THE RADIOLYSIS OF ETHANOL

I. VAPOR PHASE[1]

J. M. RAMARADHYA[2] AND G. R. FREEMAN

ABSTRACT

The alpha radiolysis of ethanol vapor at 108° C produced hydrogen as the major single product, with smaller amounts of methane, carbon monoxide, ethylene, ethane, acetaldehyde, formaldehyde, water, 2,3-butanediol, 1,2-propanediol, propanol, and butanol. The initial yield of hydrogen was $G(H_2) = 8.9 \pm 0.4$, which is much higher than the values reported for the liquid phase $(G(H_2) \approx 4)$.

A mechanism is proposed to account for the formation of the products. However, the observed value of $G(H_2O) = 5.4$ is over four times larger than can be explained by the mechanism.

There is a good material balance in the observed reaction products, which indicates that little polymerization occurred during the radiolysis. This is in marked contrast with the vapor phase radiolysis of cyclohexane.

INTRODUCTION

Although the radiolysis of liquid ethanol has been studied using helium ions (1, 2) and Co[60] gamma rays (3), very little attention has been paid to the vapor phase radiolysis of ethanol. In the liquid phase radiolysis of ethanol, the gaseous products were hydrogen, carbon monoxide, methane, ethylene, and ethane and the liquid products were formaldehyde, acetaldehyde, and vicinal glycols.

One previous study of ethanol vapor by cathode-ray bombardment has been reported by McLennan and Patrick (4). The products reported were hydrogen, carbon monoxide, carbon dioxide, methane, ethane, formaldehyde, and acetaldehyde. In this paper, an investigation of the radiolysis of ethanol vapor by Po[210] alpha particles is described.

EXPERIMENTAL

The apparatus and the general experimental technique used in this investigation are similar to those described in an earlier paper (5).

The ethanol was from Reliance Chemical Ltd., containing about 0.11 mole% water. Three and one-half grams of sodium was dissolved in 500 ml of ethanol and 14 g of diethyl phthalate was added to the solution (6). This solution was refluxed for 2 hours and was distilled in a system protected from moist air by passing dry hydrogen through it. The hydrogen was dried by passing it through a trap containing silica gel, immersed in liquid nitrogen. Only the middle one-third of the distillate was retained. After the purification the ethanol contained only 0.005 mole% water.

The purified ethanol was degassed and stored under vacuum in a reservoir. Prior to irradiation, 1.6 ml of the ethanol was distilled into a calibrated tube, where its volume was accurately measured at 0° C, and then volatilized into the reaction chamber.

The reaction chamber was a 1-liter bulb, heated to 108° C, containing a nominally 100-mc Po[210] source (5). The polonium source was calibrated by Fricke dosimetry, using $G(Fe^{+++}) = 5.5$ (5). All the energy of the alpha particles was absorbed by the ethanol vapor during an experiment.

The products of the ethanol vapor radiolysis were analyzed by low-temperature distillation and by gas chromatography. The fraction of gaseous products that was volatile

at $-196°$ C consisted of hydrogen, carbon monoxide, and methane. It was collected and measured in a McLeod–Toepler apparatus and then analyzed on a 1-m activated charcoal column. Another gaseous fraction, noncondensable at $-112°$ C and consisting of residual methane and C_2, C_3, and trace amounts of C_4 hydrocarbons, was analyzed using a 2.5-m silica gel column. The analyses of the various liquid products were performed using 2.5-m carbowax 1500, 2.5-m didecyl phthalate, and 1-m ucon columns.

Anhydrous ethanol is very hygroscopic. Water was also a reaction product. When the yield of water was being determined, samples of unirradiated ethanol were put through the entire analytical procedure and then analyzed for water on a 2.5-m carbowax 1500 column. The differences between the blanks and the irradiated samples were used to calculate the G of water.

The acetaldehyde yield was determined polarographically (7).

The amount of formaldehyde was measured by the chromotropic acid method. Analyses were done in triplicate and three standard samples and a blank were done concurrently with the unknowns. The procedure for an individual analysis was as follows. Chromotropic acid (110 ± 1 mg) was weighed into each of seven 10-ml Erlenmeyer flasks and 0.80 ml of distilled water was added to each. Only a small portion of the chromotropic acid dissolved. Then 0.20 ml of irradiated ethanol, or of pure ethanol or standard ethanolic solution of formaldehyde, was added to the various flasks. Three different standard concentrations of formaldehyde were used to bracket the concentration in the unknowns. The solutions were then evaporated to dryness by suspending the flasks for 25 minutes in an oil bath at $110\pm2°$ C. The oil was stirred to obtain a uniform temperature for all the flasks in the bath. The flasks were then removed from the bath and allowed to cool for 3 or 4 minutes. Five milliliters of concentrated sulphuric acid was pipetted into each flask and they were then heated for 30 minutes in an oil bath at $130\pm2°$ C. After the flasks were removed from the bath and cooled, the acid solutions were transferred into 50-ml, glass-stoppered flasks. The solutions were diluted with 15.0 ml of distilled water, cooled, and their optical densities measured at 570 mμ. The temperatures and times in the analytical procedure should be kept as constant as possible and the diluted solution should not stand more than 1 hour before being measured in a spectrophotometer (the color fades). The sensitivity of the method decreases markedly if the water/ethanol ratio in the initial chromotropic acid solution decreases below 4/1. Acetaldehyde does not interfere with the analysis.

RESULTS

Pure ethanol was subjected to alpha radiation and the gaseous-product yield distribution was studied as a function of dose over the range 0.50×10^{19} ev to 3.77×10^{19} ev. The total yield of gases noncondensable at $-196°$ C, $G(-196)$, appears to be constant at 10.1 ± 0.4 over this dose range, while that of gases volatile at $-112°$ C, $G(-112)$, decreases with increasing dose.

The products that constituted the fractions volatile at $-196°$ C and $-112°$ C were measured and their G values are presented as a function of dose in Fig. 1.

The yields of methane are the combined yields obtained from the two gas fractions. The portion of the total methane, derived from the $-112°$ C fraction, increased from 21% at the lowest dose to 58% at the highest dose. However, the methane yield obtained from the gases volatile at $-196°$ C remained approximately constant with a G of 1.1 ± 0.1 except for the lowest-dose experiment.
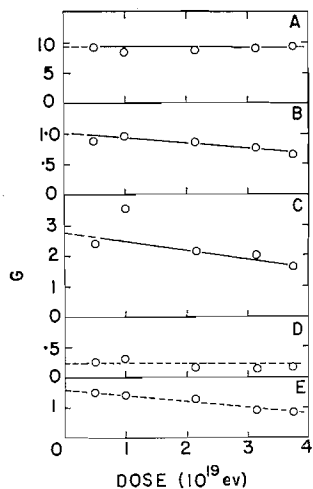
FIG. 1. G values of products volatile at $-196°$ C and $-112°$ C, as a function of dose: (A) hydrogen, (B) carbon monoxide, (C) methane, (D) ethane, (E) ethylene. The sample was 1.6 ml liquid ethanol volatilized into a 1-l. bulb at $108°$ C.

Since the amounts of liquid products were too small to be measured in these dose-function experiments, appreciably higher doses, about 8×10^{20} ev, were given to three ethanol samples and the liquid products were measured. The average yields are given in Table I along with the yields of the gaseous products obtained at the same dose. Comparison of the gaseous product yields in Table I and Fig. 1 indicates little change in the

TABLE I

G values of products obtained by irradiating ethanol vapor
(Irradiation temperature $108°$ C, dose $\approx 8 \times 10^{20}$ ev)

Product	G	Product	G
Hydrogen	7.6	Formaldehyde	0.9
Carbon monoxide	1.1	Acetaldehyde	4.5
Methane	1.66	Propanol	0.6
Ethane	0.23	Butanol	0.19
Ethylene	0.72	1,2-Propanediol	0.15
Acetylene	0.03	2,3-Butanediol	1.2
C_3 and C_4 hydrocarbons	Trace	Total glycols	1.6
Water	5.4		

dose region from about 4 to 80×10^{19} ev.

There is fair agreement between the total glycols (ucon column) and the sum of the vicinal glycols (carbowax column). Ethylene glycol, 1,3-butanediol, and 1,4-butanediol were not present in detectable amounts.

DISCUSSION

The values of $G(H_2)$ obtained in the previous investigations of liquid ethanol (1–3) are around 4. The present vapor phase radiolysis of ethanol has yielded an average value of $G(H_2) = 8.9 \pm 0.4$ in the dose region from 0.5 to 3×10^{19} ev/g. In hydrocarbon

radiolyses, the 100-ev hydrogen yields are also larger in the gas phase reactions than in the liquid phase reactions (5).

The following mechanism is suggested to account for the observed reaction products:

$$CH_3CH_2OH \ \longrightarrow \ CH_3CH_2OH^* \tag{1a}$$

$$\longrightarrow \ CH_3CH_2OH^+ + e \tag{1b}$$

$$CH_3CH_2OH^* \rightarrow CH_3CHOH + H \tag{2a}$$

$$\rightarrow CH_3 + CH_2OH \tag{2b}$$

$$CH_3CH_2OH^* \rightarrow CH_3CHO + H_2 \tag{3a}$$

$$\rightarrow CH_2O + CH_4 \tag{3b}$$

$$\rightarrow C_2H_4 + H_2O \tag{3c}$$

$$CH_3CH_2OH^+ + CH_3CH_2OH \rightarrow CH_3CH_2OH_2^+ + CH_3CHOH \tag{4}$$

$$CH_3CH_2OH_2^+ + e \rightarrow CH_3CH_2 + H_2O \tag{5a}$$

$$\rightarrow CH_3CH_2O + H_2 \tag{5b}$$

$$H + CH_3CH_2OH \rightarrow H_2 + CH_3CHOH \tag{6}$$

$$CH_3 + CH_3CH_2OH \rightarrow CH_4 + CH_3CHOH \tag{7}$$

$$C_2H_5 + CH_3CH_2OH \rightarrow C_2H_6 + CH_3CHOH \tag{8}$$

$$CH_3CH_2O + CH_3CH_2OH \rightarrow CH_3CH_2OH + CH_3CHOH \tag{9}$$

$$C_2H_4 + H \rightarrow C_2H_5 \tag{10}$$

$$CH_3 + CH_3CHOH \rightarrow CH_3\underset{\underset{\displaystyle CH_3}{|}}{CHOH} \tag{11a}$$

$$\rightarrow CH_4 + CH_3CHO \tag{11b}$$

$$C_2H_5 + CH_3CHOH \rightarrow CH_3\underset{\underset{\displaystyle C_2H_5}{|}}{CHOH} \tag{12a}$$

$$\rightarrow C_2H_6 + CH_3CHO \tag{12b}$$

$$\rightarrow C_2H_4 + C_2H_5OH \tag{12c}$$

$$2CH_3CHOH \rightarrow CH_3CHOHCHOHCH_3 \tag{13a}$$

$$\rightarrow CH_3CH_2OH + CH_3CHO \tag{13b}$$

$$CH_3CHOH + CH_2OH \rightarrow CH_3CHOHCH_2OH \tag{14a}$$

$$\rightarrow CH_3CH_2OH + CH_2O \tag{14b}$$

$$\rightarrow CH_3CHO + CH_3OH \tag{14c}$$

$$CH_3CHOH + CH_3CH_2O \rightarrow CH_3CHO + C_2H_5OH \tag{15a}$$

$$\rightarrow CH_3\underset{\underset{\displaystyle OC_2H_5}{|}}{CHOH} \rightarrow CH_3CHO + C_2H_5OH. \tag{15b}$$

Reactions [4] and [5a, b] are quite speculative but they are being considered in an investigation of the radiolysis of liquid ethanol in this laboratory. It is assumed that the positive charge on the species in reactions [4] and [5a, b] is localized on the oxygen atom.

Acetaldehyde may be formed by reactions [3a], [11b], [12b], [13b], [14c], and [15a, b]. The radicals involved in these reactions are CH_3, C_2H_5, CH_3CH_2O, CH_3CHOH, and CH_2OH. From the G values of products which require these radicals for their formation, the amounts of CH_3, C_2H_5, ($CH_3CHOH + CH_3CH_2O$), and CH_2OH radicals can be calculated to be respectively 1.1–2.3 (depending on the mechanism of formation of CO), 0.43, 12.35, and 1.05 G units. Since the amount, and therefore the concentration, of ($CH_3CHOH + CH_3CH_2O$) radicals is much greater than that of any other radical, the disproportionation reaction of these radicals (reactions [13b] and [15]) might be considered as a major source of acetaldehyde. The steady-state concentration of CH_3CH_2O will probably be much smaller than that of CH_3CHOH because of reaction [9] and because the latter radicals can be generated in many more reactions than can the former radicals (see the above mechanism).

Since the C—C bond is the weakest bond in the ethanol molecule, one might have expected a large yield of products resulting from CH_3 and CH_2OH radicals in the gas phase. In the liquid phase, there may be recombination of the CH_3 and CH_2OH radicals in the Franck–Rabinowitch cages and hence the yields of the corresponding products would be low. Low yields of methane (0.43) and formaldehyde (0.3) were experimentally observed by McDonell and Newton (1). In the gas phase, where the cage effect is not operative, larger yields of methane (1.7) and formaldehyde (0.9) were observed in the present work.

Carbon monoxide might be formed by decomposition of formaldehyde and acetaldehyde.

Propanol and butanol are probably formed by the addition of methyl and ethyl radicals to CH_3CHOH radicals (reactions [11a] and [12a]).

The vicinal glycols (2,3-butanediol and 1,2-propanediol) that were measured in the present investigation were probably formed by combination of CH_3CHOH radicals with themselves and with CH_2OH radicals (reactions [13a] and [14a]). From the relative yields of these two glycols it may readily be calculated that the yield of ethylene glycol would be negligible. If CH_2CH_2OH radicals were present in appreciable concentration during the decomposition of ethanol, the combination of CH_2CH_2OH radicals with each other and with CH_3CHOH would have led to the formation of 1,4-butanediol and 1,3-butanediol. Since these products were not produced to a measurable extent, the concentration of CH_2CH_2OH radicals was negligible in the present system.

The ethyl radicals produced by reactions [5a] and [10] might abstract (reaction [8]) or disproportionate to give ethane.

$$2C_2H_5 \rightarrow C_4H_{10} \qquad\qquad [16a]$$
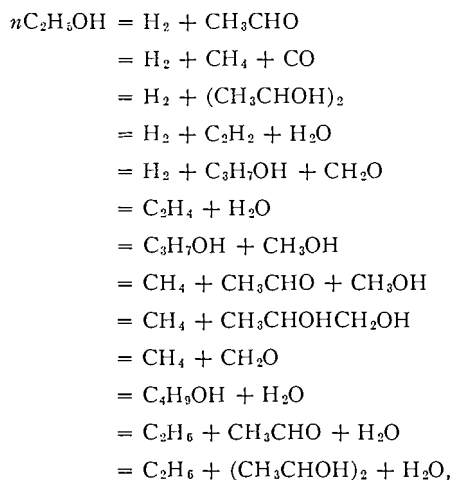$$\rightarrow C_2H_4 + C_2H_6 \qquad\qquad [16b]$$

Since the value of the ratio of disproportionation to combination of ethyl radicals is about 0.12 (9), the amount of ethane from reaction [16b] would be about one-eighth of the amount of butane. The yield of butane in the present work was only a trace, and thus a negligible amount of ethane originates from the disproportionation reaction. Therefore the major source of ethane is probably reaction [8].

Ethylene, which has an appreciable yield, is assumed to be formed by reactions [3c], [12c], and [16b]. Since [16b] was precluded as a significant source of ethane, it may also be neglected as a source of ethylene.

It is not known whether the acetylene is a primary or a secondary product but it will be assumed to be mechanistically as well as stoichiometrically equivalent to ($C_2H_4 - H_2$).

The preceding mechanism can be reduced to the following stoichiometric equations:

$$nC_2H_5OH = H_2 + CH_3CHO$$
$$= H_2 + CH_4 + CO$$
$$= H_2 + (CH_3CHOH)_2$$
$$= H_2 + C_2H_2 + H_2O$$
$$= H_2 + C_3H_7OH + CH_2O$$
$$= C_2H_4 + H_2O$$
$$= C_3H_7OH + CH_3OH$$
$$= CH_4 + CH_3CHO + CH_3OH$$
$$= CH_4 + CH_3CHOHCH_2OH$$
$$= CH_4 + CH_2O$$
$$= C_4H_9OH + H_2O$$
$$= C_2H_6 + CH_3CHO + H_2O$$
$$= C_2H_6 + (CH_3CHOH)_2 + H_2O,$$

where $n = 1$, 2, or 3. The products can be written in several equivalent combinations. Equations such as

$$3C_2H_5OH = CH_4 + (CH_3CHOH)_2 + CH_3OH$$
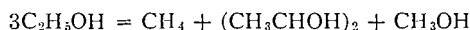
can be included without altering the over-all picture or the calculations that follow.

From the above equations, the yields of hydrogen, water, and methane were correlated to the yields of other products.

$$G(H_2) = G(CH_3CHO+CO+(CH_3CHOH)_2+C_2H_2+C_3H_7OH-CH_3OH-C_2H_6)$$

Using Table I, the sum of the G values of the products on the right-hand side of this equation is equal to $7.2-G(CH_3OH)$.

Similarly

$$G(H_2O) = G(C_2H_2+C_2H_4+C_4H_9OH+C_2H_6)$$
$$= 1.2,$$

$$G(CH_4) = G(CO+CH_3OH+CH_3CHOHCH_2OH+CH_2O-C_3H_7OH)$$
$$= 1.55+G(CH_2OH).$$

The values of $G(H_2) = 7.2-G(CH_3OH)$ and $G(CH_4) = 1.55+G(CH_2OH)$ are in approximate agreement with the observed values, $G(H_2) = 7.6$ and $G(CH_4) = 1.66$, if $G(CH_3OH)$ is small.

From the above, an approximate expected yield of methanol would be $G(CH_4)-1.55 \approx 0.1$. In the liquid phase radiolysis of ethanol (1), the value of the ratio of the yields of formaldehyde to methanol is 0.2. If this ratio had the same value in the vapor phase, the expected yield of methanol would be about 0.2. Thus the methanol yield is probably quite small, although methanol could not be measured by the present analytical system.

The predicted value of $G(H_2O) = 1.2$ is much lower than the observed value of 5.4. The source of this excess water is not obvious. It might have been formed by reactions not considered in the mechanism, or the sample might have absorbed water from the atmosphere during the analytical procedure. However, the analysis of the blank samples should have compensated for the latter possibility. An unaccountable excess of water was also observed by McDonell and Newton (1) in the liquid phase radiolysis of ethanol.

A mass balance for carbon, hydrogen, and oxygen has been worked out from the products and is presented in Table II. This mass balance corresponds to an empirical

TABLE II

Mass balance of carbon, hydrogen, and oxygen in the products obtained in the radiolysis of ethanol vapor

Product	G	Mass balance		
		C	H	O
Hydrogen	7.6	—	15.2	—
Carbon monoxide	1.1	1.1	—	1.1
Methane	1.66	1.7	6.6	—
Ethylene	0.72	1.4	2.9	—
Ethane	0.23	0.5	1.4	—
Acetylene	0.03	0.1	0.1	—
Water	5.4	—	10.8	5.4
Formaldehyde	0.9	0.9	1.8	0.9
Acetaldehyde	4.5	9.0	18.0	4.5
Propanol	0.6	1.8	4.8	0.6
Butanol	0.19	0.8	1.9	0.2
1,2-Propanediol	0.15	0.5	1.2	0.3
2,3-Butanediol	1.2	4.8	12.0	2.4
Total		22.2	76.7	15.4

NOTE: The numbers under C, H, and O in the table were obtained by multiplying the G value of the product by the respective number of atoms of C, H, or O in that product.

formula $C_{2.00}H_{6.76}O_{1.36}$, which has slightly more hydrogen and oxygen in it than does ethanol, C_2H_6O.

If water is generated only by reactions [3c] and [5a], then $G(H_2O)$ should be equal to 1.2. The excess water in G units is $(5.4 - 1.2) = 4.2$. If the corresponding amounts of H (8.4) and O (4.2) are subtracted from the mass balance in Table II, the empirical formula of the total products becomes $C_{2.00}H_{6.02}O_{0.99}$.

This good mass balance indicates that little or no polymer was formed during irradiation, unless polymer was a coproduct of the observed excess of water. It was also observed that the Po^{210}-alpha-particle source intensity showed no decrease during the ethanol irradiations. In the radiolysis of hydrocarbons (5, 8), there was a poor mass balance and a decrease in source intensity due to the deposition of polymer on the surface of the source. The lack of decrease in source intensity and a good mass balance in the ethanol products corroborate little or no polymer formation during the radiolysis of ethanol.

It might be mentioned that the decrease in the yields of CO, CH_4, and C_2H_4 between 0.5 and 4×10^{19} ev does not appear to be accompanied by a comparable decrease in the hydrogen yield (Fig. 1). Thus the decrease does not appear to be entirely a scavenging effect.

REFERENCES

1. W. R. McDONELL and A. S. NEWTON.　J. Am. Chem. Soc. 76, 4651 (1954).
2. A. S. NEWTON and W. R. McDONELL.　J. Am. Chem. Soc. 78, 4554 (1956).
3. J. G. BURR.　J. Phys. Chem. 61, 1477 (1957).
4. J. C. McLENNON and W. L. PATRICK.　Can. J. Research, 5, 470 (1931).
5. J. M. RAMARADHYA and G. R. FREEMAN.　J. Chem. Phys. 34, 1726 (1961).
6. L. F. FIESER.　Experiments in organic chemistry. 3rd ed. D. C. Heath and Co., New York. 1955. p. 286.
7. G. W. C. MILNER.　The principles and applications of polarography. Longmans Green and Co., New York. 1957.
8. J. M. RAMARADHYA and G. R. FREEMAN.　To be published.
9. S. J. LAPPORTE.　Angew. Chem. 72, 759 (1960).