Free-Radical Chain Reactions in the Radiation-Sensitized Pyrolysis of Ethanol Vapor[1]

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Abstract: The study of pyrolysis reactions can be assisted by use of the radiation sensitization technique. In this way the over-all kinetics are simplified and information can be obtained about the chain-propagation reactions. At temperatures above 300° in the radiolysis of ethanol vapor, free-radical chain reactions account for most of the decomposition of ethanol. The mechanisms were tested by the addition of propylene (free-radical scavenger), sulfur hexafluoride (electron scavenger), and ammonia (proton scavenger). Between 300 and 375°, at pressures in the range 10^2–10^3 torr, three modes of decomposition occur to similar extents. The stoichiometric equations are: I, $C_2H_5OH \rightarrow H_2 + CH_3CHO$; II, $C_2H_5OH \rightarrow CH_4 + CH_2O$; III, $C_2H_5OH \rightarrow C_2H_4 + H_2O$. The activation energies, in kilocalories/mole, and orders of the respective rate-limiting chain propagation reactions at 350° and 300–500 torr are: $CH_3CHOH \rightarrow CH_3CHO + H$, ≥ 30, 1.2; $CH_3CH_2O \rightarrow CH_3 + CH_2O$, 20, 1.9; $CH_2CH_2OH \rightarrow C_2H_4 + OH$, 27, 1.5. These unimolecular reactions are in their pressure-dependent regions under the present experimental conditions. As the temperature of the system is increased, the relative extents of occurrence of the three mechanisms becomes I > III > II at about 420°, and the difference between their contributions increases with further increase in temperature. This conclusion also applies to the normal pyrolysis system. Based upon $k(e^- + (C_2H_5OH)_mH^+) = 1 \times 10^{-6}$ cm^3/(ion sec), the value $k(e^- + SF_6) = 3 \times 10^{-12}$ cm^3/(ion sec) was obtained.

The technique of radiation-sensitized pyrolysis[3,4] has been extended to the study of ethanol. The pyrolysis of ethanol has received little attention.[5,6] At the high temperatures (>500°) required for the normal pyrolysis to occur at a convenient rate, secondary reactions of the products are very important. Furthermore, pyrolysis reactions are normally done in "aged" reaction vessels that have carbonaceous deposits on the inner surfaces. These carbonaceous deposits doubtlessly contain free-radical centers, so it is uncertain whether the chain-initiation and -termination reactions occur mainly on the wall or mainly in the gas phase. The system can be simplified to some extent by initiating the chains by the absorption of high-energy radiation. The initiation reaction can be assumed to be of the first order, and lower temperatures can be used to study the chains.

γ radiation is a convenient sensitizer for these studies because it readily penetrates the walls of the furnace and reaction vessel. It has the slight disadvantage that it generates ions as well as neutral free radicals, but it is usually possible to sort out the ionic and free-radical reactions by the use of suitable inhibitors.

During the radiolysis of ethanol vapor at temperatures above 300°, diethyl ether and methanol were formed by ionic chain reactions.[7] The present article reports free-radical chains that occurred in the same system. The inhibitors used to test the mechanisms were propylene (free-radical scavenger), ammonia (proton scavenger), and sulfur hexafluoride (electron scavenger).

Experimental Section

The materials and experimental techniques were described earlier.[8] The irradiation dose rate was 4×10^{19} eV/(g hr), measured with ethylene and assuming $G(H_2) = 1.31$.[8]

Products were analyzed by gas chromatography. A preliminary analysis of the gaseous products was made by low-temperature distillation in a vacuum line and measurement in a McLeod–Toepler apparatus. Separate samples were usually used for the gaseous and the liquid product analyses.

Gas chromatography was not suitable for formaldehyde measurement, so a chromotropic acid method was used.[9]

Results

Effect of Temperature at Constant Density. Samples of ethanol, 500 ml at a density of 0.66 g/l., were irradiated to a dose of 1.2×10^{20} eV/g at the desired temperature in the range 200–375°. The measured product yields are shown as functions of temperature in Figures 1–3. The yields of hydrogen, acetaldehyde, methane, formaldehyde, methanol, carbon monoxide, ethylene, and ethane increased rapidly as the temperature was raised above 280° (Figures 1 and 2). Formaldehyde was changed into methanol under the conditions of this work,[7] so the sum of their yields is plotted in Figure 1B.

The yield of 2,3-butanediol decreased while those of 1,2-propanediol and *sec*-butyl alcohol increased as the temperature was raised above 230° (Figure 3A). Diethoxymethane was a minor product ($G = 0.1$ at 260°) and its yield increased slightly at temperatures above 280° (Figure 3B).

The value of $G(H_2O)$ was only measured at two temperatures. It was 66 at 350° and 77 at 375°.

Isopropyl alcohol was believed to be a possible chain-termination product at the higher temperatures, but it was not observable ($G < 0.4$) at 350 or 375°. To be mechanistically significant the G value would have had to be greater than one.

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[1] This work was assisted financially by the National Research Council of Canada.

[2] Holder of National Research Council of Canada Studentship and University of Alberta Graduate Fellowship.

[3] A. V. Topchiev, "Radiolysis of Hydrocarbons," Elsevier Publishing Co., London, 1964.

[4] K. M. Bansal and G. R. Freeman, *J. Am. Chem. Soc.*, **88**, 4326 (1966).

[5] G. R. Freeman, *Proc. Roy. Soc.* (London), **A245**, 75 (1958).

[6] J. A. Barnard and H. W. D. Hughes, *Trans. Faraday Soc.*, **56**, 55 (1960).

[7] K. M. Bansal and G. R. Freeman, *J. Am. Chem. Soc.*, 90, 5632 (1968).

[8] K. M. Bansal and G. R. Freeman, *ibid.*, **90**, 7183 (1968).

[9] J. M. Ramaradhya and G. R. Freeman, *Can. J. Chem.*, **39**, 1836 (1961).

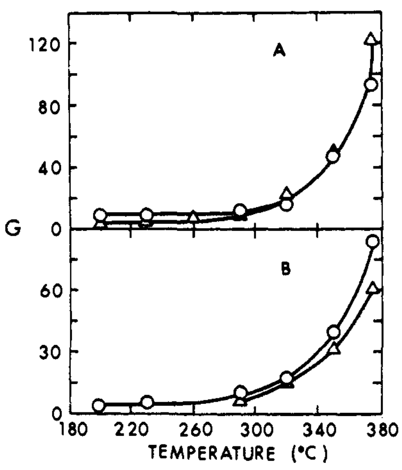

Figure 1. Product yields as a function of temperature in the radiolysis of ethanol vapor (ethanol density = 0.66 g/l.): (A) ○, hydrogen; △, acetaldehyde; (B) ○, methane; △, formaldehyde plus methanol.

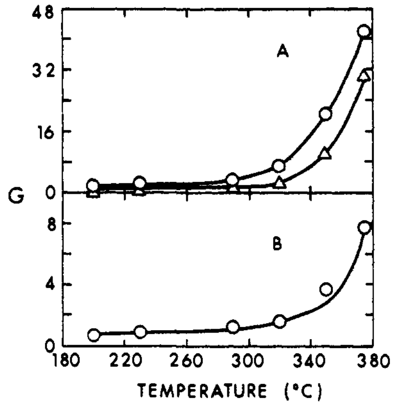

Figure 2. Product yields as a function of temperature in the radiolysis of ethanol vapor (ethanol density = 0.66 g/l.): (A) ○, ethylene; △, carbon monoxide; (B) ethane.

Effect of Ethanol Pressure at 350°. The pressure was varied over the range 67–1790 torr (0.080–2.12 g/l.). The samples were given a dose of 7.5 × 10^{19} eV/g. The measured product yields are listed in Table I. The yields of methane, carbon monoxide, methanol, and *sec*-butyl alcohol increased with increasing pressure; those of ethane and ethylene were nearly constant while that of hydrogen decreased. The yields of acetaldehyde were somewhat scattered but the decrease with increasing pressure was less pronounced than in the case of the hydrogen yields.

Table I. Product Yields as a Function of Pressure in the Radiolysis of Ethanol at 350°

	Pressure, torr			
Product	67	279	568	1790
	G			
Hydrogen	77	60	47	30
Methane	19	33	40	54
Carbon monoxide	3.4	6.0	10.0	10.7
Ethane	2.6	2.5	3.6	2.3
Ethylene	19	19	20	17
Acetaldehyde	75	81	50	61
Methanol	4.6	10.5	17.4	26.4
sec-Butyl alcohol	1.5	1.6	2.9	3.3

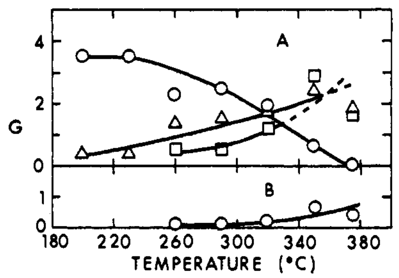

Figure 3. Product yields as a function of temperature in the radiolysis of ethanol vapor (ethanol density = 0.66 g/l.): (A) ○, 2,3-butanediol; △, 1,2-propanediol; □, *sec*-butyl alcohol; (B) diethoxymethane.

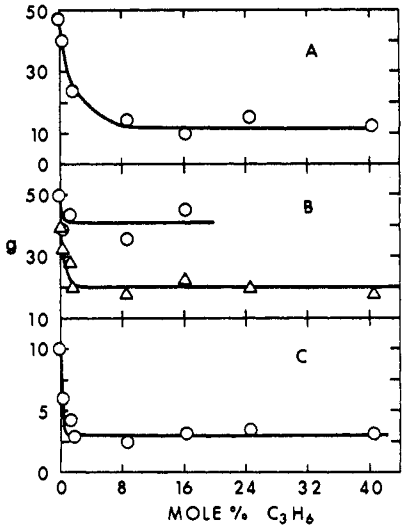

Figure 4. Product yields in the radiolysis of ethanol–propylene mixtures (temperature, 350°; ethanol density = 0.66 g/l.): (A) hydrogen; (B) ○, acetaldehyde; △, methane; (C) carbon monoxide.

Ethanol–Additive Mixtures. The effects of the presence of propylene, sulfur hexafluoride, or ammonia on product yields at 350° were measured. The samples were irradiated to a dose of 7.5 × 10^{19} eV/g. The ethanol density was 0.66 g/l. (568 torr). The product yields from the ethanol–additive mixtures are reported as *g* values

$$g(\mathrm{P}) = \frac{G(\mathrm{P})_{\mathrm{obsd}} - G(\mathrm{P})_{\mathrm{ad}}\epsilon_{\mathrm{ad}}}{\epsilon_{\mathrm{C_2H_5OH}}} \qquad \text{(i)}$$

where $G(\mathrm{P})_{\mathrm{obsd}}$ is the yield of P in the mixture, $G(\mathrm{P})_{\mathrm{ad}}$ is the yield from the radiolysis of pure additive, and ϵ_{ad} and $\epsilon_{\mathrm{C_2H_5OH}}$ are the electron fractions of additive and ethanol, respectively, in the mixture.

1. **Hydrogen.** Propylene reduced $g(H_2)$ from 47 to 12, and about 8 mol % of propylene was required to cause the maximum inhibition (Figure 4A). Radiolysis of pure propylene at 350° and 805 torr gave $G(H_2)_{C_3H_6}$ = 1.36. Sulfur hexafluoride reduced $g(H_2)$ from 47 to 21, but only 0.2 mol % was required to cause the maximum inhibition (Figure 5A). Up to 16 mol % of ammonia had no effect on $g(H_2)$.

2. **Methane.** Propylene reduced $g(CH_4)$ from 40 to 20 (Figure 4B). The value of $G(CH_4)_{C_3H_6}$ was 2.64 at 350° and 805 torr of propylene. Sulfur hexafluoride reduced $g(CH_4)$ to 9 (Figure 5A), whereas ammonia had no effect on the methane yield. The sulfur hexafluoride inhibition curve for methane is similar to that for hy-

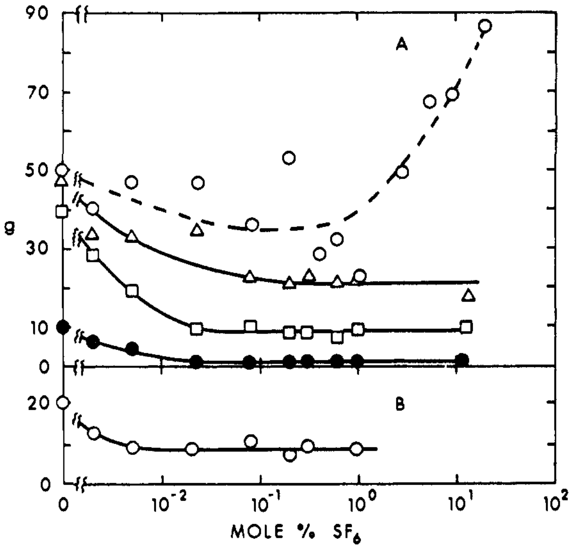

Figure 5. Product yields in the radiolysis of ethanol–sulfur hexafluoride mixtures (temperature, 350°; ethanol density = 0.66 g/l.): (A) ○, acetaldehyde plus acetal; △, hydrogen; □, methane; ●, carbon monoxide; (B) ethylene.

drogen. The same is true of the propylene inhibition curves for these two products.

3. **Carbon Monoxide.** The value of $g(CO)$ was reduced from 10.0 to 3.1 by propylene (Figure 4C), to 1.0 by sulfur hexafluoride (Figure 5A), and to 5.0 by ammonia (Figure 6A).

4. **Ethylene.** $g(C_2H_4)$ was decreased from 20 in pure ethanol to 15 in the presence of 1.4 mol % of propylene. The yield could not be measured at higher propylene concentrations because of analytical interference of the latter compound. Sulfur hexafluoride reduced $g(C_2H_4)$ to 8 (Figure 5B), whereas ammonia had no effect.

5. **Other Products.** The yield of ethane was not affected by the presence of propylene, but was reduced from 2.5 to 1.6 by ammonia (Figure 6B). The effect of sulfur hexafluoride was not determined, due to analytical difficulties. Propylene decreased $g(CH_3CHO)$ from 50 to about 41 (Figure 4B), so $\Delta g(CH_3CHO)$ was only about 25 % of $\Delta g(H_2)$.

In the presence of sulfur hexafluoride the acetaldehyde was mostly converted to acetal. This reaction was presumably catalyzed by hydrogen fluoride formed as a radiolysis product. The sum of acetaldehyde and acetal was taken to represent the amount of the former compound produced. Unfortunately, the precision of the results was poor, but small amounts of sulfur hexafluoride appeared to inhibit the formation of acetaldehyde somewhat and large amounts catalyzed it (Figure 5).

Ammonia reacts with acetaldehyde,[10] so the effect of the former on the rate of formation of the latter could not be determined.

Discussion

The marked increases in the yields of hydrogen, acetaldehyde, methane, carbon monoxide, formaldehyde + methanol, and ethylene at temperatures above 280° can be explained by free-radical chain mechanisms. For the sake of simplicity the over-all chain reactions can be represented by the following stoichiometric equations.

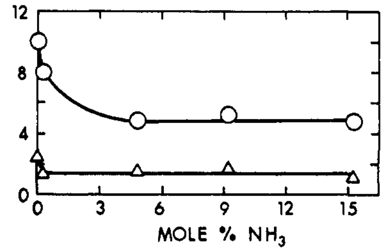

Figure 6. Product yields in the radiolysis of ethanol–ammonia mixtures (temperature, 350°; ethanol density = 0.66 g/l.): (A, top) ○, carbon monoxide; (B, bottom) △, ethane.

$$C_2H_5OH \longrightarrow H_2 + CH_3CHO \qquad \text{(I)}$$

$$C_2H_5OH \longrightarrow CH_4 + CH_2O \qquad \text{(II)}$$

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O \qquad \text{(III)}$$

$$CH_2O + C_2H_5OH \longrightarrow CH_3OH + CH_3CHO \qquad \text{(IV)}$$

The last reaction has been suggested to occur by an ionic mechanism[7] and will not be discussed here. The chain mechanisms that correspond to reactions I–III will be discussed separately. However, the three mechanisms occur simultaneously, so their initiation and termination steps are intermingled. It is therefore necessary to consider the total free-radical concentration in the system.

Radical Concentration

$$C_2H_5OH \overset{I}{\rightsquigarrow} 2R \qquad (1)$$

$$2R \longrightarrow \text{termination} \qquad (2)$$

where R is any radical and I is the rate of the reaction step 1. Any radical can initiate any chain and any radical can participate in the termination of any chain. To terminate a given chain, only one of the carriers of that chain need take part in the termination step; the other termination reactant may be a radical from another chain. Therefore, the total concentration of radicals R must be considered in each chain mechanism. The total concentration of radicals is given by

$$[R] = (I/k_2)^{1/2} \qquad \text{(ii)}$$

where

$$I = {}^1/_2 10^{-2} DG(R) \qquad \text{(iii)}$$

where D is the dose rate in eV/(cm^3 sec) and $G(R)$ is the 100-eV yield of R. The factor $^1/_2$ is included in eq iii because two radicals are formed in each reaction step 1.

I. $C_2H_5OH \rightarrow H_2 + CH_3CHO$. The formation of hydrogen and acetaldehyde is explained by reactions 3–6.

$$C_2H_5OH \rightsquigarrow CH_3CHOH + H \qquad (3)$$

$$H + C_2H_5OH \longrightarrow H_2 + CH_3CHOH \qquad (4)$$

$$CH_3CHOH \longrightarrow CH_3CHO + H \qquad (5)$$

$$CH_3CHOH + R \longrightarrow \text{termination} \qquad (6)$$

To simplify the presentation of an individual chain mechanism, the initiation step is written in terms of the carriers of that chain. The termination step is written in terms of one specific chain carrier and one general

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[10] J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 442.

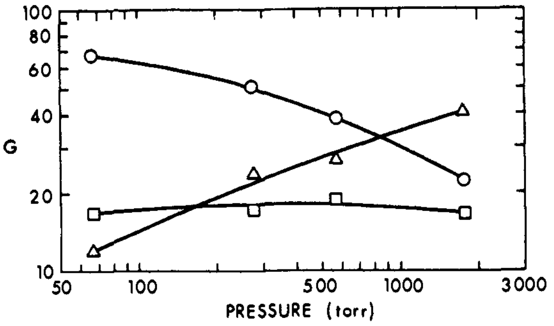

Figure 7. Chain product yields from ethanol radiolysis as a function of pressure (temperature, 350°): ○, hydrogen; △, methane; □, ethylene. $G(H_2)_{chain} = G(H_2)_{350°} - G(H_2)_{150°}$; $G(CH_4)_{chain} = G(CH_4) - G(CO) - 3.1$; $G(C_2H_4)_{chain} = G(C_2H_4)_{350°} - G(C_2H_4)_{150°}$. The 350 and 150° yields were taken at the same ethanol density. The yields at 150° were obtained from ref 8.

radical R. These simplifications do not alter the forms of the derived rate equations because the initiation step is always first order and termination is always second order under the present conditions. It is assumed that the rate constants of all the free-radical chain termination reactions are equal to k_2, *e.g.*, $k_6 = k_2$. Hence, in the present mechanism

$$[R] = (I/k_6)^{1/2} \quad \text{(iv)}$$

Some of the acetaldehyde decomposes to methane and carbon monoxide, but for the sake of simplicity in the discussion, this secondary decomposition will be ignored. The total acetaldehyde yield will be taken as the sum of those of acetaldehyde and carbon monoxide.

Steady-state treatment of reactions 3–6 gives eq v and vi.

$$d[CH_3CHO]/dt = k_5(I/k_6)^{1/2} \quad \text{(v)}$$

$$d[H_2]/dt = I + k_5(I/k_6)^{1/2} \quad \text{(vi)}$$

For long chains, eq vi reduces to

$$d[H_2]/dt = k_5(I/k_6)^{1/2} \quad \text{(vii)}$$

Now

$$I = A[C_2H_5OH] \quad \text{(viii)}$$

where A is a constant that is proportional to the product of the radiation intensity, the ethanol molecular absorption coefficient, and the efficiency of reaction 3. Therefore

$$d[H_2]/dt = k_5(A/k_6)^{1/2}[C_2H_5OH]^{1/2} \quad \text{(ix)}$$

Thus this mechanism predicts that the formation of hydrogen and acetaldehyde should be 0.5 order.

The G value of a product P may be expressed as

$$G(P) = (d[P]/dt)/B[C_2H_5OH] \quad \text{(x)}$$

where B is a constant proportional to the product of the radiation intensity and the ethanol molecular absorption coefficient. Thus a plot of log $G(P)$ against ethanol pressure has a slope n, and $n + 1$ is the order of formation of P.

The slope of the plot of $G(H_2)$ against ethanol pressure varies from -0.2 at the lower pressures to -0.5 at the higher pressures (Figure 7), so the order of formation of hydrogen is 0.8 at the lower and 0.5 at the higher pressures. Only the amount of hydrogen that resulted from reaction 5 was used in the plot. The nonchain portion was assumed to be equal to the yield at 150°, measured at the same ethanol density and reported earlier.[8] This portion, which includes the I of eq vi, was subtracted from the hydrogen yield measured at 350° and the difference was plotted in Figure 7.

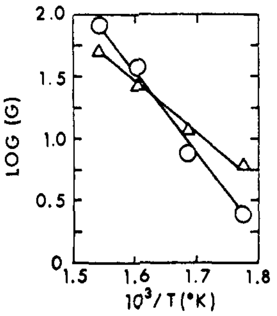

Figure 8. Arrhenius plot of (○) hydrogen and (△) methane yields $G(H_2)_{chain} = G(H_2) - 9.0$; $G(CH_4)_{chain} = [G(CH_4) - G(CO) - 3.1]$. Ethanol density = 0.66 g/l.

The fact that the order is greater than 0.5 at lower pressures indicates that under these conditions the decomposition of the CH_3CHOH radicals is in the pressure-dependent region. Reaction 5 should in fact be written as the combination of reactions 5a–c,

$$CH_3CHOH + M \longrightarrow CH_3CHOH^* + M \quad \text{(5a)}$$

$$CH_3CHOH^* + M \longrightarrow CH_3CHOH + M \quad \text{(5b)}$$

$$CH_3CHOH^* \longrightarrow CH_3CHO + H \quad \text{(5c)}$$

where M can be any molecule, but is ethanol in the present case. Substitution of reactions 5a–c for 5 in the preceding mechanism leads to eq xi for the rate of formation of hydrogen.

$$\frac{d[H_2]}{dt} = \frac{k_{5a}k_{5c}}{k_{5c} + k_{5b}[C_2H_5OH]}\left(\frac{A}{k_6}\right)^{1/2}[C_2H_5OH]^{3/2} \quad \text{(xi)}$$

This illustrates that at low enough pressures the formation of hydrogen should be 1.5 order, and at high pressures it should be 0.5 order. The observed transition from 0.8 to 0.5 order indicates that the reaction had reached the high-pressure limit at 1790 torr.

From an Arrhenius plot of the hydrogen yields (Figure 8), it was determined that $(E_5 - 0.5E_6) = 30$ kcal/mol. Only the amount of hydrogen produced by the chain reaction was used in the plot, so the nonchain portion (9.0 units, which includes the I in eq vi) was subtracted from the total yields at the higher temperatures. The value of E_6 is zero, which leaves $E_5 = 30$ kcal/mol.

Reaction 5 is 30 kcal/mol endothermic.[11] Previous observations of the decomposition of oxy radicals to form carbonyl compounds indicate that the activation energy is higher than the enthalpy change for such reactions.[4,12,13] For this reason it is believed that the present estimate of E_5 might be too low. Some of the acetaldehyde could be formed by the chain-propaga-

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[11] Estimated from the following heats of formation and bond dissociation energies, in kilocalories/mole: (a) CH_3CHO, -39.7, and H, 52.1 (S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); (b) D(H–CH(OH)-CH_3), 90 ("Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1965–1966, pp F154–155).

[12] L. F. Loucks and K. J. Laidler, *Can. J. Chem.*, **45**, 2767 (1967).

[13] P. Gray, R. Shaw, and J. C. J. Thynne, *Progr. Reaction Kinetics*, **4**, 63 (1967).

tion reactions 7 and 8. The above estimate of the activation energy would then correspond to some average value between E_5 and E_7. The value of E_8 has been reported to be 21 kcal/mol, whereas ΔH_8 = 19 kcal/mol.[13] We therefore conclude that $E_5 \geq 30$ kcal/mol.

$$H + C_2H_5OH \longrightarrow H_2 + C_2H_5O \qquad (7)$$

$$C_2H_5O \longrightarrow CH_3CHO + H \qquad (8)$$

The chain represented by reactions 7 and 8 may be terminated by reaction 9. The inclusion of reactions

$$C_2H_5O + R \longrightarrow \text{termination} \qquad (9)$$

7–9 in the mechanism does not alter the kinetic conclusions reached earlier because the formation of hydrogen and acetaldehyde from either CH_3CHOH or CH_3CH_2O involves the competition between the unimolecular decomposition of a radical (reaction 5 or 8) and a bimolecular termination reaction (6 or 9).

Hydrogen atoms add readily to propylene,[14] so the addition of propylene to the sytem is expected to inhibit hydrogen formation through the competition of reaction 10 with 4.

$$H + C_3H_6 \longrightarrow C_3H_7 \qquad (10)$$

The formation of acetaldehyde is less inhibited than that of hydrogen because the propyl radicals formed in reaction 10 propagate the chain through reaction 11.

$$C_3H_7 + C_2H_5OH \longrightarrow C_3H_8 + CH_3CHOH \qquad (11)$$

Further evidence for the occurrence of reaction 11 is the fact that the addition of 1.4 mol % of propylene increased $g(C_3H_8)$ from 0.1 to 9.1 and decreased $g(H_2)$ from 47 to 33. $\Delta g(C_3H_8) = 9$ is smaller than $-\Delta g(H_2) = 14$ because reaction 11 is less efficient than reaction 4 in propagating the chain.

Ammonia did not affect the hydrogen yield at 350° for the same reason that it had no effect at 150°,[8] namely, that the neutralization of either $(C_2H_5OH)_mH^+$ or $(C_2H_5OH)_nNH_4{}^+$ by an electron leads to the formation of a hydrogen atom.

Sulfur hexafluoride has a large capture cross section for thermal electrons,[15] so it alters the neutralization reaction in the system from (12) to (14). The addition

$$(C_2H_5OH)_mH^+ + e^- \longrightarrow mC_2H_5OH + H \qquad (12)$$

$$e^- + SF_6 \longrightarrow SF_6{}^- \qquad (13)$$

$$(C_2H_5OH)_mH^+ + SF_6{}^- \longrightarrow mC_2H_5OH + HF + SF_5 \qquad (14)$$

of sulfur hexafluoride to the ethanol vapor therefore decreases the hydrogen yield. Half of the maximum effect was caused by 5×10^{-3} mol % of the additive (Figure 5) which corresponds to a concentration of 7×10^{-7} *M*. The absorbed dose rate was 2.6×10^{19} eV/l. hr and *G*(ionization) = 4.0. Assuming $k_{12} = 1 \times 10^{-6}$ cm^3/(ion sec), one can obtain $k_{13} = 3 \times 10^{-12}$ cc/(ion sec) from kinetic analysis of the results. This value of k_{13} is the same as that obtained from the radiolysis of methylcyclohexane vapor in the presence of sulfur hexafluoride.[16] However, values of k_{13} determined by different methods can differ by several orders of magnitude and the reason for this is not understood.[16]

The effect of sulfur hexafluoride on the acetaldehyde yield is complex (Figure 5). The initial inhibition is doubtlessly related to the occurrence of reactions 13 and 14, but the catalysis caused by the presence of more than 1 mol % of sulfur hexafluoride is not well understood. Sulfur hexafluoride is evidently able to take part in a chain reaction that generates acetaldehyde.

II. $C_2H_5OH \rightarrow CH_4 + CH_2O$. The formation of methane and formaldehyde can be explained by the following reactions.

$$C_2H_5OH \rightsquigarrow CH_3 + CH_2OH \qquad (15)$$

$$CH_2OH + C_2H_5OH \longrightarrow CH_3OH + C_2H_5O \qquad (16)$$

$$C_2H_5O \longrightarrow CH_3 + CH_2O \qquad (17)$$

$$CH_3 + C_2H_5OH \longrightarrow CH_4 + C_2H_5O \qquad (18)$$

$$C_2H_5O + R \longrightarrow \text{termination} \qquad (9)$$

It should be emphasized that for the sake of presentation this mechanism has been oversimplified. Only one set of chain carriers has been included, except in the termination reaction. Methyl radicals do not in reality abstract exclusively from the oxygen in ethanol, nor do hydrogen atoms abstract exclusively from the α-carbon atom, as depicted in mechanism I. However, the simplified mechanisms are sufficient to illustrate the kinetic behavior of the system.

Steady-state treatment of reactions 15–18 and 9, using

$$[R] = (I/k_9)^{1/2} \qquad (xii)$$

gives

$$d[CH_2O]/dt = k_{17}(A/k_9)^{1/2}[C_2H_5OH]^{1/2} \qquad (xiii)$$

and

$$d[CH_4]/dt = I + k_{17}(A/k_9)^{1/2}[C_2H_5OH]^{1/2} \qquad (xiv)$$

which for long chains reduces to

$$d[CH_4]/dt = k_{17}(A/k_9)^{1/2}[C_2H_5OH]^{1/2} \qquad (xv)$$

This mechanism indicates that the formation of formaldehyde and methane should be 0.5 order.

The secondary decomposition of acetaldehyde also forms methane, along with carbon monoxide. The amount of methane formed "directly" from ethanol is therefore taken as $G(CH_4) - G(CO)$.

The amount of methane formed from the methyl radicals generated by reaction 17 at 350° is taken as $G(CH_4) - G(CO) - 3.1$, where 3.1 is the difference between the methane and carbon monoxide yields at 200°. Reaction 17 is negligible at 200°, and the methane is independent of ethanol pressure in the nonchain temperature region.[8] A plot of log $[G(CH_4) - G(CO) - 3.1]$ against log [ethanol pressure] has a slope of 0.4 at 100 torr and 0.3 at 1000 torr (Figure 7). This means that the chain formation of methane at 350° is 1.4 order at the lower and 1.3 order at the higher pressures.

The fact that the order is greater than 0.5 is probably due to the pressure dependence of the decomposition of the C_2H_5O radicals under the conditions of the present work. Reaction 17 should be written as the combination of reactions 17a–c

$$C_2H_5O + M \longrightarrow C_2H_5O^* + M \qquad (17a)$$

$$C_2H_5O^* + M \longrightarrow C_2H_5O + M \qquad (17b)$$

$$C_2H_5O^* \longrightarrow CH_3 + CH_2O \qquad (17c)$$

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(14) R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

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where M can be any molecule, but is ethanol in the present system. Substitution of reactions 17a–c for 17 in the preceding mechanism leads to eq xvi for the rate of formation of methane.

$$\frac{d[CH_4]}{dt} = \frac{k_{17a}k_{17c}}{k_{17c} + k_{17b}[C_2H_5OH]}\left(\frac{A}{k_9}\right)^{1/2}[C_2H_5OH]^{3/2} \quad \text{(xvi)}$$

Thus at low enough pressures the formation of methane should be 1.5 order, and at high pressures it should be 0.5 order. The observed order of 1.3–1.4 indicates that the decomposition of C_2H_5O radicals is 1.8–1.9 order, *i.e.*, near the "low-pressure limit" of 2.0, under the present conditions.

A contribution of reaction 9′ to the termination of the chain would lower the estimated order of reaction 17.

$$CH_3 + R \longrightarrow \text{termination} \quad (9')$$

However, even if termination were entirely by (9′), the estimated order of 17 would only be reduced to 1.4.

From an Arrhenius plot of the methane yields (Figure 8) it was determined that $E_{17} - 0.5E_9 = 19$ kcal/mol. Only the amount of methane that resulted from reaction 17 was used in the plot. The value of E_9 is zero, so $E_{17} = 19$ kcal/mol. The value of E_{17} is greater than the $\Delta H_{17} = 12$ kcal/mol,[11a] as expected.[4,12,13]

About 70% of the product formaldehyde was converted into methanol under the present conditions,[7] so the total amount of formaldehyde was taken as the sum of the measured yields of the two compounds. The nonchain G value was 0.8,[8] which was subtracted from the G_{total} to get G_{chain}. The Arrhenius plot of $G(CH_2O + CH_3OH)_{\text{chain}}$ in Figure 9 gives $E_{17} - 0.5E_9 = E_{17} = 20$ kcal/mol, in close agreement with the value obtained from the methane yields.

Previous estimates of E_{17} range from 13 to 23 kcal/mol, but the lower value might be due to hot-radical effects.[13]

Propylene decreases the yield of methane (Figure 4C). This is presumably due to competition between reactions 18 and 19.

$$CH_3 + C_3H_6 \longrightarrow C_4H_9 \quad (19)$$

Sulfur hexafluoride decreases the methane yield at 350° (Figure 5A), presumably by inhibiting the chain initiation reaction, although the possibility that it scavenges methyl radicals at this temperature has not been ruled out. Sulfur hexafluoride has no effect on the formation of methane in the nonchain temperature region.[8]

Ammonia does not affect the methane yield, as expected for a free-radical mechanism.

III. $C_2H_5OH \rightarrow C_2H_4 + H_2O$. The following simplified mechanism explains the formation of ethylene and water.

$$C_2H_5OH \overset{I}{\rightsquigarrow} CH_2CH_2OH + H \quad (20)$$

$$H + C_2H_5OH \longrightarrow H_2 + CH_2CH_2OH \quad (21)$$

$$CH_2CH_2OH \longrightarrow C_2H_4 + OH \quad (22)$$

$$OH + C_2H_5OH \longrightarrow H_2O + CH_2CH_2OH \quad (23)$$

$$CH_2CH_2OH + R \longrightarrow \text{termination} \quad (24)$$

Steady-state treatment of reactions 20–24, using

$$[R] = (I/k_{24})^{1/2} \quad \text{(xvii)}$$

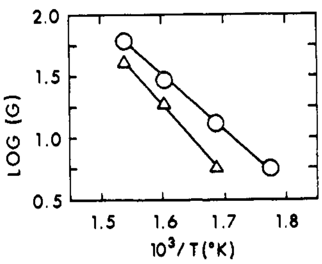

Figure 9. Arrhenius plot of (○) formaldehyde plus methanol and (△) ethylene. $G(CH_2O + CH_3OH)_{\text{chain}} = [G(CH_2O + CH_3OH) - 0.8]$; $G(C_2H_4)_{\text{chain}} = [G(C_2H_4) - 1.3]$. Ethanol density = 0.66 g/l.

gives

$$d[C_2H_4]/dt = k_{22}(A/k_{24})^{1/2}[C_2H_5OH]^{1/2} \quad \text{(xviii)}$$

This mechanism indicates that the formation of ethylene should be 0.5 order.

The amount of ethylene formed in the chain reaction at a given pressure at 350° was estimated by subtracting from the measured yield the amount formed at 150° at the same ethanol density.[8] The values of $G(C_2H_4)_{\text{chain}}$ are plotted against the ethanol pressure in Figure 7. The slope of the curve varies from 0.1 at the lower pressures to −0.1 at the higher pressures. This indicates that the chain formation of ethylene varies from 1.1 to 0.9 as the ethanol pressure increases from 67 to 1790 torr at 350°. The fact that the order is greater than 0.5 is ascribed to the pressure dependence of the decomposition of the CH_2CH_2OH radicals. As before, substitution of reactions 22a–c for 22 in the mechanism leads to eq xix instead of xviii

$$CH_2CH_2OH + M \longrightarrow CH_2CH_2OH^* + M \quad (22a)$$

$$CH_2CH_2OH^* + M \longrightarrow CH_2CH_2OH + M \quad (22b)$$

$$CH_2CH_2OH^* \longrightarrow C_2H_4 + OH \quad (22c)$$

where M can be any molecule, but is ethanol in the present system. The observed order of ethylene formation changed from 1.1 to 0.9 as the pressure was increased over the present range, which implies that the order of reaction 22 changed from 1.6 to 1.4 over this pressure range.

$$\frac{d[C_2H_4]}{dt} = \frac{k_{22a}k_{22c}}{k_{22c} + k_{22b}[C_2H_5OH]}\left(\frac{A}{k_{24}}\right)^{1/2}[C_2H_5OH]^{3/2} \quad \text{(xix)}$$

At an ethanol density of 0.66 g/l., the nonchain yield of ethylene is 1.3.[8] Hence, at this density, $G(C_2H_4)_{\text{chain}} = G(C_2H_4) - 1.3$. An Arrhenius plot of $G(C_2H_4)_{\text{chain}}$, shown in Figure 9, gives $E_{22} - 0.5E_{24} = E_{22} = 27$ kcal/mol.

The value of D(H–CH_2CH_2OH) is not known, but if a value of 96 kcal/mol is assumed one obtains $\Delta H_{22} = 30$ kcal/mol. By analogy with the decomposition of the ethyl radical,[17] the activation energy of reaction 22 at "infinite" pressure, where the order of the reaction is 1.0, should be 1–2 kcal/mol greater than ΔH_{22}. At "zero" pressure, where the order of the decomposition is 2.0, E_{22} should be 6–7 kcal/mol less than ΔH_{22}. At an intermediate pressure where the order of the reaction is 1.5, one would expect $\Delta H_{22} - E_{22} \simeq 2$–3 kcal/mol, which agrees with the value, 3 kcal/mol, observed under

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these conditions. Reaction 22 is therefore analogous to the decomposition of the ethyl radical, as might be expected.

Propylene and sulfur hexafluoride decreased the ethylene yield, while ammonia had no effect. The reasons are the same as those given for mechanisms I and II.

Ethane, *sec*-Butyl Alcohol, and 1,2-Propanediol. The increase of $G(C_2H_6)$ from 1.5 to 7.5 when the temperature was increased from 320 to 375° (Figure 2B) indicates that ethane was produced by a minor chain reaction in this temperature region. The yield was not affected by propylene but was reduced by ammonia at 350°, so cations appear to be involved in the chain. The mechanism will be investigated further.

The mechanisms of formation of *sec*-butyl alcohol and 1,2-propanediol are not known.

General Comment. In the radiation-sensitized pyrolysis of ethanol at 350° the three different modes of decomposition of ethanol, represented by mechanisms I, II, and III, all occurred to similar extents. The relative extents were I:II:III::2:2:1. In the normal pyrolysis at 525° the relative extents were 4:0:1,[5] whereas at 600°, only mechanism I was observed.[6] In both the normal and radiation-sensitized pyrolyses the initiation and termination reactions of the three mechanisms are intermingled, so this trend of the relative extents of the mechanisms with increasing temperature should be related to the relative activation energies of the chain-propagation reactions: $E_{\mathrm{Ip}} > E_{\mathrm{IIIp}} > E_{\mathrm{IIp}}$, where E_{Ip} is the activation energy of propagation of mechanism I, and so on. This is in agreement with observation, since $E_5 \geq 30$ kcal/mol, $E_{22} = 27$ kcal/mol, and $E_{17} = 20$ kcal/mol. A parallel implication of the trend is that the frequency factors of the propagation reactions are in the order $A_{\mathrm{Ip}} > A_{\mathrm{IIIp}} > A_{\mathrm{IIp}}$. This might be due to the relative values of the frequency factors of reactions 5, 22, and 17, or to the relative frequencies of production of the CH_3CHOH, CH_2CH_2OH, and CH_3CH_2O radicals, or both.

In agreement with the above discussion, extrapolation of the present results indicates that at about 420° the relative extents of the different mechanisms becomes I > III > II, and that the difference between their relative contributions increases with further increase in temperature.

Fluorescence of Zinc and Magnesium Etioporphyrin I. Quenching and Wavelength Shifts Due to Complex Formation[1]

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Abstract: Emission spectra of zinc and magnesium etioporphyrin I are red shifted and decrease in intensity on coordination with several ligands. These shifts parallel absorption spectral changes and are probably due to steric interactions between the ligand and the porphyrin π cloud. Ligand exchange for excited magnesium complexes is probably close to diffusion controlled. Nitrobenzene and other nitro compounds quench zinc and magnesium porphyrin fluorescence, probably through an excited complex which has some charge-transfer character. Studies of excited porphyrin-induced *cis–trans* isomerization of 4-nitrostilbene indicate that the zinc porphyrin triplet must be the precursor to the isomerizable species. The results suggest that zinc porphyrin triplets are better electron donors than the corresponding excited singlets.

Numerous investigations have dealt with energy transfer and electron transfer phenomena involving porphyrins and related compounds. Much of the interest of these systems centers around the mechanism of chlorophyll action and the role of other biologically important systems. It has been demonstrated that photoexcited porphyrins can serve either as electron donors[3–7] or electron acceptors[5–7] and that the porphyrin may or may not be altered permanently in the process. Excited porphyrins can also act as sensitizers in ordinary energy transfer processes.[8,9] Many of the phenomena concerned with chlorophyll and other porphyrins are very dependent on environment. Aggregated and coordinated species are common and it may well be such forms that are the reactive species in several photoreactions involving porphyrins.[10–13] Recent work has shown that amines,[14] conjugated dienes,[15]

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[2] National Science Foundation Predoctoral Fellow, 1965–present.

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