the gas phase to form the observed products. Of the two possible reactions, *i.e.*, a reaction with a gas phase OH radical or H atom to form $H_2 + O_2$, the reaction with the H atom should again have the lower activation energy.

We suggest, therefore, that the mechanism of this surface reaction is

$$S + OH = S\text{-}OH \tag{15}$$
$$S\text{-}OH + H = S\text{-}O + H_2 \tag{16}$$
$$S\text{-}O + S\text{-}O = 2S + O_2 \tag{17}$$

where S is the surface. The OH radical is probably bound to the surface through the oxygen atom. This orientation would greatly increase the probability of forming $H_2 + O_2$ upon reaction of an H atom from the gas phase, as is experimentally observed.

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PHILADELPHIA, PA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MANCHESTER]

Radical and Molecular Yields in the γ-Irradiation of Liquid Methanol

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Fe(III) salts and benzoquinone are reduced during the γ-irradiation of methanol and the extent of reduction is a measure of *G*(radicals). These solutes also decrease $G(H_2)$, $G(CH_4)$ and *G*(glycol) while at the same time increasing $G(CH_2O)$. The observations are accounted for by the oxidants reacting with the radicals H, CH_2OH and CH_3 and the results are analyzed to give *G*(H), $G_m(H_2)$, $G(CH_2OH)$, $G(CH_3)$, $G_m(CH_2O)$, G_m(glycol) and $G_m(CH_4)$. Appreciable differences in *G*(H) and $G(CH_3)$ are observed between pure methanol and methanol which is 0.1 *N* in sulfuric acid.

Values of the total radical yields have been obtained for various organic solvents subjected to ionizing radiation by using scavengers such as iodine[1] and diphenylpicryl hydrazyl,[2] and also from measurements of the initiation rates of polymerization.[3] So far the separation of these total yields into the yields of individual radicals has not been made as it has for water. The present work is an application to methanol of the use of ferric salts and quinones as radical scavengers.[4-6] These have been fruitful in aqueous systems where the radicals reduce the scavengers and, in suitable conditions, the extent of this reduction is a measure of $G_w(H) + G_w(HO)$. More detailed analyses of the product yields in various conditions also enables the individual radical and molecular yields to be obtained.

We found in preliminary experiments that Fe(III) and quinones are also reduced during the irradiation of their solutions in organic liquids. Methanol was chosen for a detailed study because the work of McDonell and Newton[7] and McDonell and Gordon[8] has shown that the irradiation products are ethylene glycol, formaldehyde, hydrogen, methane and carbon monoxide, all of which can be determined at low conversions.

Experimental

Materials.—Methanol of analytical reagent grade was dried by refluxing with magnesium methoxide. Traces of formaldehyde were removed by refluxing with dinitrophenylhydrazine. Benzoquinone was purified by low temperature sublimation *in vacuo*. Ferric chloride hydrate (described as $FeCl_3 \cdot 6H_2O$) was analytical reagent grade and was used without further purification.

Analyses.—Gases were collected and measured as described previously[5] and analyzed mass spectroscopically. The formaldehyde in the irradiated methanol (10^{-4} to 10^{-3} *M*) was determined with chromotropic acid[9] and glycol by treating with periodic acid.[10]

We found it possible to extend the latter method to concentrations of the order 10^{-4} *M*. With a 50% excess of periodic acid the time for complete reaction was about 12 hours when the analysis mixture contained about 20% methanol + 80% water. More than 20% methanol slowed the reaction considerably and also gave rise to a reduction of periodic acid over and above that due to glycol. Hence to determine the smaller amounts of glycol, the original methanol solution was concentrated by distillation *in vacuo* and then diluted with water.

Fe(III), because of its absorption in the ultraviolet, interferes with this method of analysis and was removed before the addition of periodate by running the solution (diluted to 20% methanol) through an ion-exchange resin (Amberlite I.R. 120) in the sodium form. Tests showed that the eluent gave some reaction with periodic acid even in the absence of glycol, due presumably to traces of material from the resin. This was corrected for by running blanks through the same resin but the procedure introduced an error of about ±0.05 into the glycol yields. Since in the presence of Fe(III) these are only of the order of 0.2 the possible error in the yields in these conditions is considerable. Benzoquinone interferes with both glycol and formaldehyde analyses and we have been unable to overcome this difficulty. Hence in benzoquinone + methanol mixtures we can only report the gas yields.

With these exceptions tests with known solutions containing all the materials present in the irradiated solutions established the reliability of the analytical methods for glycol and formaldehyde.

When the extent of reduction of Fe(III) or quinone was small, the Fe(II) and hydroquinone produced were determined by their reduction of ferriin as described previously.[5,6] When the change was appreciable, as at the lower Fe(III) and quinone concentrations, it was measured by the decrease in absorption of Fe(III) at 249 mμ and of benzoquinone at 246 mμ. We have been unable to obtain hydroquinone

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[1] F. N. Weber, P. F. Forsyth and R. H. Schuler, *Radiation Research*, **3**, 68 (1955).

[2] A. Prevost-Bernas, A. Chapiro, C. Cousin, Y. Landler and M. Magat, *Disc. Faraday Soc.*, **12**, 98 (1952).

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[6] J. H. Baxendale and G. Hughes, *ibid.*, **14**, 324 (1958).

[7] W. R. McDonell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

[8] W. R. McDonell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955).

[9] C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem.* (*Anal. Ed.*), **17**, 400 (1945).

[10] G. O. Aspinall and R. J. Ferrier, *Chem. Ind.*, 1216 (1957).

yields in the acidified methanol because some reduction of the quinone occurs in these conditions even in the absence of radiation.

Irradiations.—These were done on about 50 cc. of methanol in 100-cc. Pyrex vessels using a Co^{60} source. Dose rates were between 3×10^{15} and 7×10^{15} e.v./g. min. with total doses from 8×10^{17} to 2×10^{19} e.v./g. Doses were calculated from calibrations using the ferrous sulfate dosimeter assuming the energy absorbed by the liquids to be proportional to their densities and taking 15.6 Fe^{3+} per 100 e.v. as the yield in the dosimeter liquid.

All methanol solutions were deaerated by shaking and pumping as described previously.[5,6]

Results

In their γ-irradiations of pure methanol, McDonell and Gordon[8] used very high doses to obtain the yields of the oxidation products and it seemed desirable to repeat the experiments at the lower doses used here to ensure the absence of secondary reactions with the products. As is shown below there are appreciable differences between the two sets of observations. We have also compared the irradiation of pure methanol with that of methanol containing 0.1 *N* sulfuric acid and up to 3% of water (henceforth referred to as acid methanol). This was done because in addition to using ferric chloride and benzoquinone as radical scavengers, we have also used ferric sulfate (as in the aqueous methanol work[6]), which is insoluble in pure methanol but is sufficiently soluble in the acid methanol.

Neutral and Acid Methanol.—The yields for pure methanol over a large dose range are shown in Fig. 1. $G(H_2)$, $G(CH_2O)$ and $G(CO)$ are constant at 4.1, 2.05 and 0.15, respectively, while G(glycol) increases and $G(CH_4)$ decreases slightly with increasing dose. Extrapolation to zero dose gives $G(\text{glycol}) = 3.1$ and $G(CH_4) = 1.2$. These results are compared with McDonell and Gordon's[8] in Table I. The main differences are in $G(CH_2O)$ and $G(CH_4)$. The former might arise from secondary reactions since their doses were at least thirty times higher than ours in this determination, but we are unable to explain the difference in the $G(CH_4)$ which were obtained with similar doses.

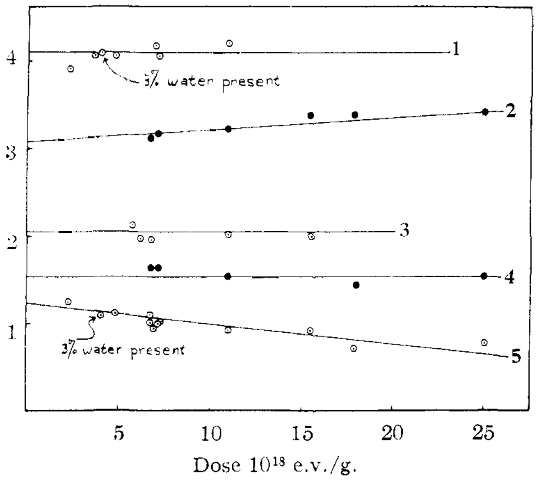

Fig. 1.—Yields of products for neutral methanol: 1, $G(H_2)$; 2, G(glycol); 3, $G(CH_2O)$; 4, $G(CO) \times 10$; 5, $G(CH_4)$.

Table I

Yields from Methanol with γ-Irradiation

	$G(H_2)$	$G(CH_2O)$	G(glycol)	$G(CH_4)$	G(CO)
a	4.0	1.3	3.0	0.24	0.16
b	4.1	2.05	3.1	1.23	.15
c	5.6	2.25	3.3	0.38	.14
d	5.4	. .	. .	.41	.17
e	5.4	. .	. .	.41	.14

[a] Neutral, McDonell and Gordon's results. [b] Neutral, present results. Extrapolated to zero dose. [c] 97%, containing 0.1 *N* H_2SO_4. Extrapolated to zero dose. [d] 97%, containing 0.5 *N* H_2SO_4. Dose 3.2×10^{18} e.v./g. [e] 97%, containing 1.0 *N* H_2SO_4. Dose 6.0×10^{18} e.v./g.

It will be noted from Fig. 1 that $G(H_2)$ and $G(CH_4)$ are unchanged when the methanol contains 3% water. However considerable differences arise when the 97% methanol is made 0.1 *N* in sulfuric acid as is shown in Fig. 2. An increase in acidity does not cause any further change (Table I).

Fe(III) Sulfate in Acid Methanol.—Table II shows the changes in product yields for acid methanol when ferric sulfate is introduced. G(CO), $G(CH_4)$ and $G(H_2)$ are unaffected. There is a big increase in $G(CH_2O)$, a decrease in G(glycol) and at the same time Fe(II) is formed. G(FeII), $G(CH_2O)$ and G(glycol) are reasonably constant for a fivefold change both in Fe(III) concentration and in dose.

Table II

Yields in 97% Methanol, 0.1 *N* in H_2SO_4 and Containing Ferric Sulfate

Doses *ca.* 4×10^{18} e.v./g. except where indicated.

Fe-(III) $\times 10^4$	$G(H_2)$	G(Fe II)	$G(CH_2O)$	G-(glycol)	G(CO)	G-(CH_4)
0	5.6	0	2.25	3.3	0.14	0.38
3.3	5.55	6.25	8.4	. .	.14	.39
4.8	5.55	6.5	8.5	. .	.16	.35
10[a]	5.55	6.45	8.7	0.2	.15	.41
24	5.65	6.55	8.4	. .	.17	.40
50[b]	5.65	6.6	8.6	0.2	.17	.40
100	5.55	6.55	7.9	. .	.17	.39

[a,b] Doses increased 2 × and 5 ×, respectively.

These observations suggest that, as in aqueous alcohol,[6] Fe(III) reacts with the CH_2OH radicals which otherwise dimerize to glycol

$$\cdot CH_2OH + Fe(III) \longrightarrow CH_2O + Fe(II) + H^+$$

and also that at these Fe(III) concentrations all the radicals are oxidized in this way. It will be noted that there is a reasonable balance between the loss of glycol, the increase in aldehyde, and the Fe(II) produced as required by this mechanism.

By analogy with the dilute aqueous methanol system we would expect the hydrogen to be formed both as molecular hydrogen and also from atomic hydrogen by the reaction

$$H + CH_3OH \xrightarrow{k_1} H_2 + CH_2OH \qquad (1)$$

The observation that $G(H_2)$ is unchanged by Fe(III) means that the competing reaction

$$H + Fe(III) \xrightarrow{k_2} H^+ + Fe(II) \qquad (2)$$

which is observed in the aqueous system, does not occur appreciably in the present conditions. This would be expected if k_1/k_2 were of the same order in 97% methanol as found in water,[6] *i.e.*, 2.1, since reaction 1 would predominate. Whatever the

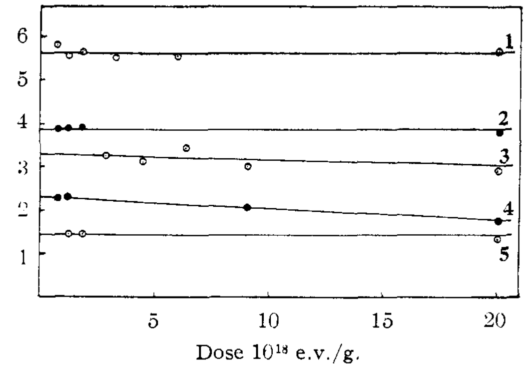

Fig. 2.—Yields of products for 97% methanol + 3% water, 0.1 *N* in sulfuric acid: 1, $G(H_2)$; 2, $G(CH_4) \times 10$; 3, *G*(glycol); 4, $G(CH_2O)$; 5, $G(CO) \times 10$.

source of the hydrogen, it follows that since *G*(FeII) is constant then Fe(III) must be reacting with all the available radicals and hence *G*(FeII) = *G*(radicals) = 6.5.

We saw that the decrease in glycol was balanced by the increase in formaldehyde and the formation of Fe(II) so that the Fe(III) apparently only interferes with the formation of glycol. Hence the formaldehyde produced in the absence of Fe(III) must be a "molecular" product in the sense that if there are precursors these give formaldehyde rapidly and dot not react with low concentrations of the scavenger.

It would also appear that the small amount of glycol which remains under these conditions is not formed by the same process as the bulk of the product. Since it is unaffected by Fe(III) concentration this residual amount can also be termed the "molecular" yield of glycol.

Fe(III) Chloride and Benzoquinone in Acid Methanol.—Hydrated ferric chloride and benzoquinone are much more efficient scavengers than ferric sulfate as is shown in Tables III and IV.

TABLE III

YIELDS IN 97% METHANOL CONTAINING 0.1 *N* H_2SO_4 AND HYDRATED FERRIC CHLORIDE

Doses *ca.* 4×10^{18} e.v./g.

$Fe(III) \times 10^4$	$G(H_2)$	$G(CH_4)$	$G(CO)$	$G(FeII)$
0	5.6	0.38	0.14	0
1.0	5.65	.38	..	..
22.7	4.6	.31	.15	6.8
47.5	4.2	.22	.16	7.2
71.1	3.5	.24	.15	7.3
143.5	3.0	.23	.14	..

TABLE IV

YIELDS IN 97% METHANOL CONTAINING 0.1 *N* H_2SO_4 AND BENZOQUINONE (*Q*)

Doses *ca.* 5×10^{18} e.v./g.

$Q \times 10^3$	$G(H_2)$	$G(CH_4)$	$G(CO)$
0	5.6	0.38	0.14
1.2	5.1	.27	..
4.9	4.6	.24	.15
7.4	4.2	.19	.13
10.2	4.0	.18	.11
18.6	3.4	.21	.15
25.1	3.15	.24	.14
50	2.4	.20	..

Not only is *G*(glycol) decreased and $G(CH_2O)$ increased as before, but $G(H_2)$ progressively decreases with increasing scavenger concentration. Also $G(CH_4)$ appears to reach a lower constant value of about 0.2, but *G*(CO) is unaffected.

These observations suggest that at least part of the hydrogen is produced from atomic hydrogen by reaction 1 above and that Fe(III) competes with methanol for the atoms by reaction 2, and benzoquinone by the reaction

$$Q + H \longrightarrow QH \longrightarrow {}^1/_2Q + {}^1/_2QH_2$$

Assuming that a certain amount of hydrogen $G_m(H_2)$ is produced as molecules and that the yield of atoms is *G*(H), then the observed yield $G(H_2)$ in the presence of Fe(III) should be given by

$$G(H)_2 = G_m(H_2) + \frac{k_1(MeOH)}{k_1(MeOH) + k_2(FeIII)} \times G(H)$$

This derivation assumes $G_m(H_2)$ and *G*(H) are unaffected by the scavenger. In the absence of Fe(III), $G(H_2)$ has a maximum value $G_{max} = G_m(H_2) + G(H) = 5.6$, and hence

$$1/[G_{max} - G(H_2)] = [1 + k_1(MeOH)/k_2(FeIII)]/G(H) \qquad (I)$$

Figure 3 shows plots of this equation and the analogous one for quinone which are linear as required. Both lines give the same intercept, the value of which from the above equation gives *G*(H) = 3.8 and $G_m(H_2) = 1.8$.

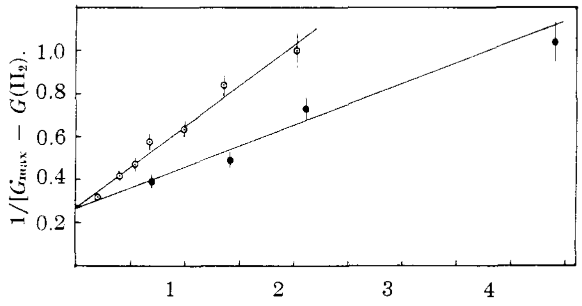

Fig. 3.– Plot of data in Tables III and IV according to equation I: ○, quinone; ●, Fe(III).

The decrease of $G(CH_4)$ from 0.38 to 0.2 suggests that part of the methane also had a radical precursor which reacts with the scavengers. This is probably the methyl radical which, in the absence of scavenger, will react

$$CH_3 + CH_3OH \longrightarrow CH_4 + CH_2OH$$

With ferric chloride it may react

$$FeCl_3 + CH_3 \longrightarrow FeCl_2 + CH_3Cl$$

and with benzoquinone it will probably give an addition product as do other radicals which are not readily oxidized.[11] In both cases $G(CH_4)$ will decrease. The residual methane found with constant yield of about 0.23 at the higher scavenger concentrations comes in the category of a "molecular" yield and hence $G_m(CH_4) = 0.2$ and $G(CH_3) = 0.2$.

Another feature of the results in Table III is that *G*(FeII) increases with increasing Fe(III) con-

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[11] A. F. Bickel and W. A. Waters, *J. Chem. Soc.*, 1764 (1950).

centration and is generally higher than the constant value found with ferric sulfate (Table II). The same effect occurs in dilute aqueous methanol at high Fe(III) concentrations.[6] In order to establish whether there existed a lower constant limit of G(FeII), the production of Fe(II) was followed over a fourfold change in Fe(III) at low concentration. This is shown in Fig. 4. A constant rate of Fe(II) production is observed which gives G(FeII) = 6.4 in reasonable agreement with Table II.

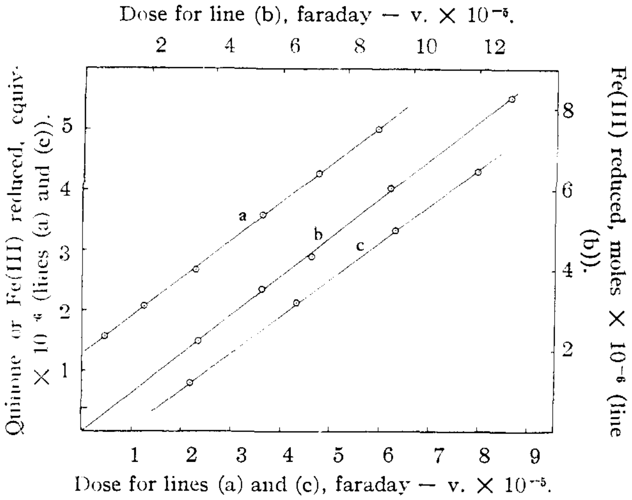

Fig. 4.—Rates of reduction in γ-irradiated methanol: (a) 4.8 × 10^{-5} M benzoquinone in neutral methanol, G = 6.2; (b) 2.5 × 10^{-4} M Fe(III) chloride in 0.1 N acid methanol, G = 6.4; (c) 1.2 × 10^{-4} M Fe(III) chloride in neutral methanol, G = 6.1. In (a) the ordinate, and in (c) the abscissa axis has been shifted to separate the lines.

This increase in G(FeII) would occur if what we have called the "molecular" hydrogen and glycol were produced by the combination of radical precursors and this process were prevented in part by high concentrations of the scavenger. However the "molecular" yield of glycol is too small to account for all the effect in this way and a change in $G_m(H_2)$ would show up in the plot of equation I in Fig. 3. An alternative explanation of the increase is that excitation of Fe(III) is induced by subexcitation electrons. It is known from photochemical investigations that such excitation could lead to further oxidation of methanol with the accompanied reduction of Fe(III).

At low Fe(III) concentrations both H and CH_3 react with methanol to give CH_2OH radicals and we have seen that the total radical yield in these conditions is 6.5. We find $G(H) + G(CH_3)$ = 4.0 hence another radical is present with a yield of 2.5. Since in the absence of scavenger the amount of glycol is greater than can be accounted for in terms of the "molecular" glycol and the dimerization of the CH_2OH formed from H and CH_3, and since these other radicals give aldehyde with Fe(III), it is highly probable that they are primarily produced CH_2OH radicals, *i.e.*, $G(CH_2OH)$ = 2.5.

Fe(III) Chloride and Benzoquinone in Neutral Methanol.—Figure 4 shows that in neutral methanol at low Fe(III) and benzoquinone concentrations G(FeII) = $G(QH_2)$ = G(Radicals) = 6.1. Tables V and VI show that Fe(III) and benzoquinone have the same qualitative effect on the products as in acid methanol. However, although the benzoquinone results are reasonably consistent with equation I above, as is shown in Fig. 5, those with ferric chloride show deviations which suggest that Fe(III) at the higher concentrations is more reactive with H than would be expected. This may occur because Fe(III) is not present as a single species, and that other forms, possibly polymeric, of increasing activity become more important at the higher concentrations. Whatever the reason for this behavior, the important observation for the present purpose is that $G(H_2)$ reaches a lower limiting value, *viz.*, 1.7, which is constant over a fourfold change in Fe(III) concentration. The extrapolated limit for the benzoquinone results (Fig. 5) is consistent with this value and it can therefore be identified with $G_m(H_2)$ as before. Hence $G_m(H_2)$ = 1.7 and G(H) = 2.4 in neutral methanol.

Tables V and VI also show that although $G(CH_4)$ is higher than in acid methanol (1.2 compared with 0.38), Fe(III) and benzoquinone reduce it to the same value 0.2 in both media. Assuming as before that the methyl radical is the precursor to part of the methane we obtain $G_m(CH_4)$ = 0.2 and $G(CH_3)$ = 1.0.

As in acid methanol G(CO) is unchanged and G(FeII) increases appreciably with Fe(III) concentration. Since $G(H_2)$ at the high concentration end, which we have identified with $G_m(H_2)$, is constant when G(FeII) increases it confirms that this increase does not arise by Fe(III) interfering with the molecular hydrogen formation.

TABLE V

YIELDS FROM NEUTRAL METHANOL CONTAINING HYDRATED FERRIC CHLORIDE

Doses *ca.* 4 × 10^{18} e.v./g.

Fe(III) × 10^3	$G(H_2)$	$G(CH_2O)$	$G(CH_4)$	G(CO)	G(FeII)
0[a]	4.1	2.05	1.23	0.15	0
1.0[b]	4.0	7.35	0.38	.16	6.55
2.0	3.20	6.85	.37	.19	6.8
4.0	2.70	5.55	.29	.18	6.8
5.0	..	..	..	..	6.9
6.0	2.43	5.6	.28	.20	7.3
24	1.70	..	.21	.18	7.2
50	1.71	..	.22	.16	7.5
100	1.73	..	.23	..	7.6

[a] G(glycol) = 3.1. [b] G(glycol) = 0.15.

TABLE VI

YIELDS IN NEUTRAL METHANOL CONTAINING BENZOQUINONE (Q)

Doses *ca.* 4 × 10^{18} e.v./g.

Q × 10^3	$G(H_2)$	$G(CH_4)$	G(CO)
0.10	4.1	0.52	0.22
2.3	3.23	.25	.15
5.6	2.86	.25	.15
13.3	2.52	.25	.18
14.4	2.44	.23	.14
27.7	2.11	.21	.14

Discussion

The radical and molecular yields are collected in Table VII. These products will be formed as a result of the excitation of methanol and/or from various positive ions produced in the ionization of methanol. The two mechanisms of formation of primary species from positive ions which have been proposed for water[12,13] must be considered as possibilities with other substances. In brief, the one theory supposes that the electron leaving the ion loses its energy rapidly and returns to the parent ion to give a highly excited molecule which may dissociate into atomic and molecular fragments. The other theory assumes that the electron escapes leaving a positive ion which may dissociate. Further dissociation may occur when the electron is captured by either the solvent or a positive ion.

TABLE VII

RADICAL AND MOLECULAR YIELDS PER 100 e.v. FOR METHANOL

	Neutral	Acid
H	2.4	3.8
CH_2OH	2.7	2.5
CH_3	1.0	0.2
H_2	1.7	1.8
CH_2O	2.05	2.2
$(CH_2OH)_2$	0.2	0.2
CH_4	0.2	0.2
CO	0.15	0.16

An idea of the positive ions to be expected can be obtained from the mass spectrum of methanol vapor.[14] With 50–100 v. electrons, CH_3OH^+, CH_2OH^+, CHO^+, CH_3^+ and CH_2O^+ are observed with relative abundances 1.0, 1.5, 0.8, 0.35 and 0.1, respectively. It is unlikely that the same abundances will hold for the liquid since the solvent cage effect will tend to prevent dissociative processes, but in the absence of other information we must assume that the above ions are likely to be produced in the liquid.

On the electron return theory it can readily be imagined how all the primary products which have been observed, could be formed from excited species resulting from the neutralization of these ions. On the electron escape theory the three main products H, CH_2OH and CH_2O would result from the formation and dissociation of the two most abundant ions

$$CH_3OH \rightsquigarrow CH_2OH^+ + H + e^- \longrightarrow CH_2O + H^+ + H + e^- \quad (a)$$

$$CH_3OH \rightsquigarrow CH_3OH^+ + e^- \longrightarrow CH_2OH + H^+ + e^- \quad (b)$$

The "molecular" hydrogen, which also has an appreciable yield, may be produced initially as molecules or be formed from atoms, either by dimerization, or possibly in a "hot" atom reaction with methanol. The observation that high Fe(III) concentrations do not decrease $G_m(H_2)$, as they do in aqueous systems,[6] argues against the dimerization mechanism.

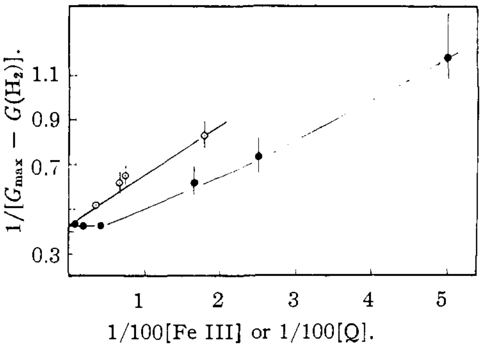

Fig. 5.—Plot of data in Tables V and VI according to equation I: ○, quinone; ●, Fe(III).

On the electron escape theory the fate of the escaping electron also must be considered. Apart from the neutralization of positive ions dissociative capture could occur in two ways

$$CH_3OH + e^- \longrightarrow CH_3O^- + H \quad (c)$$

$$CH_3OH + e^- \longrightarrow CH_3 + OH^- \quad (d)$$

Information about solvation energies in methanol is required before we can say which, if any, of these reactions is important, but (d) is interesting as a possible source of the methyl radical. However, this could not be the sole fate of the electrons if reactions (a) and (b) are responsible for the bulk of the H, CH_2OH and CH_2O, since $G(CH_3)$ is too small.

The above are the most obvious of the multitude of reactions between the primary ions, the electrons and the solvent molecules which can be formulated to give rise to the observed products. A more detailed picture must await information on such things as electron capture and ion-molecule reactions in methanol.

It is interesting to note that the effect of acid in increasing G(H) is also observed in water.[6] In methanol it is accompanied by a decrease in $G(CH_3)$. These observations suggest that the ion $CH_3OH_2^+$ in acid methanol presents an alternative reaction path and, by analogy, H_3O^+ may do similarly in water. The obvious possibility is that the ion is neutralized by electron capture and gives rise, among other things, to hydrogen atoms. If this is the case then the methyl radical would seem to be a product of the alternative capture process which occurs in neutral methanol.

We gratefully acknowledge the financial support of the U.K. Atomic Energy Authority (Research Group, Harwell).

MANCHESTER, ENGLAND

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[12] R. L. Platzman, *Radiation Research*, **2**, 1 (1955).

[13] Summarized by H. A. Dewhurst, A. H. Samuel and J. L. Magee, *ibid.*, **1**, 62 (1954).

[14] L. Friedman, F. A. Long and M. Wolfsberg, *J. Chem. Phys.*, **27**, 613 (1957).