_2\text{OH}} \geq \sim 1$.

Most of the observed $DG(\text{CO})$ of about +0.9 can be rationalized on the basis of processes higher than second order in CH_2O and primary radicals. Thus $DG(\text{CH}_2\text{O} + \text{C}_2\text{H}_6\text{O}_2)$ of ca. $-1\frac{1}{3}$ corresponds to $DG(\text{CO})$ of +0.7 and at the high concentrations characteristic of the track this may arise from such processes as 8-11. The data of Landsman and Butterfield



indicate that the yields of primary CO and H_2 increase substantially at LET above 30 e.v./Å.

The conclusion that virtually all ethylene glycol from recoil radiolysis is formed in the ionization track leads to the corollary that very few H atoms (or solvated electrons) escape into the bulk solution under this condition. H atoms apparently disappear largely by combination with each other and other radicals in the track. Investigation of the effect of efficient scavengers of H_2 precursors² on $G(\text{H}_2)$ at high LET is much in order.

It does not seem possible to rationalize the increase in $G(\text{CH}_4)$ with increase in LET if it is assumed that CH_4 is formed from CH_3 , the yield of which is independent of LET. Diminution of $G(\text{CH}_4)$ and production of C_2H_6 , which was not detected, and CH_3OCH_3 or $\text{CH}_3\text{-CH}_2\text{OH}$, which were not determined, would result from

addition of CH_3 to itself or to CH_3O or CH_2OH . Addition of CH_3 to H or abstraction of H from CH_3O or CH_2OH would have no effect on $G(\text{CH}_4)$.

The Effect of KI and Other Halides on γ -Radiolysis.—The effect of KI on $G(\text{CH}_2\text{O})$ and $G(\text{C}_2\text{H}_6\text{O}_2)$ is, in agreement with Theard and Burton,⁴ clearly a property of coupled oxidation and reduction of iodide ion and iodine atom, e.g., by CH_3O and CH_2OH , respectively, as they suggest. The present data indicate that reaction 12 does not compete significantly with 3b and the oxidation of CH_2OH to CH_2O by I since, if it did, the decrease in $G(\text{C}_2\text{H}_6\text{O}_2)$ would be greater than the increase in $G(\text{CH}_2\text{O})$. Since Theard and Burton



report⁴ just such an inequality, however, reaction 12 cannot be excluded.

Reaction 12 could account for reduction of $G(\text{H}_2)$ by iodide but the dependence of this reduction on the history of the methanol suggests a role other than scavenging of hydrogen atoms. Elucidation of this role must probably await an improved understanding of the sensitivity of $G(\text{H}_2)$ to purity of methanol. The same conclusion may also hold for the other alkali halides, all of which reduce $G(\text{H}_2)$ more or less. Whether the effects are due to the halides themselves or to impurities in the halides is not known at present.

Acknowledgment.—The authors are indebted to Dr. Robert Woodley for his assistance in neutron irradiations. N. N. L. is also indebted to the National Science Foundation for a Senior Postdoctoral Fellowship and to the Isotope Department of the Weizmann Institute of Science for its hospitality, both of which facilitated preparation of this paper.

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH 13, PENNA.]

The Adsorption of Alkanes on Cracking Catalysts. I. A Study of the Exchange between Isobutane and its Adsorbed Radioactive Analog

BY JOHN G. LARSON AND W. KEITH HALL

RECEIVED JUNE 10, 1963

Isobutane- C^{14} is chemisorbed on silica-alumina in three forms; two of these may be regenerated into the gas phase unchanged by exchange with nonradioactive $i\text{-C}_4\text{H}_{10}$; the third is irreversibly adsorbed and cannot be so regenerated. The exchange kinetics have been studied as a function of the pretreatment of the catalyst and of the evacuation temperature following contact with the radioactive gas. It has been found that the amount of the most loosely held form, V(1), can be reduced virtually to zero without altering the amount of the more strongly held chemisorbed forms by raising the evacuation temperature from 27 to 150°; further, V(1) is nearly independent of the manner in which the catalyst is pretreated. The more strongly held, exchangeable isobutane is unaffected by altering the evacuation temperature, but is quite sensitive to the pretreatment of the catalyst. The amount of this species, V(2), is greatly reduced by treating the catalyst with H_2 at elevated temperature, by base-exchanging it with KAc, or by adding back H_2O , following the initial evacuation at 500°; it is increased by cooling the catalyst from 500° to room temperature in O_2 before evacuation. The nonexchangeable species V(NE) responds similarly except that it is unaffected by base-exchange or by adding back H_2O . As the rate constants per molecule for exchange (probability of desorption), $k(i)$, are unaffected by these variables, the equilibrium adsorption-desorption rates, $R(i)$, are proportional to the adsorbed amounts. Since $R(2)$ is lowered by small amounts of added-back H_2O while the rate of exchange of $i\text{-C}_4\text{H}_{10}$ hydrogen for catalyst deuterons is simultaneously increased, the enhanced rate of the latter reaction cannot be attributed to an increase in $R(2)$ by a cocatalyst effect. Moreover, direct comparison of the rate of deuterium exchange, using $i\text{-C}_4\text{D}_{10}$, with $R(2)$ reveals that the former rate is much too fast to be accounted for solely by the latter when H_2O has been added back, whereas these same rates compare favorably when the catalyst is dry. It is concluded, therefore, that an additional process for H-exchange becomes important when H_2O has been added back.

Introduction

The effects of small amounts of water on the rates of reactions of hydrocarbons being catalyzed by strong Lewis acids are not well understood. Hindin, Oblad, and Mills¹ reported that the rates of isomerization and cracking of C_5 - to C_8 -paraffins were increased by as much as 25-fold by the addition of as little as 0.05%

H_2O to cracking catalysts which had previously been evacuated at 525°. Related findings exist for butane cracking,² cumene dealkylation,³ and propylene poly-

(1) S. G. Hindin, A. G. Oblad, and G. A. Mills, *J. Am. Chem. Soc.*, **77**, 535, 538 (1955).

(2) R. C. Hansford, *Ind. Eng. Chem.*, **39**, 849 (1947).

(3) C. D. Prater and R. M. Lago, "Advances in Catalysis," Vol. VIII, Academic Press, Inc., New York, N. Y., 1956, p. 293.