Radiolysis of Diethyl Ether. III.
Effect of Temperature on the Vapor Phase[1]

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Abstract: The γ radiolysis of diethyl ether vapor was studied over the temperature range from 33 to 220°. At temperatures greater than 80°, acetaldehyde and ethane are formed mainly by a free-radical chain reaction. The activation energies of reactions 4 and 5 were found to be $E_4 = 19$ kcal/mole and $E_5 = 9$ kcal/mole. The main chain termination reaction in the temperature range 100 to 140° is that of reaction 7, whereas at higher temperatures the main termination reaction is that of reaction 8. The disproportionation reaction (11) occurs only to a small extent; $k_{11}/k_7 \leqslant 0.07$. Furthermore, as shown by reactions 6 and 9, $k_9/k_6 \leqslant 0.14$. At temperatures greater than 80°, the total primary yield of radicals is $G(\text{ether} \rightarrow \text{R} + \text{R}') = 5.8$.

The present work extends the study of the radiolysis of diethyl ether.[2,3] It has been found that radiation sensitization will provide a useful method to extend normal pyrolysis studies. The radiation-sensitized pyrolysis of diethyl ether is much less complex than the normal pyrolysis of this compound,[4] because the sensitized chain reaction occurs at appreciable rates at relatively low temperatures.

Experimental Section

Materials. The diethyl ether used was Spectrograde from Eastman Organic Chemicals Co. This was dried over sodium and was stored in a reservoir in the vacuum system. No impurities were detected by gas chromatographic analysis of the diethyl ether on the columns silicone grease, di-2-ethyl hexyl sebacate, and tetraethylene glycol dimethyl ether, each on Chromosorb W.

The compounds ethane, acetaldehyde, methane, carbon monoxide, *sec*-butyl ethyl ether, *n*-butane, ethanol, ethylene, ethyl isopropyl ether, formaldehyde, diethoxymethane, propane, acetylene, ethyl vinyl ether, and diethyl acetal used as calibration standards in gas chromatographic analysis were obtained commercially.

2,3-Diethoxybutane was prepared by Moore's method[5] and was distilled before use. This was further purified by gas chromatography. Ethyl methyl acetal was prepared by the method described by Juvet and Chiu[6] and was distilled before use. The 2-ethoxypropanol-1 and 1-ethoxypropanol-2 were prepared from propylene oxide.[7]

Sample Preparation. Most of the irradiation bulbs were 500-ml round-bottom Pyrex glass flasks with breakseals and filling tubes attached. The bulbs were baked at a temperature of about 450°, while being evacuated, for 3–4 hr before filling. In some experiments, smaller samples were irradiated in 125-ml bulbs and the entire contents were transferred directly on to a gas chromatographic column to measure the yields of the C_2–C_4 gaseous products.

Irradiation of Samples. The samples were irradiated in a 10,000-curie Co^{60} γ-ray source. The dose rate was 5.3×10^{19} ev/g hr. The samples received a dose of 1.6×10^{20} ev/g. The bulbs were kept at the desired constant temperature (±3°) by completely enclosing them in a special electrical heating mantle.

Vapor phase dosimetry was done with ethylene, using $G(H_2) = 1.28$.[8] Sufficient ethylene was placed in the bulb so that the electron density of ethylene was similar to that of ether in the ether samples.

Analysis. Hydrogen, methane, and carbon monoxide were separated from the irradiated samples by distillation through two traps, the first of which was maintained at −196° and the other at −210°. The total amount of this gas fraction was measured in a Toepler–McLeod apparatus and analyzed by gas chromatography, using a molecular sieve 13X column. A second fraction, volatile at −130° and consisting of C_2–C_4 hydrocarbon products, was analyzed by gas chromatography on a silica gel column. The C_2–C_4 hydrocarbons were sometimes analyzed by condensing the entire irradiated sample into a small thin-walled bulb and transferring the contents of the bulb directly into the gas chromatographic carrier gas stream using a bulb crushing apparatus. The silica gel column was used.

The liquid products were analyzed by gas chromatography using three columns: 2.5 m, 10% silicone grease on Diato-port WAW; 2.5 m, 10% di-2-ethyl hexyl sebacate on Diato-port WAW; a 6.5-m column, the first half of which was packed with 10% tetraethylene glycol dimethyl ether on Diaport WAW and the other half with 25% Ucon LB 1800X on Celite.

Authentic samples of all the identified products were used to determine the analytical calibration factors.

Formaldehyde was analyzed by a chromotropic acid method.[9] The method was slightly modified for formaldehyde analysis in the irradiated ether vapor samples.[3]

Results

Effect of Temperature. Samples (0.58 g) of liquid diethyl ether were vaporized into 500-ml bulbs and irradiated to a dose of 1.6×10^{20} ev/g at temperatures in the range 33 to 220°. The amount of ether in the bulb corresponded to a pressure of 404 torr at 140°.

The G values of the products at 33° are presented in Table I together with the results of an earlier study.[3] The agreement between the two sets of results is quite good. The G values of the products are plotted as a function of temperature in Figures 1 and 2.

Temperature has a very large effect on the yields of ethane, acetaldehyde, methane, carbon monoxide, butane, *sec*-butyl ethyl ether, and 2,3-diethoxybutane (Figure 1) and a smaller effect on the yields of the other products (Figure 2).

Effect of Pressure on Product Distribution at 140°. The pressures were varied by varying the volume of liquid diethyl ether that was vaporized into the irradiation bulb. The pressure was calculated on the basis of the ideal gas law equation. The dose used was 1.6×10^{20} ev/g. The results of the variation of product yields with pressure are presented in Figure 3.

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[1] This work received financial assistance from the National Research Council of Canada.

[2] M. K. M. Ng and G. R. Freeman, *J. Am. Chem. Soc.*, **87**, 1635 (1965).

[3] M. K. M. Ng and G. R. Freeman, *ibid.*, **87**, 1639 (1965).

[4] Seen for example, (a) K. J. Laidler and D. J. McKenney, *Proc. Roy. Soc.* (London), **A278**, 505, (1964); (b) G. R. Freeman, *ibid.*, **A245**, 49 (1958).

[5] C. G. Moore, *J. Chem. Soc.*, 236 (1951).

[6] R. S. Juvet and J. Chiu, *J. Am. Chem. Soc.*, **83**, 1560 (1961).

[7] D. Gagnaire, *Bull. Soc. Chim. France*, 1813 (1960).

[8] R. A. Back, T. W. Woodward, and K. A. McLauchlan, *Can. J. Chem.*, 40, 1380 (1962).

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

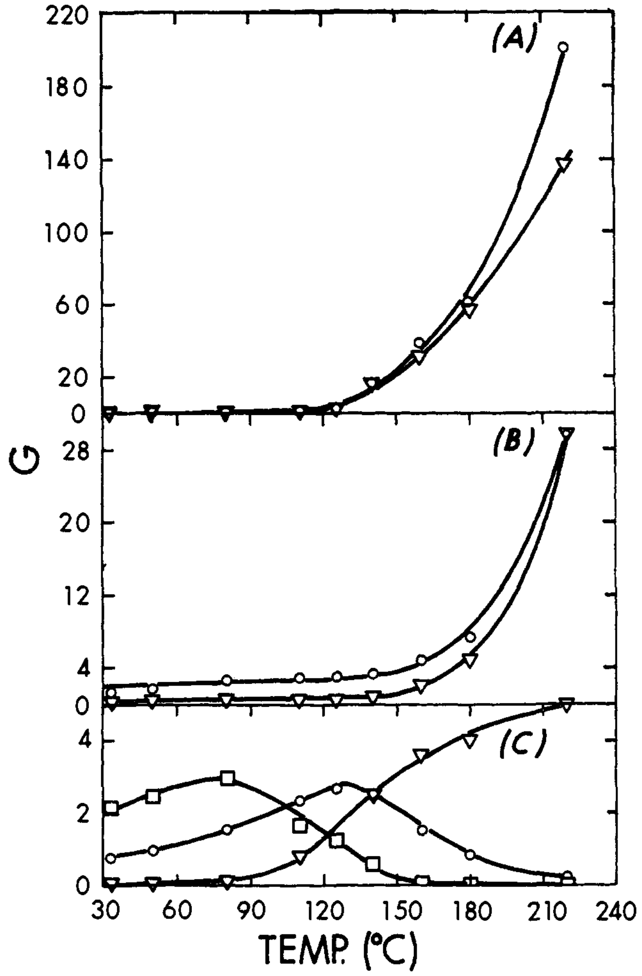


Figure 1. Effect of temperature on product yields: (A) ○ ethane, ▽ acetaldehyde; (B) ○ methane, ▽ carbon monoxide; (C) □ 2,3-diethoxybutane, ○ *sec*-butyl ethyl ether, ▽ *n*-butane.

Pressure has a small effect on the yields of 2,3-diethoxybutane, *sec*-butyl ethyl ether, *n*-butane, and hydrogen (Figure 3C, F) and no effect on the yields of the other products.

Table I. Gas Phase Radiolytic Product Yields at 33°

Product	This study	Ref 3
Hydrogen	5.85	6.40
2,3-Diethoxybutane	2.12	2.40
Ethylene	1.79	2.10
Acetaldehyde	1.40	1.40
Methane	1.55	1.30
Ethyl isopropyl ether	1.08	1.00
Formaldehyde	0.64	0.90
Ethyl *sec*-butyl ether	0.78	0.83
Ethanol	0.63	0.65
Ethane	0.40	0.44
Carbon monoxide	0.47	0.40
Ethyl vinyl ether	0.37	0.40
Ethyl methyl acetal	0.34	0.22
Propane	0.22	0.14
Acetal	<.03	0.09
Acetylene	0.23	0.03
n-Butane	0.06	. . .

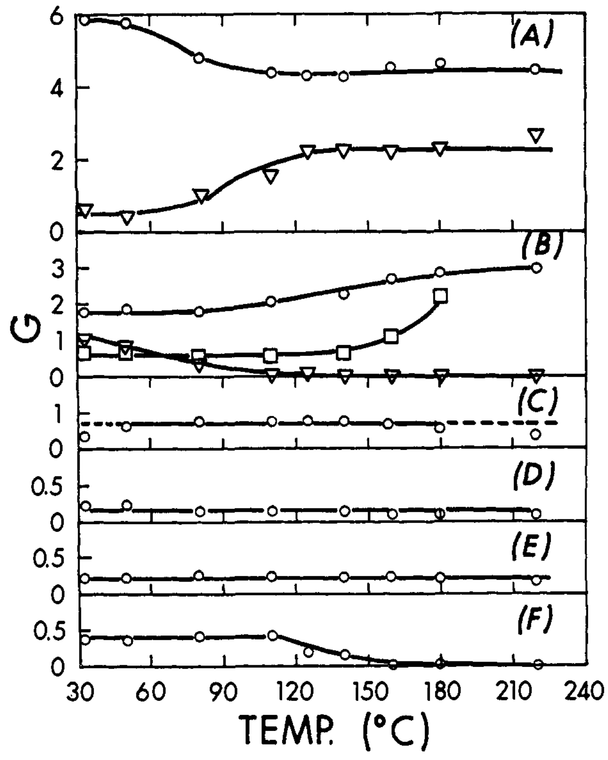


Figure 2. Effect of temperature on product yields: (A) ○ hydrogen, ▽ ethanol; (B) ○ ethylene, ▽ ethyl isopropyl ether, □ formaldehyde; (C) ethyl methyl acetal; (D) propane; (E) acetylene; (F) ethyl vinyl ether.

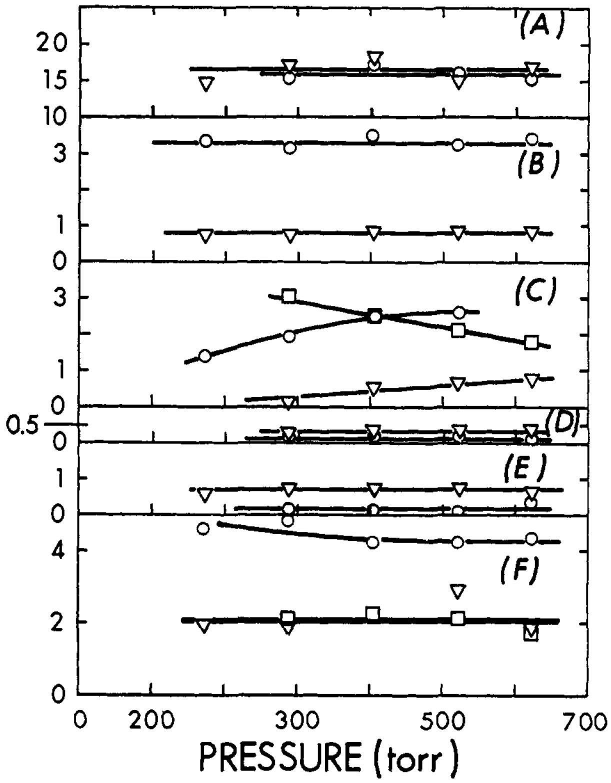


Figure 3. Effect of pressure on product yields at 140°: (A) ○ ethane, ▽ acetaldehyde; (B) ○ methane, ▽ carbon monoxide; (C) ○ *sec*-butyl ethyl ether, ▽ 2,3-diethoxybutane, □ *n*-butane; (D) ○ propane, ▽ acetylene; (E) ○ ethyl vinyl ether, ▽ ethyl methyl acetal; (F) ○ hydrogen, ▽ ethanol, □ ethylene.

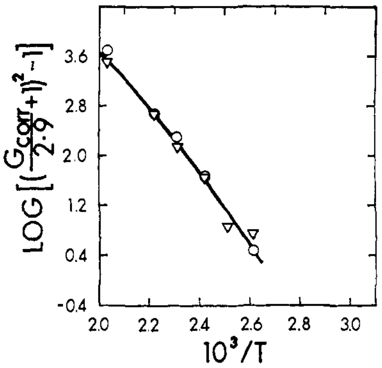


Figure 4. Arrhenius' plot of ethane (○) and acetaldehyde (▽) yields: $G(C_2H_6)_{cor} = G(C_2H_6) - 0.40$; $G(CH_3CHO + CO)_{cor} = G(CH_3CHO + CO) - 1.8$.

Discussion

The Chain Reaction. At high temperatures, the products ethane and acetaldehyde are produced mainly by a chain reaction (Figure 1A). Methane and carbon monoxide are also produced by the chain decomposition of acetaldehyde at these temperatures (Figure 1B), but for the sake of simplicity in this discussion the decomposition of acetaldehyde will be ignored and the total acetaldehyde yield will be taken as the sum of the acetaldehyde and carbon monoxide yields.

The formation of the products ethane, acetaldehyde, *n*-butane, *sec*-butyl ethyl ether, and 2,3-diethoxybutane are explained by the following mechanism.

$$C_2H_5OC_2H_5 \overset{I}{\rightsquigarrow} R + R' \tag{1}$$

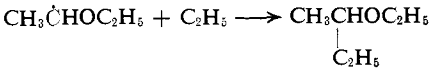
$$R + C_2H_5OC_2H_5 \longrightarrow RH + CH_3\dot{C}HOC_2H_5 \tag{2}$$

$$R' + C_2H_5OC_2H_5 \longrightarrow R'H + CH_3\dot{C}HOC_2H_5 \tag{3}$$

$$CH_3\dot{C}HOC_2H_5 \longrightarrow CH_3CHO + C_2H_5 \tag{4}$$

$$C_2H_5 + C_2H_5OC_2H_5 \longrightarrow C_2H_6 + CH_3\dot{C}HOC_2H_5 \tag{5}$$

$$2CH_3\dot{C}HOC_2H_5 \longrightarrow (CH_3CHOC_2H_5)_2 \tag{6}$$



$$CH_3\dot{C}HOC_2H_5 + C_2H_5 \longrightarrow CH_3\underset{\displaystyle C_2H_5}{\underset{|}{C}}HOC_2H_5 \tag{7}$$

$$2C_2H_5 \longrightarrow C_4H_{10} \tag{8}$$

where R and R′ are radicals and

$$I = 10^{-2}DG(\mathrm{R}) \tag{i}$$

where D is the dose rate (ev/cc sec) and G(R) is the 100-ev yield of R.

The disproportionation counterparts of reactions 6, 7, and 8 occur to a smaller extent.

$$2CH_3\dot{C}HOC_2H_5 \longrightarrow C_2H_5OC_2H_5 + CH_2{=}CHOC_2H_5 \tag{9}$$

$$CH_3\dot{C}HOC_2H_5 + C_2H_5 \longrightarrow C_2H_5OC_2H_5 + C_2H_4 \tag{10}$$

$$\longrightarrow CH_2{=}CHOC_2H_5 + C_2H_6 \tag{11}$$

$$2C_2H_5 \longrightarrow C_2H_6 + C_2H_4 \tag{12}$$

It is known that $k_{12}/k_8 = 0.14$.[10] An upper limit of $k_9/k_6 \leqslant 0.14$ is obtained from the ratio of the yields of ethyl vinyl ether and 2,3-diethoxybutane at 80°. An upper limit of $k_{11}/k_7 \leqslant 0.07$ is obtained from the ratio of the yields of ethyl vinyl ether and *sec*-butyl ethyl ether at 125°, and it is reasonable to assume that $(k_{10} + k_{11})/k_7 \leqslant 0.14$.

Since reactions 9–12 occur to a much smaller extent than do reactions 6–8, the discussion of the chain mechanism will be further simplified by neglecting the disproportionation reactions. This will not alter the conclusions or the values of the activation energies obtained.

The sum of the G values of the products of the chain-terminating reactions 6–8 is constant at 5.1 ± 0.3 at temperatures greater than 80°, so steady-state kinetics can be applied to the simplified chain mechanism in this temperature region. The value of G(R) is approximately $5.1 \times 1.14 = 5.8$.

The yields of the chain-termination products (Figure 1C) indicate that, in the temperature region from about 100 to 140°, the rate of formation of ethane should be described by the following rate equation.

$$\frac{d[C_2H_6]}{dt} = -\frac{I}{2} + \left\{\left(\frac{I}{2}\right)^2 + \frac{k_4k_5}{k_7}I[C_2H_5OC_2H_5]\right\}^{1/2} \tag{ii}$$

This is because the average kinetic effects of reactions 6–8 in this temperature region are approximately the same as those that would be observed if chain termination occurred only by reaction 7. Furthermore, chain initiation is first order in ether concentration, *i.e.*

$$I = A'[C_2H_5OC_2H_5] \tag{iii}$$

where A' is a proportionality constant that depends on the γ-beam intensity, the ether molecular absorption coefficient, and the efficiency of reaction 1. Therefore

$$\frac{d[C_2H_6]}{dt} = \left\{-A + \left(A^2 + \frac{2k_4k_5}{k_7}A\right)^{1/2}\right\}[C_2H_5OC_2H_5] \tag{iv}$$

where $A = A'/2$. The value of $G(C_2H_6)$ is given by

$$G(C_2H_6) = \frac{10^2}{D}\frac{d[C_2H_6]}{dt} \tag{v}$$

From eq i, iii, iv, and v we obtain

$$G(C_2H_6) = \frac{G(\mathrm{R})}{2}\left\{-1 + \left(1 + \frac{2k_4k_5}{k_7A}\right)^{1/2}\right\} \tag{vi}$$

Since G(R) is expected to be independent of ether concentration, $G(C_2H_6)$ should also be independent of ether concentration in this temperature region.

It can readily be shown that $G(CH_3CHO)$ should also be independent of ether concentration in this temperature region. Values of $G(C_2H_6)$ and $G(CH_3CHO)$ at 140° were found to be independent of ether pressure over the range 172 to 622 torr (Figure 3A), as expected. At temperatures greater than 80°, $G(\mathrm{R})/2 = 2.9$. Thus eq vi can be rearranged to

$$\left[\frac{G(C_2H_6)}{2.9} + 1\right]^2 - 1 = \frac{2k_4k_5}{k_7A} \tag{vii}$$

The logarithm of the left-hand side of eq vii was plotted against $1/T$, where T is the absolute temperature (Figure 4). A small amount of ethane is formed by another mechanism ($G = 0.40$ at 33 and 50°), so this was subtracted from the higher temperature yields in the present treatment. The net G value is designated as G_{cor}. The acetaldehyde yields were similarly treated and are also plotted in Figure 4. From the slope of the

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(10) J. C. J. Thynne, *Trans. Faraday Soc.*, **58**, 676 (1962).

curve in the region that corresponds to temperatures 110 to 140°, the value $(E_4 + E_5 - E_7) = 28$ kcal/mole was calculated, where E_4 is the activation energy of reaction 4, and so on. However, $E_7 \approx 0$, so $(E_4 + E_5) = 28$ kcal/mole.

At temperatures greater than 200°, the main chain termination product is *n*-butane (Figure 1C), so termination occurs mainly by reaction 8. Under these conditions, the value of $G(C_2H_6)$ can be shown to be

$$G(C_2H_6) = \frac{k_5}{k_8^{1/2}}\left\{\frac{[C_2H_5OC_2H_5]}{A'}\right\}^{1/2} G(R) \qquad \text{(viii)}$$

The concentration of ether was constant in these experiments, so one could obtain the value of $(E_5 - {}^1/_2E_8)$ by plotting log $G(C_2H_6)$ *vs.* $1/T$. The yields of ethane are so large at temperatures greater than 160° that the left-hand side of eq vii is essentially equal to $[G(C_2H_6)/2.9]^2$. Thus the value of $(2E_5 - E_8)$ can be calculated from the slope of the upper portion of the curve in Figure 4. The value of E_8 is zero, so $E_5 = 9$ kcal/mole. Furthermore, $E_4 = 19$ kcal/mole. Long and Skirrow[11] have reported $E_4 = 23.5 \pm 2$ kcal/mole and $E_{13} = 9.75 \pm 0.5$ kcal/mole.

$$CH_3 + C_2H_5OC_2H_5 \longrightarrow CH_4 + CH_3\dot{C}HOC_2H_5 \qquad (13)$$

When the ether pressure is increased, the increased rate of reaction 5 decreases the lifetime of the ethyl radicals in the system. The rate of reaction 4 is not expected to be affected by pressure at these high pressures, so the lifetime of the $CH_3\dot{C}HOC_2H_5$ radicals should be independent of ether pressure. One therefore expects the yield of *n*-butane to decrease and that of 2,3-diethoxybutane to increase with increasing ether pressure. This was observed (Figure 3C).

The value of the ratio $G(C_4H_9OC_2H_5)/[G(n\text{-}C_4H_{10}) \times G((CH_3CHOC_2H_5)_2)]^{1/2}$ is 2.2 ± 0.2 at all temperatures at which it could be determined (Table II). This value is consistent with the suggestion that these products are formed exclusively by reactions 6–8.

Table II. Ratio of Products of Radical–Radical Reactions

Temp, °C	$G(C_4H_9OC_2H_5)/[G(n\text{-}C_4H_{10}) \times G(CH_3CHOC_2H_5)_2]^{1/2}$
33	2.18
50	2.58
80	1.98
110	2.01
140	2.13
	Average 2.2 ± 0.2

Energetics of Reactions 4. Reaction 4 is 5 kcal/mole endothermic.[12] The fact that $E_4 = 19$ kcal/mole indicates that the activation energy of the reverse reaction

$$C_2H_5 + CH_3CHO \longrightarrow C_2H_5O\dot{C}HCH_3 \qquad (14)$$

is $E_{14} = 14$ kcal/mole. This accounts for the fact that reaction 14 has never been observed to occur. The more favorable metathetical reaction occurs instead.[17]

$$C_2H_5 + CH_3CHO \longrightarrow C_2H_6 + CH_3CO \qquad (15)$$

Similar energetics have been observed in the decomposition of other oxygen-containing radicals.

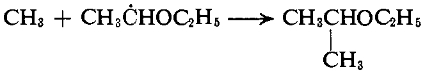
	ΔH, kcal/mole	E, kcal/mole
$CH_3CH_2O \longrightarrow CH_3 + CH_2O$	13[16]	21[16]
$(CH_3)_3CO \longrightarrow CH_3 + (CH_3)_2CO$	4.7[16]	12[18]

Other Reactions. The hydrogen yield decreased $(\Delta G(H_2) = 1.5)$ by approximately the same amount as the ethanol yield increased $(\Delta G(C_2H_5OH) = 1.6)$ as the temperature was increased from 33 to 125° (Figure 2A). The yields of these products are independent of temperature in the range 125 to 220° and at these temperatures are nearly the same as the yields in the liquid phase radiolysis at 33°. In the high-temperature vapor, $G(H_2) = 4.4$ and $G(C_2H_5OH) = 2.3$, whereas the liquid phase yields at 33° are $G(H_2) = 3.7$ and $G(C_2H_5OH) = 2.1$.[2] The reason for this similarity is not obvious.

The inverse parallelism in the changes of the hydrogen and ethanol yields with increasing temperature in the gas phase indicates that one of the low temperature precursors of hydrogen becomes a precursor of ethanol at higher temperatures.

Most of the increase in ethylene yield (Figure 2B) with increasing temperature results from the disproportionation of ethyl radicals. The nonradical yield of ethylene is constant at $G = 1.8$ up to 140°, then increases gradually to 2.2 at 220°.

Ethyl isopropyl ether is presumably formed by the reaction

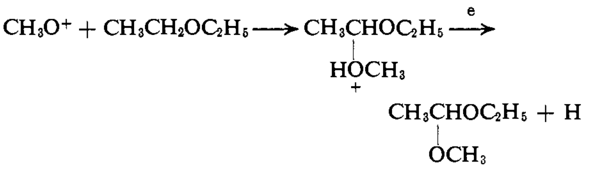


$$CH_3 + CH_3\dot{C}HOC_2H_5 \longrightarrow \underset{\displaystyle CH_3}{CH_3CHOC_2H_5} \qquad (16)$$

The yield of this product decreases with increasing temperature (Figure 2B) because the ether radicals decompose (reaction 4) and the methyl radicals react metathetically.

$$CH_3 + C_2H_5OC_2H_5 \longrightarrow CH_4 + CH_3\dot{C}HOC_2H_5 \qquad (17)$$

The yield of ethyl methyl acetal is independent of temperature over the range 50 to 180° (Figure 2C). This product was probably formed by the reactions



$$CH_3O^+ + CH_3CH_2OC_2H_5 \longrightarrow \underset{\displaystyle H\overset{+}{O}CH_3}{CH_3CHOC_2H_5} \xrightarrow{e} \underset{\displaystyle OCH_3}{CH_3CHOC_2H_5} + H \qquad (18)$$

The product identified as diethoxymethane in the earlier work[3] was probably ethyl methyl acetal.

There is not sufficient information to make speculation about the modes of formation of the other products worthwhile.

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[11] J. Long and G. Skirrow, *Trans. Faraday Soc.*, **58**, 1403 (1962).

[12] Calculated from the following heats of formation and bond dissociation energies (in kcal/mole), at 25°: $C_2H_5OC_2H_5$, −60.3;[13] CH_3CHO, −39.8;[14] C_2H_5, 26.7;[15] H, 52.1;[15] $D(C_2H_5OCH(CH_3){-}H$, 94.[16] Therefore, $\Delta H_f°(CH_3\dot{C}HOC_2H_5) = -18.4$ kcal/mole.

[13] G. Pilcher, H. A. Skinner, A. S. Pell, and A. E. Pope, *Trans. Faraday Soc.*, **59**, 316 (1963).

[14] F. T. Wall, "Chemical Thermodynamics," 2nd ed, W. H. Freeman and Co., San Francisco, Calif., 1965, p 54.

[15] "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Co., Cleveland, Ohio, 1965–1966, pp F-126 and F-128.

[16] P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

[17] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 117 (1961).

[18] L. M. Terman, *Russ. Chem. Rev.*, **34**, 185 (1965).