

The method used by Rathjens and Pitzer did not involve the isolation of diammoniate at any stage. Diborane was distilled into a calorimeter containing solid ammonia. Successive portions of ammonia were melted by supplying electrical energy. The process of melting the ammonia was a slow, controlled one, requiring a good many hours.¹³ Under such conditions, it is conceivable that diborane was not converted to the diammoniate but that an intermediate species was formed.

The technique used in this investigation does not provide the control of melting that was available to Rathjens and Pitzer in their calorimeter; it required a relatively harsh treatment of the solutions involving warming to several degrees above their melting points and the use of vigorous stirring. As a result, intermediate molecular species could not be detected in freshly prepared solutions. The apparent cryoscopic constants obtained for such solutions were never below 1.17, indicating essentially complete conversion of diborane to the diammoniate. Nevertheless, it has been recognized that under sufficiently mild conditions of addition of diborane to ammonia, complete conversion to the diammoniate does not necessarily

(13) K. S. Pitzer, private communication.

take place.^{3,14,15} Comparison of the results of this investigation with those of Rathjens and Pitzer provides additional support to this interpretation of the chemical observations.

The nature of the intermediate material in solution is unknown, except that it would be a non-dissociated two boron atom molecule. It might be molecular diborane in ammonia or perhaps a single hydrogen bridge structure $\text{H}_2\text{B}-\text{H}-\text{BH}_3$



as suggested by Parry and Shore.³ This structure seems to be particularly attractive since Brown and co-workers¹⁶ have been able to provide evidence for the existence of $\text{H}_2\text{B}-\text{H}-\text{BH}_3$ and other analogous materials.



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(14) G. W. Schaeffer, M. D. Adams and F. J. Koenig, *J. Am. Chem. Soc.*, **78**, 725 (1956).

(15) A. B. Burg and G. W. Campbell, Jr., *ibid.*, **74**, 3744 (1952).

(16) H. C. Brown, P. F. Stehle and P. A. Tierney, *ibid.*, **79**, 2020 (1957).

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The γ -Radiolysis of Methanol and Methanol Solutions

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Product yields from γ -irradiated neutral methanol agree with those obtained by Meshitsuka and Burton. It is suggested that trace impurities which scavenge a reactive precursor to hydrogen are responsible for the lower yields which have been reported. The variation of yields with temperature, acid and various solutes has been investigated. The presence of two precursors to hydrogen is indicated by the results and a reasonable interpretation is obtained by assuming that one is the H atom and the other an electron.

The major products from the γ -radiolysis of liquid methanol are hydrogen, formaldehyde, ethylene glycol and small amounts of methane and carbon monoxide. There is still a considerable lack of agreement among the various investigators¹⁻⁴ on the 100 e.v. yields (G) of these products. Values of $G(\text{H}_2)$ have been reported from 4.0 to 5.4, $G(\text{CH}_2\text{O})$ from 1.3 to 2.2, $G(\text{glycol})$ from 2.9 to 3.6 and $G(\text{CH}_4)$ from 0.2 to 1.2. It seems probable that, as in the radiation chemistry of water, trace amounts of impurities can affect the yields by acting as radical and atom scavengers.

In extending earlier work³ we have observed a slight increase in $G(\text{H}_2)$ with increasing time of irradiation, which continued on prolonged irradiation but ultimately reached a constant value. Since none of the products affect $G(\text{H}_2)$, we were led to suspect the presence of impurities which were consumed during irradiation. We have therefore investigated the purification procedure and in the

(1) G. Meshitsuka and M. Burton, *Radiation Research*, **8**, 285 (1958).

(2) W. R. McDonnell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955).

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

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

light of this repeated and extended the earlier work.

Experimental

Materials.—The purification of methanol is described subsequently. Ferric chloride hexahydrate, 2,4-dinitrophenylhydrazine, hydrochloric, periodic and sulfuric acids, benzene, naphthalene and anthracene were of analytical reagent grade and were used without further purification. Benzoquinone was subjected to two sublimations from room temperature to liquid nitrogen. Biphenyl was recrystallized from methanol. Chromotropic acid was a specially purified grade for formaldehyde determination. A 30% solution of methyl borate was obtained by refluxing boric anhydride with methanol and collecting the middle cut of the azeotropic mixture.

Irradiations.—These were done on 50 or 25 cc. samples contained in 4 cm. diameter tubes fitted with a stopcock attached by a cone and socket. Deaeration was accomplished by short periods of pumping at room temperature after equilibrating gas and liquid with a vibro-shaker. Two Co^{60} sources were used, giving maximum dose rates in the vessels of 2×10^{15} and 3×10^{16} e.v. cc.⁻¹ min.⁻¹. Doses were calculated from calibrations using the ferrous sulfate dosimeter assuming the energies absorbed proportional to the liquid densities and $G(\text{Fe}^{3+}) = 15.6$.

Analyses.—Hydrogen and carbon monoxide were measured by first equilibrating the irradiated liquid with the gas phase and then expanding the gas from the vessel cooled in Dry Ice through a liquid nitrogen trap into the sample bulb of a mass spectrometer, thus eliminating the collection procedure used previously.³ This technique gave lower meth-

ane yields than the collection method, due to the fact that methane was entrained with the methanol in the trap. Hence for methane a Dry Ice trap was used first and, after the expansion into the sample bulb, this was replaced by liquid nitrogen which removed traces of methanol vapor. The spectrometer was calibrated, using gases of known compositions and pressures in the range of those obtained in the irradiations.

Formaldehyde was determined with chromotropic acid⁵ and glycol with periodic acid.⁶ In methanol-aromatic mixtures it was necessary to dilute with water and extract the aromatic with low-boiling benzene-free petroleum ether before determining formaldehyde. The glycol reaction is very pH sensitive and methanol containing acid or alkali was first neutralized to methyl red at the aqueous stage just prior to adding the periodic acid.

The disappearance of Fe(III), benzoquinone and duroquinone during irradiation was followed spectrophotometrically using a reaction vessel fitted with a 1 cm. quartz cell into which the liquids could be poured after successive irradiations on the same sample.

Results

Purification of Methanol.—In the previous work,³ the methanol was purified by refluxing with dinitrophenylhydrazine (DNP) and hydrochloric acid, to remove ketonic impurities, and then fractionated from this solution. As mentioned above, such a preparation gives increasing $G(\text{H}_2)$ with increasing dose and points to the presence of substances which react with the precursors of hydrogen gas. In view of the lack of agreement between various investigations it seemed worth while to examine the effects of possible impurities and of other purification procedures. Values of $G(\text{H}_2)$ in various conditions are given in Table I.

TABLE I
 $G(\text{H}_2)$ for aerated methanol, doses 2×10^8 e.v. cc.⁻¹, temperature 19°

Expt.	Conditions	$G(\text{H}_2)$
1	Methanol fractionated from DNP + HCl (sample A)	4.0
2	Sample A subjected to prolonged irradiation (sample B)	5.4
3	B + 10^{-2} M methyl borate	5.4
4	B + 3 mm. oxygen	5.4
5	Methanol fractionated from NaBH ₄	5.4
6	A refractionated	5.3
7	Methanol fractionated from DNP + H ₂ SO ₄ (sample C)	5.4
8	C + HCl fractionated	4.3
9	C + 2×10^{-5} M methyl iodide	5.0
10	C + 2.16×10^{-6} M anthracene	5.0
11	C + 5×10^{-4} M naphthalene	4.17
12	C + 6.8×10^{-4} M biphenyl	4.1
13	C + 10^{-4} M acetone	4.7
14	C + 1.9×10^{-5} M benzoquinone	4.5
15	C + 3.6×10^{-4} M ferric chloride	4.8

It seems likely that the increase in yield of 4.0 to 5.4 obtained after prolonged irradiation (expt. 2) is due to the consumption of an adventitious impurity. Possible impurities are methyl borate⁶ and oxygen, but neither of these at concentrations well in excess of those expected to be present, seems to be effective (expts. 3, 4). Removal of carbonyl compounds with sodium borohydride (expt. 5) gives the higher yield and suggests that

(5) C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem.*, **22**, 720 (1956).

(6) R. P. Porter, *J. Phys. Chem.*, **61**, 1260 (1957).

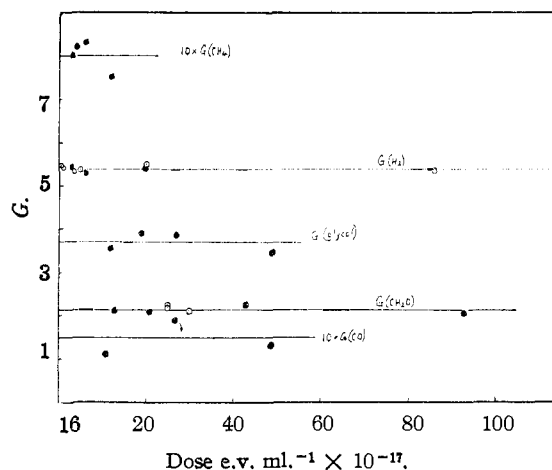


Fig. 1.—Yields of products from neutral methanol. open circles are at dose rate 2×10^{16} e.v. cc.⁻¹ min.⁻¹; others at 3×10^{16} e.v. cc.⁻¹ min.⁻¹.

the effective impurity originates in the DNP + HCl. This is confirmed by a second fractionation (expt. 6). The higher yield using H₂SO₄ + DNP (expt. 7) and the fact that fractionation in the presence of HCl decreases the yield (expt. 8) points to HCl as the source of the impurity. It seems likely that the latter is methyl chloride and the mass spectrum of the methanol Sample A did show small peaks consistent with this, although there was not sufficient to identify with certainty.

The sensitivity of $G(\text{H}_2)$ to small concentrations of solute is illustrated by expts. 9–15 in Table I. Thus 20 μM methyl iodide, which might be expected to behave similarly to methyl chloride, produces a measurable decrease, and only 2 μM anthracene is enough to give the same effect. Acetone, a common impurity in methanol, is slightly less effective but might account for some of the low yields which have been reported. If, as has been concluded from previous work,⁸ the major part of the hydrogen arises by hydrogen atoms abstracting from methanol, it is remarkable that such low concentrations of solutes can compete effectively with methanol for these hydrogen atoms.

From these experiments we conclude that the higher hydrogen yields reported previously¹ are probably correct.

For the work reported below the methanol was obtained by first refluxing analytical grade methanol for about 12 hr., to remove the bulk of the formaldehyde, then fractionating in a 50 plate column and retaining the middle 80%. This was refluxed for a further 12 hr. with 5 g. DNP + 2 g. H₂SO₄ per l. and again fractionated, the middle 60% being retained for the experiments. The liquid was protected throughout by drying tubes of silica gel. We have repeated some of the previous work using this methanol and also extended it to Dry Ice temperature.

Product Yields.—These are shown for pure neutral methanol as a function of dose in Fig. 1. Mean values are collected in Table II and are very similar to those first reported by Meshitsuka and Burton.¹ There is a reasonable numerical balance between oxidation and reduction products,

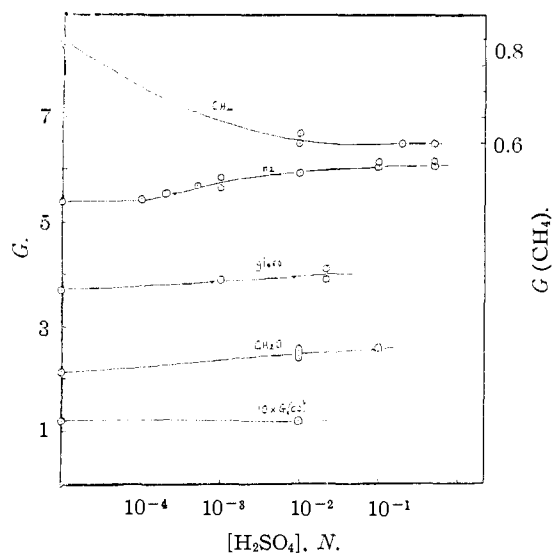


Fig. 2.—Variation of yields from methanol with acid concentration: doses $5\text{--}50 \times 10^{17}$ e.v. cc.⁻¹, at 3×10^{16} e.v. cc.⁻¹ min.⁻¹.

and from the mass balance we calculate $G(\text{H}_2\text{O}) = 0.8$, $G(-\text{CH}_3\text{OH}) = 13.5$.

Adams and Baxendale³ and Lichtin⁴ reported that some of the product yields were changed on adding sulfuric acid to the methanol. We have confirmed this and, as shown in Fig. 2, have found that the yields became independent of acid concentration above about $10^{-2}N$. These limiting yields are given in Table II. The main changes are in $G(\text{H}_2)$, $G(\text{CH}_4)$ and $G(\text{CH}_2\text{O})$, whereas $G(\text{CO})$ is unaffected and the slight increase in $G(\text{glycol})$ is not outside possible experimental error. On the other hand, the addition of alkali in the form of sodium methoxide gives yields which are within experimental error the same as those in neutral methanol.

TABLE II
YIELDS FROM PURE METHANOL

	$G(\text{H}_2)$	$G(\text{CH}_2\text{O})$	$G(\text{glycol})$	$G(\text{CH}_4)$	$G(\text{CO})$
Neutral 19°	5.40	2.15	3.7	0.80	0.15
Above $10^{-2} N \text{H}_2\text{SO}_4$					
19°	6.05	2.55	3.8	.60	.12
$10^{-2} N \text{CH}_3\text{ONa}^a$ 19°	5.50	2.05	3.9	.87	.11
Neutral ^b -78°	4.15	0.65	4.0	.45	.13
$10^{-2} N \text{H}_2\text{SO}_4^c$ -78°	5.70	2.53	3.9	.40	.12
$3 \times 10^{-2} N \text{H}_2\text{SO}_4^d$					
-78°	5.90	2.55	3.8	.42	..

^a $G(\text{H}_2)$ is the mean of three experiments which agree to ± 0.1 over a dose range $1\text{--}5 \times 10^{17}$ e.v. cc.⁻¹. The rest are single determinations in the same dose-range. ^b $G(\text{H}_2)$ is the mean of 4 measurements agreeing to ± 0.1 , $G(\text{CH}_2\text{O})$ mean of 3 agreeing to ± 0.03 , $G(\text{glycol})$ mean of 3 agreeing to ± 0.3 , $G(\text{CH}_4)$ mean of 2 agreeing to 0.05 and $G(\text{CO})$ a single measurement. Doses as in ^a. ^c $G(\text{H}_2)$ and $G(\text{CH}_2\text{O})$ means of 3 measurements, $G(\text{glycol})$ of 2, with deviations as in ^b. $G(\text{CH}_4)$ and $G(\text{CO})$ are from a single experiment. ^d From one experiment only.

It has been reported^{1,4} that small amounts of water also affect $G(\text{H}_2)$. We found no differences with the methanol prepared as above either on drying by a molecular sieve (Union Carbide 5A) or on adding 3% water.

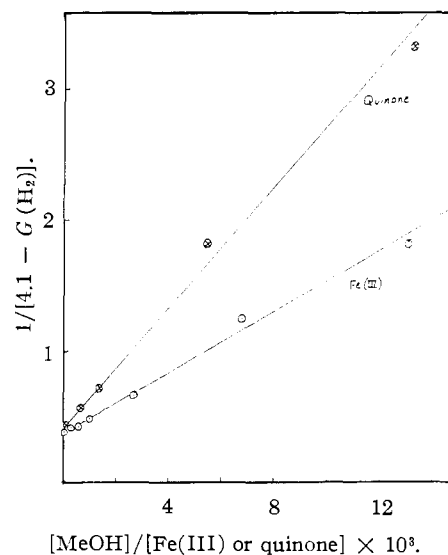
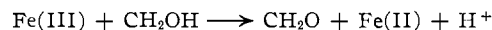
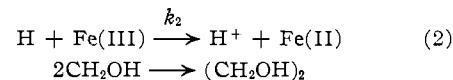
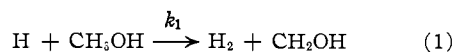


Fig. 3.—Plot of data in Table III using $G_{\text{max}} = 4.1$.

Decreasing the temperature to -78° has a marked effect on $G(\text{H}_2)$, $G(\text{CH}_2\text{O})$ and $G(\text{CH}_4)$ but leaves $G(\text{glycol})$ and $G(\text{CO})$ unchanged (Table II). $G(\text{H}_2)$ and $G(\text{CH}_2\text{O})$ however recover almost to the 19° values on adding acid.

Radical Yields.—Previous work^{3,7,8} has shown that oxidizing agents such as Fe(III) and benzoquinone can be used as radical scavengers and that the extent of reduction is a measure of the radical yield $G(\text{R})$. In the case of methanol $G(\text{R}) = 6.3 \pm 0.1$ has been reported.^{3,7} We have confirmed this value, using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, benzoquinone and duroquinone as scavengers.

Effect of Fe(III) and Benzoquinone $G(\text{H}_2)$.—The presence of these solutes has been shown³ to decrease $G(\text{H}_2)$ and $G(\text{glycol})$ while at the same time increasing $G(\text{CH}_2\text{O})$. This is attributed to the reactions:



At sufficiently high scavenger concentrations all H reacts in (2) and then $G(\text{H}_2)$ is a measure of the hydrogen produced either as molecules or by precursors which do not react with the scavenger. This yield has been called the molecular yield $G_m(\text{H}_2)$ so that on the above interpretation, the maximum yield obtained in the absence of scavengers is given by

$$G_{\text{max}} = G_m(\text{H}_2) + G(\text{H})$$

Reactions 1 and 2 should give the relationship

$$1/[G_{\text{max}} - G(\text{H}_2)] = [1 + k_1(\text{MeOH})/k_2(\text{Fe(III)})]/G(\text{H})$$

Adams and Baxendale³ found reasonable agreement with this equation, using their lower value of $G(\text{H}_2)$ for pure methanol, *viz.*: $G_{\text{max}} = 4.1$.

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

(8) E. A. Chernick, F. S. Dainton, E. Collinson and G. M. Meaburn, *Proc. Chem. Soc. (London)*, 54 (1958).

TABLE III
EFFECT OF FERRIC CHLORIDE AND BENZOQUINONE ON HYDROGEN YIELDS FROM METHANOL AT 19°
At 0.296 M ferric chloride $G(\text{CH}_4) = 0.22$

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ mM	0.036	0.362	1.88	3.62	9.05	23.6	40	296
$G(\text{H}_2)$	5.30	4.80	3.55	3.30	2.60	2.05	1.78	1.50
Benzoquinone mM	0.0185	0.185	4.50	17.9	35.6	179		
$G(\text{H}_2)$	4.45	3.80	3.55	2.70	2.35	1.75		

We have repeated the work with the results given in Table III. However, using the value $G_{\text{max}} = 5.4$, the equation does not fit the observations and the deviations are in the sense that the effect of Fe(III) or benzoquinone falls off more rapidly with concentration than the equation predicts. This is in line with the sensitivity of $G(\text{H}_2)$ to low solute concentrations shown in Table I and suggests that there may be two precursors to the hydrogen having different reactivities with the solutes.

If we plot the results in Table III, using $G_{\text{max}} = 4.1$ as was done by Adams and Baxendale, then they fit the equation reasonably well as shown in Fig. 3. Both Fe(III) and benzoquinone data extrapolate to $G_{\text{m}}(\text{H}_2) = 1.6$, which agrees with the value obtained by Adams and Baxendale for the "molecular" yield. From this we infer that a more reactive precursor is removed at low solute concentrations and $G(\text{H}_2)$ is reduced readily from 5.4 to 4.1, *i.e.*, this precursor has a yield of 1.3. The less reactive precursor with a yield of 2.5 then reacts according to the above equation. The frequently observed $G(\text{H}_2) \sim 4$ would then be explained by the presence of amounts of impurities sufficient to remove the more reactive precursor but insufficient to interfere with the less reactive one.

It will be noted from Table III that $G(\text{CH}_4)$ is also decreased by high Fe(III) concentrations from 0.8 to 0.22. This confirms that most of the methane has a reactive precursor—possibly the radical CH_3 as previously suggested.³

Methanol-Methyl Iodide Mixtures.—Table IV shows the effect of methyl iodide on $G(\text{H}_2)$ and $G(\text{CH}_4)$ over a bigger concentration range. The decrease in $G(\text{H}_2)$ is accompanied by an increase in $G(\text{CH}_4)$ and the high value of the latter beyond $10^{-3}M$ methyl iodide indicates the presence of a chain reaction. A similar effect was observed by Schuler⁹ in cyclohexane-methyl iodide mixtures. It is reasonable to suppose that methyl chloride would behave similarly and if, as suggested, it was present as an impurity in the methanol used by Adams and Baxendale,³ it would account for the higher $G(\text{CH}_4)$ and lower $G(\text{H}_2)$ reported by them.

TABLE IV
EFFECT OF METHYL IODIDE ON $G(\text{H}_2)$ AND $G(\text{CH}_4)$ FROM METHANOL

$[\text{CH}_3\text{I}]$ μM	0	3.4	17	85	8500	85,000
$G(\text{H}_2)$	5.4	5.3	4.95	4.45	3.05	1.87
$G(\text{CH}_4)$	0.8	1.0	1.45	2.05	10.0	380

Methanol-Benzene Mixtures.—Values of $G(\text{H}_2)$ and $G(\text{CH}_2\text{O})$ obtained at 19 and -78° are shown as a function of volume composition in Fig. 6. If the benzene acts merely as a diluent, the yields

should be linear with composition since, to this accuracy, volume fraction and electron fraction are numerically the same. This appears to be the case for $G(\text{CH}_2\text{O})$, hence we conclude that benzene does not interact with the precursor of formaldehyde.

$G(\text{H}_2)$ is much more sensitive to small amounts of benzene and the curve in Fig. 4 resembles that

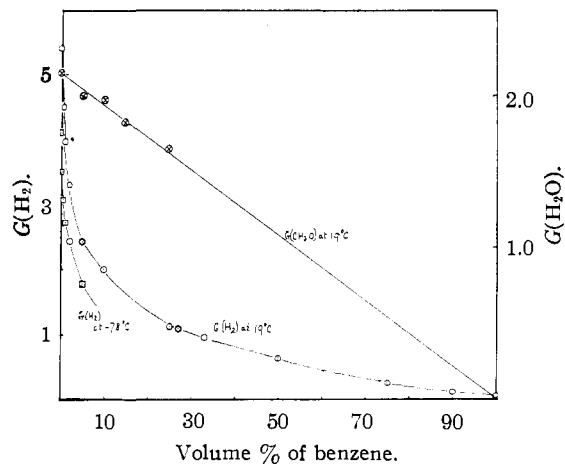


Fig. 4.—Variation of $G(\text{H}_2)$ with composition for methanol-benzene mixtures. Yields calculated in terms of energy absorbed by mixture.

obtained by Burton, *et al.*,¹⁰ for cyclohexane-benzene mixtures. If benzene competes with methanol for hydrogen atoms in reactions analogous to (1) and (2) above, then the hydrogen yields should follow the equation derived from these, providing we use yields calculated in terms of the energy absorbed in the methanol only, *i.e.*, $G_{\text{M}}(\text{H}_2)$ in the equation

$$\text{obsd. } G(\text{H}_2) = E_{\text{M}}G_{\text{M}}(\text{H}_2) + E_{\text{B}}G_{\text{B}}(\text{H}_2)$$

where E is electron fraction and the subscripts refer to methanol and benzene. $G_{\text{M}}(\text{H}_2)$ have been calculated using $G_{\text{B}}(\text{H}_2) = 0.035$ ¹⁰ and are shown in Fig. 5.

Plots of $1/[G_{\text{max}} - G_{\text{M}}(\text{H}_2)]$ vs. $[\text{CH}_3\text{OH}]/[\text{C}_6\text{H}_6]$ are shown in Fig. 6 where $G_{\text{max}} = 5.4$ and 4.15 have been used for 19 and -78° , respectively. These are reasonably linear up to about 10% benzene (*i.e.*, $\sim 1.5 M$) at 19° and over the whole range of solubility at -78° . Extrapolation of the lines gives $G_{\text{m}}(\text{H}_2) = 1.7$ in both cases, which is close to the value obtained above using Fe(III) and benzoquinone. If the precursor is H, then the plots give relative rates of reaction with benzene and methanol of 140 and 330 at 19° and -78° , *i.e.*, the methanol reaction has an activation energy of ~ 1 kcal. more than the benzene reaction.

At benzene concentrations $>10\%$, $G_{\text{M}}(\text{H}_2)$ is lower than predicted by the equation and from the

(9) R. H. Schuler, *J. Phys. Chem.*, **61**, 1472 (1957).

(10) J. P. Manion and M. Burton, *ibid.*, **58**, 421 (1954).

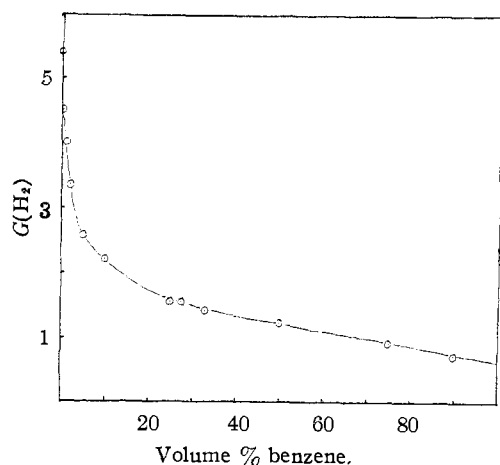


Fig. 5.—Variation of hydrogen yield with composition for methanol-benzene mixtures. $G_M(H_2)$ is the yield calculated in terms of the energy absorbed in methanol only, *i.e.*, the observed $G(H_2)$ is corrected for energy absorbed by and H_2 arising from benzene.

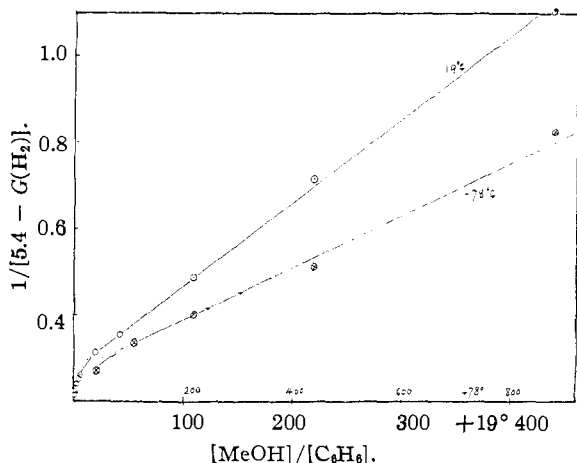


Fig. 6.—Plot of data in Fig. 7 according to equation from competition kinetics

curve in Fig. 5 would appear to extrapolate to $G_M(H_2) = 0.6$ at very high benzene concentrations. At these concentrations the environment of the methanol molecule will be mainly benzene and the difference between 0.6 and 1.7 presumably derives from this. Thus, if some "molecular" hydrogen is produced in a process requiring the co-operation of several methanol molecules or if "hot" H atoms, not normally scavenged by low benzene concentrations, contribute to the "molecular" hydrogen, then such a difference would be expected. This is in contrast to $G(CH_4)$ which was found to decrease to 0.2 at high Fe(III) concentrations and maintains this value even in 90% benzene.

Methanol Solutions of Other Aromatics.—The effects of naphthalene, biphenyl and anthracene on $G(H_2)$ and $G(CH_2O)$ are shown in Table V and Fig. 7. As with benzene $G(CH_2O)$ is unchanged, but $G(H_2)$ shows a very steep fall at the lower concentrations and then decreases more gradually. The expanded curve for anthracene in Fig. 7 shows clearly that the decrease occurs in two well defined steps, the first being to $G(H_2) \sim$

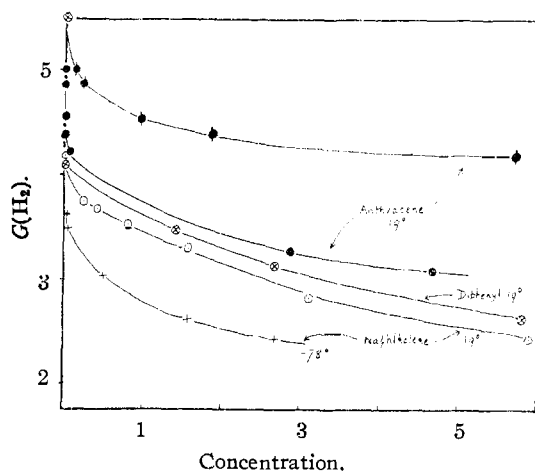


Fig. 7.—Effect of diphenyl, naphthalene and anthracene on $G(H_2)$ from methanol. Abscissa are $M \times 10^{-2}$ for diphenyl and naphthalene, $M \times 10^{-3}$ for the lower anthracene curve and $M \times 10^{-5}$ for upper curve.

4.1. This phenomenon was not observed with benzene, although a similar but not so pronounced effect was found above for Fe(III) and benzoquinone. It was interpreted in terms of the successive reactions of two precursors of hydrogen, the first decreasing $G(H_2)$ to 4.1.

TABLE V
EFFECT OF AROMATICS ON $G(H_2)$ AND $G(CH_2O)$ FROM METHANOL
Doses ca. 2×10^{18} e.v. cc.⁻¹ at 19°, 2×10^{17} e.v. cc.⁻¹ at -78°

Solute	Temp., °C.	M	$G(CH_2O)$	$G(H_2)$
....	19	0.00	2.15	5.40
Naphthalene	19	.51	1.98, 2.03, 2.20	..
Biphenyl	19	.32	2.3, 2.1	1.65
Anthracene	19	.0047	2.25, 2.20	3.07
....	-78	.00	0.65	4.15
Benzene	-78	.20	.70	2.4
Naphthalene	-78	.027	.65	2.4

Plotting the data using $G_{max} = 4.1$ as before, again gives reasonable lines as shown in Fig. 8 and again the extrapolation to the "molecular" yield gives $G_m(H_2) = 1.7$. The lines in Fig. 8 show the relative rates for the reaction of diphenyl, naphthalene and anthracene with this precursor to be 600, 940 and 4000, respectively. It is interesting to note that the relative rates follow the sequence found by Levy and Szwarc¹¹ for reactions of these aromatics with methyl radicals, and a similar linear relationship is found between the aromatic singlet-triplet excitation energies and the logarithms of the rates.

For the more reactive precursor we have data for anthracene only and, assuming again that it is competed for by anthracene and methanol, the rate constant ratio is about 5×10^6 . The high value reflects the fact that as little as $2 \mu M$ anthracene produces a detectable fall in $G(H_2)$ from 5.4 to 5.0.

We also find, as shown in Table VI, that $G(H_2)$ in this range of anthracene concentration is very sensitive to acid. Thus $3 \times 10^{-5} N H_2SO_4$ is

(11) M. Szwarc and M. Levy, *J. Am. Chem. Soc.*, **77**, 4468 (1955).

TABLE VI

EFFECT OF SULFURIC ACID ON $G(\text{H}_2)$ FROM METHANOL CONTAINING $5 \mu\text{M}$ ANTHRACENE^a

[H ⁺] μM	0	3.2	32	3200
$G(\text{H}_2)$	4.70	5.05	5.30	5.70
$G_0(\text{H}_2)$	5.40	5.40	5.40	5.90

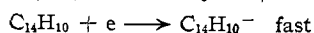
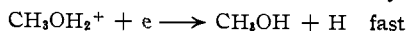
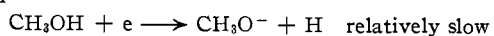
^a $G_0(\text{H}_2)$ is the value of $G(\text{H}_2)$ obtained in the absence of anthracene. At 1.6 mM CH_3ONa $G(\text{H}_2) = 4.35$, $G_0(\text{H}_2) = 5.4$.

sufficient to increase $G(\text{H}_2)$ from 4.7 to 5.3, although this amount of acid does not change $G(\text{H}_2)$ from pure methanol. From this we infer that CH_3OH_2^+ competes efficiently with anthracene for the precursor and hence that this precursor is probably not the hydrogen atom since it is unlikely that there would be much difference in reactivity toward hydrogen atoms between CH_3OH^+ and methanol itself.

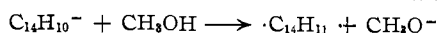
Discussion

Precursors of Hydrogen.—The observations on the effects of Fe(III), benzoquinone and the aromatics (except benzene) given above, all point to the existence of two precursors to the hydrogen produced from methanol. For the more reactive of these we have discounted the possibility that it is the hydrogen atom. Another alternative is that it is an excited state of methanol which would normally dissociate to give hydrogen atoms but may be de-excited by the above solutes. This is a process which has been invoked to account for the "protective effect" of aromatic compounds.^{10,12} However, such an excited state would need to be long-lived to account for the quenching efficiency of anthracene at such low concentrations, and there is as yet no spectroscopic evidence for such a state.

It seems more likely, in view of the effect of acid described above, that the precursor is an electron, presumably solvated by methanol, which is competed for



The first two reactions will lead to H_2 production but the anion formed from anthracene will react



This is analogous to the reactions observed between aromatic anions and water.¹³ Fe(III), benzoquinone and the other aromatics will capture the electron in the same way as anthracene, but we have seen that benzene is anomalous in this respect. Now the efficiency of the capture process will be determined to a large extent by the electron affinities of the acceptors, and Hush and Pople¹⁴ quote -0.54 , $+0.41$, $+0.65$ and $+1.19$ e.v., respectively, for benzene, biphenyl, naphthalene and anthracene in the gas phase. These would be modified to some extent in solution but the general trend is likely to remain the same, as is instanced

(12) M. Burton, J. Chang, S. Lipsky and M. P. Reddy, *Radiation Research*, **8**, 203 (1958).

(13) D. E. Paul, D. Lipkin and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

(14) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

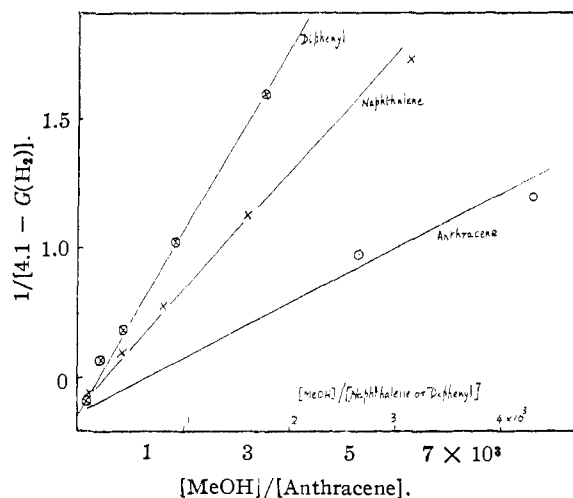
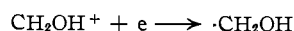
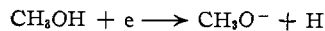


Fig. 8.—Plot of data at 19° in Fig. 9 according to equation from competition kinetics.

by the difficulty of preparing solutions of the benzene anion compared with the others. Thus the anomalous behavior of benzene would be accounted for by the inefficiency of electron capture compared with methanol. If, as we suggest, the second less reactive precursor is the hydrogen atom, this would mean that in the case of benzene, the variation of $G(\text{H}_2)$ with benzene concentration should be accounted for in terms of competition for one precursor, as is in fact observed.

The observations that in pure methanol $G(\text{H}_2)$ is increased from 5.4 to 6.05 by addition of acid again suggests that electrons are the precursors to this extra hydrogen, but unlike the electrons discussed above, they do not lead to H_2 production in the absence of acid. It will be noted that both at 19 and -78° the increase in $G(\text{H}_2)$ is accompanied by an almost equivalent increase in $G(\text{CH}_2\text{O})$, *i.e.*, the electrons either remove formaldehyde or prevent its formation. A possible explanation of these observations is that these electrons are normally captured by the ion CH_2OH^+ , *i.e.*, the protonated form of formaldehyde, so that the following reactions compete

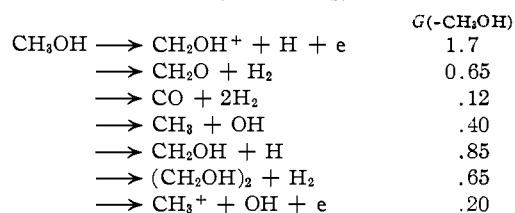


The ion CH_2OH^+ is known to be a major component in the mass spectrum of methanol and presumably will be present in the ionization spurs but will lose its proton fairly rapidly to methanol. This implies that we are concerned here with reactions in the spurs before such a transfer could occur and the relatively high concentrations of acid required to produce an effect support this suggestion.

Moreover, the decreased mobility of the electron at low temperature¹⁵ would allow more recombination with CH_2OH^+ in the spur. This explains the observations at -78° where $G(\text{CH}_2\text{O})$ and $G(\text{H}_2)$ are much lower but can be increased to the room temperature values by the addition of acid.

(15) O. H. Leblanc, *J. Chem. Phys.*, **30**, 1445 (1959).

Yields of Intermediates.—The product yields in various experimental conditions can be reasonably well accounted for in terms of intermediates formed from methanol according to the equations given below. The equations are chosen to express yields and do not necessarily represent the mechanism of formation of the intermediates.



We assume that CH_3^+ reacts rapidly with methanol and is responsible for the unscavengeable methane, $G_m(\text{CH}_4)$.

In acid solution all the electrons combine with CH_3OH_2^+ as described above and we have

$$G(\text{H}_2) = G(\text{e}) + G(\text{H}) + G_m(\text{H}_2) = 6.0$$

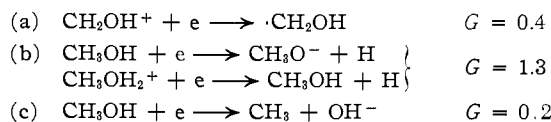
$$G(\text{CH}_3) = G(\text{CH}_2) + G(\text{CH}_3^+) = 0.6$$

$$G(\text{CO}) = 0.12, G(\text{CH}_2\text{O}) = G_m(\text{CH}_2\text{O}) + G(\text{CH}_2\text{OH}^+) + G(\text{CH}_3^+) = 2.55$$

$$G(\text{R}) = G(\text{e}) + G(\text{H}) + G(\text{CH}_3) + G(\text{CH}_2\text{OH}) + G(\text{OH}) = 6.3$$

$$G(\text{glycol}) = 1/2 G(\text{R}) + G_m(\text{glycol}) = 3.8$$

in agreement with the experimental results in Table II. In neutral solution $G(\text{H}_2)$ and $G(\text{CH}_2\text{O})$ are lower, $G(\text{CH}_4)$ is higher and quantitatively the change in $G(\text{H}_2)$ is balanced by that in $G(\text{CH}_4) + G(\text{CH}_2\text{O})$. The yields in Table II are obtained if the fate of the electrons is



We identify (a) as a reaction in the spurs and the electrons in (b) and (c) as those which are scavenged by low concentrations of solutes thus decreasing $G(\text{H}_2)$ from 5.4 to 4.1. Higher solute concentrations reduce $G(\text{H}_2)$ to $G_m(\text{H}_2)$ by scavenging H atoms.

In neutral methanol at -78° , CH_2OH^+ captures all the electrons because of their decreased mobility and/or a favorable activation energy thus decreasing $G(\text{CH}_2\text{O})$ to 0.6 and $G(\text{H}_2)$ to 4.2. In acid at -78° CH_3OH_2^+ captures all the electrons thus bringing the yields up to those in acid at 19° .

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH, SALT LAKE CITY, UTAH]

The Dependence of Geminal Proton Spin-Spin Coupling Constants on Electron Delocalization in Molecules

BY MICHAEL BARFIELD AND DAVID M. GRANT

RECEIVED MAY 22, 1961

Geminal coupling constants for a number of substituted methanes have been measured *via* deuterium substitution. In compounds with substituents containing π electrons, larger geminal coupling constants were found than predicted by existing theoretical and experimental findings for the HCH angle. This increase in the spin-spin coupling is explained in terms of hyperconjugation of the adjacent π electrons with those of the geminal hydrogens in either a methyl or a methylene group.

Introduction

Using the Hamiltonian given by Ramsey¹ for spin-spin interaction, Karplus and co-workers²⁻⁴ with a valence bond approach calculated the proton spin-spin coupling constant for methene. This work was extended by Gutowsky, Karplus and Grant⁵ to include the HCH angular dependence of the geminal coupling by considering the methylene group as a four electron valence bond system. The effect of other substituents upon the geminal coupling constant was not considered.

Banwell and Sheppard⁶ in studies of substituted vinyl compounds found significant negative deviations from the predicted values of Gutowsky, *et al.*⁵ They concluded that the decrease was due

to the withdrawal of electrons from the methylene group by electronegative substituents.

This work presents a class of compounds having geminal coupling constants which are larger than the values predicted by a four electron calculation.

Experimental

Equipment.—The proton magnetic resonance spectra were obtained with a Varian Associates V-4311 high resolution spectrometer operating at a frequency of 60 Mc./sec. The instrument was equipped with standard accessories such as a superstabilizer, homogeneity controls, etc. The reported coupling constants and shifts were determined by the sideband technique and represent the average values obtained from as many as ten separate measurements.

Ethyl Cyanomonodeuterioacetate.—By refluxing ethyl cyanoacetate with heavy water containing a small amount of HCl to catalyze the exchange, we were able to synthesize ethyl cyanomonodeuterioacetate. No attempt was made to separate this product from either the parent or the corresponding di-deuterio compound which undoubtedly was formed during the reaction. Other impurities and by-products were, of course, separated.

The proton magnetic resonance spectra of the mono-substituted material consists of a deuterium coupled 1:1:1 triplet shifted 0.81 ± 0.07 c.p.s. upfield from the single peak

- (1) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).
- (2) M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957).
- (3) M. Karplus and D. H. Anderson, *ibid.*, **30**, 6 (1959).
- (4) M. Karplus, *ibid.*, **30**, 11 (1959).
- (5) H. S. Gutowsky, M. Karplus and D. M. Grant, *ibid.*, **31**, 1278 (1959).
- (6) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).