Radiation-Sensitized Pyrolysis of Diethyl Ether. Free-Radical Reaction Rate Parameters[1]

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Abstract: The γ-radiation-induced pyrolysis of diethyl ether was studied at pressures from 35 to 2100 Torr and temperatures from 84 to 403°. The ether decomposed by a chain mechanism to form $CH_3CHO + C_2H_6$ at temperatures above 84°; above 230° a second chain formed C_2H_4 and presumably C_2H_5OH. The ethylene yield increased from 1 to 6% of the ethane yield as the temperature was increased from 257 to 403°. Hydrogen was not a chain product. The pressure and temperature dependences of the various product yields are consistent with the proposed free-radical mechanism. The following reaction rate parameters have been determined: $CH_3\dot{C}HOC_2H_5 \rightarrow CH_3CHO + C_2H_5$ (7), $\log k_7\ (\text{sec}^{-1}) = (9.7 \pm 1.1) - (16{,}000 \pm 2{,}000)/2.3\ RT$; $C_2H_5 + C_2H_5OC_2H_5 \rightarrow C_2H_6 + CH_3\dot{C}HOC_2H_5$ (8), $\log k_8\ [\text{cm}^3/(\text{mol sec})] = (11.9 \pm 0.2) - (10{,}500 \pm 500)/2.3RT$; $C_2H_5 + CH_3CHO \rightarrow C_2H_6 + CH_3\dot{C}O$ (13), $\log k_{13} = (12.1 \pm 0.6) - (8{,}500 \pm 1{,}500)/2.3RT$; $\dot{C}H_2CH_2OC_2H_5 \rightarrow C_2H_4 + C_2H_5O$ (20), $E_{20} = 22 \pm 4$ kcal/mol. The frequency factor and activation energy of reaction 7 are much lower than earlier estimates, but $E_7 = 16 \pm 2$ kcal/mol is still much greater than the heat of reaction, $\Delta H_7 \approx 5$ kcal/mol. The large negative entropy of activation, $\Delta S_7^{\ddagger} = -17 \pm 5$ cal/(deg mol), is not readily understood on the basis of current knowledge, but it is consistent with information derivable from other careful studies of radical decomposition reactions.

Information about the chain reactions that occur in pyrolysis systems and about free-radical reactions in general can be obtained by the radiation-sensitized pyrolysis technique. The presence of ions in the radiolysis system does not complicate the study of the neutral free-radical reactions. For example, in diethyl ether the ions are mainly the relatively inactive $(C_2H_5OC_2H_5)_nH^+$, which upon neutralization form free radicals that initiate the reaction chains.

An earlier study of the decomposition of diethyl ether by this method[2] was limited to temperatures below 230°, partly because of difficulties with the design of a suitable furnace that could be used inside a Gammacell. Some of the difficulties have now been overcome, and the results of experiments done at temperatures up to 400° are presented and discussed in this article. Additional information has been obtained about the free-radical reactions involved. The unimolecular decomposition of the $CH_3\dot{C}HOC_2H_5$ radical has a lower frequency factor than is usually ascribed to that kind of reaction.

Experimental Section

Materials and Sample Preparation. The materials and sample preparation techniques were the same as those reported earlier.[2] However, the volumes of the spherical irradiation bulbs used were 50, 100, 250, and 500 ml; higher gas density samples were contained in smaller bulbs to limit the sample size to an amount that could be totally injected onto a gas chromatographic column.

Sample Heating and Irradiation. The filled and sealed sample bulb was placed into the furnace that is sketched in Figure 1, and the furnace was put into the chamber of a Gammacell-220 (Atomic Energy of Canada, Ltd.). With the Gammacell in the nonirradiation position, the sample was heated to the desired temperature. The sample and furnace were then lowered into the radiation position. During irradiation the temperature was maintained constant within 1% of the set centigrade reading. The sample was then removed from the Gammacell, cooled with a stream of air (~4 min), and analyzed.

The furnace contained four thermocouples (Figure 1). The one in the wall was connected to an API Instrument Co. proportional temperature controller, Model 226. The three thermocouples inside the furnace chamber registered the same temperatures within 1% of their centigrade readings, but 6–9° higher than the one in the wall, depending on the temperature. The average reading of the three inside thermocouples was taken as the sample temperature.

The irradiation dose rate was 5.2×10^{17} eV/(g min) in the ether.

Analysis. All products were measured by gas chromatography, using a Hewlett-Packard 5750 instrument with dual thermal conductivity detectors. The dual columns were 6 ft × 0.25 in. Pyrex spirals, packed with various materials.

Hydrogen, methane, and carbon monoxide were separated from the irradiated sample by vacuum distillation through two traps at −196°. The mixed gases were collected and measured in a Toepler–McLeod apparatus, then injected onto a molecular sieve 5A column.

After removal of the above-mentioned gases, the sample was condensed into a 60 × 6 mm tube and sealed with a flame, taking care not to pyrolyze any of the sample. The tube was then put into a heated crushing device in the carrier gas stream of the gas chromatograph and broken. The products were separated on a temperature-programmed Porapak T column; after ethylene and ethane had come off at 25° the temperature was raised to 150° at a rate of 6°/min.

Authentic samples of the products were used to determine the gc calibration factors.

Many of the results shown in the figures are the averages from two or three samples.

Results

Effect of Temperature. Samples (0.078 g) of diethyl ether contained in 100-ml bulbs were irradiated to a dose of 1.6×10^{19} eV/g at temperatures from 84 to 403°. The amount of ether corresponds to a pressure of 348 Torr at 257° and a concentration of 1.05×10^{-5} mol/cm^3.

"Blank" samples were prepared and put through the same temperature cycle as the normal samples, but were not irradiated. The temperatures at which the various products became detectable, and their Arrhenius temperature coefficients, are listed in Table I. By comparison with the radiation-induced yields, the amounts of products formed in the blanks were negligible at $t < 350°$ and reached a maximum of 13% of the induced yield at 403°. The radiation-induced and

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

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

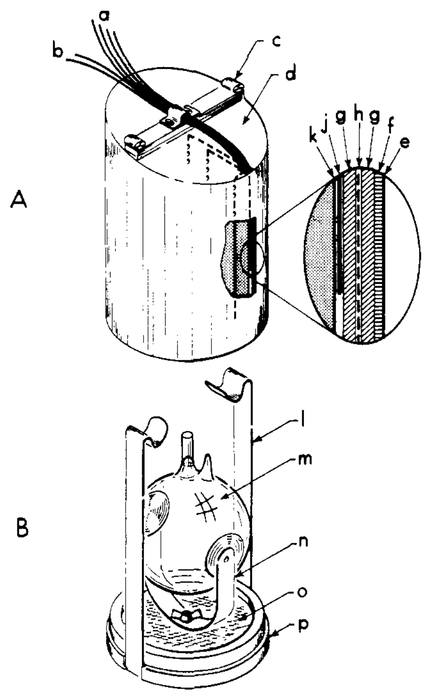

Figure 1. Furnace for irradiation cells. A, upper part: (a) four pairs of iron–constantan thermocouple leads; (b) power leads; (c) catch for spring clamp l on lower part; (d) insulated top, sloped for optimum space utilization; (e) aluminum outer wall; (f) Fyrepel heat reflector; (g) Fiberfray 9705 insulation; (h) 0.06 in. × 0.005 in. Nichrome ribbon, 32 ft, 60 ohms; (j) asbestos-coated iron–constantan thermocouple; (k) steel inner wall. The three thermocouples other than j are at different locations in the gas space inside the furnace. B, lower part: (l) spring clamp which holds lower and upper parts together; (m) sample bulb; (n) spring clamp for bulb, changeable for different bulb sizes; (o) heat reflector and insulation; (p) machined hard asbestos board base plate.

the blank reactions are kinetically linked in the radiolysis system, so a simple subtraction cannot be made. The blank correction is made during the kinetic analysis in the Discussion section.

Table I. Pyrolysis Products in Unirradiated "Blank" Samples of Diethyl Ether[a]

Product	Detection[b] temp, °C	E_a,[c] kcal/mol
C_2H_6	300	29 ± 5
CH_3CHO	300	29 ± 5[d]
CH_4	350	49 ± 5
CO	350	49 ± 5
C_2H_4	350	49 ± 5
n-C_4H_{10}	$\gtrsim$400	

[a] Ether density = 0.78 g/l. [b] Temperature at which the product became detectable after the sample had been put through a normal temperature cycle (30 min of heating + 30 min at t_{max} + 4 min of cooling), but in the absence of radiation. [c] Arrhenius temperature coefficient. These values are lower than those for homogeneous pyrolysis (ref 6) and indicate that our "blank" reactions were catalyzed by the vessel surface. [d] Obtained from a plot of the sum of the acetaldehyde and carbon monoxide yields.

To simplify the presentation of the radiolysis results they are divided into two groups: product yields from nonchain reactions and those from chain reactions. The measured products of the chain processes were acetaldehyde, ethane, ethylene, methane, and carbon monoxide. Small amounts of these compounds were also formed by nonchain mechanisms, as a result of the direct radiolysis of the ether. The nonchain yields are the total yields measured at the lower temperatures and are listed in Table II. The amounts of products formed by chain reactions at higher temperatures were determined by subtracting the nonchain yields from the measured yields: $G_{chain} = G_{measured} - G_{nonchain}$.

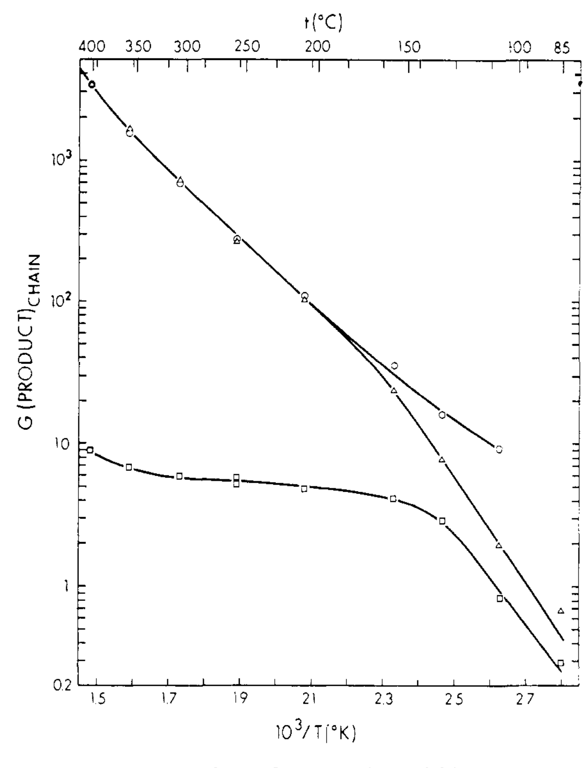

Figure 2. Arrhenius plots of the product yields from the main chain reaction: ○, $G(CH_3CHO + CO) - 2.4$; △, $G(C_2H_6) - 0.4$; □, $G(n\text{-}C_4H_{10})$. Ether density = 0.78 g/l., 1.05 × 10^{-5} mol/cm^3.

Table II. Diethyl Ether Vapor Radiolysis.
Measured Product Yields from Nonchain Reactions

Product	G_{nc}	t, °C[a]
C_2H_6[b]	0.4	80
CH_3CHO[b]	1.4	80
CH_4	3.0	160
CO	1.0	160
C_2H_4	2.7	200

[a] Nonchain yields were measured at temperatures below t°. [b] Results from ref 2.

The stoichiometric equation that represents the main chain process is

$$C_2H_5OC_2H_5 \longrightarrow CH_3CHO + C_2H_6 \qquad (1)$$

Some of the acetaldehyde formed in (1) decomposes in an induced chain reaction represented by

$$CH_3CHO \longrightarrow CH_4 + CO \qquad (2)$$

The extent of (1) is therefore represented by either the ethane yield, $G(C_2H_6)_{chain}$, or the sum of the acetaldehyde and carbon monoxide yields, $G(CH_3CHO + CO)_{chain}$. Arrhenius plots of these quantities are given in Figure 2. The activation energy of (1) is 11 kcal/mol at high temperatures and increases at temperatures below about 180°.

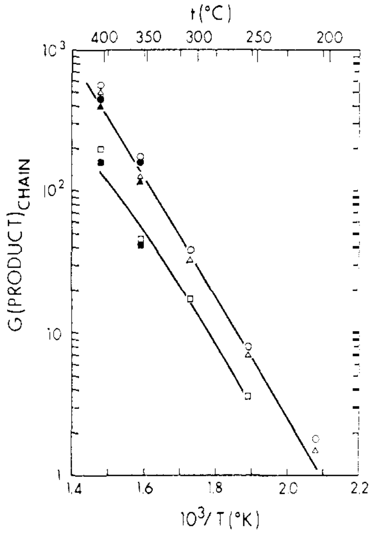

Figure 3. Arrhenius plots of the product yields from the minor chain reactions: ○, $G(CH_4)$ – 3.0; △, $G(CO)$ – 1.0; □, $G(C_2H_4)$ – 2.7; ●, ▲, and ■, yields corrected to remove the influence of thermal initiation, by dividing the chain yields by $(G(C_4H_{10})/6)^{0.5}$. Ether concentration = 1.05×10^{-5} mol/cm^3.

The chain termination product in 1×10^{-5} mol/ml of ether at temperatures above 180° is almost exclusively *n*-butane.[2] The butane yield is also shown in Figure 2. The Arrhenius temperature coefficient of butane formation at 100° is about 16 kcal/mol, and it decreases toward zero with increasing temperature. The increase in yield at $t \geq 350°$ is probably due to thermal initiation of the chain reaction.

The extent of the secondary chain process (2) is represented by either $G(CH_4)_{chain}$ or $G(CO)_{chain}$. Arrhenius plots of these quantities are presented in Figure 3. The Arrhenius temperature coefficient for the chain formation of methane and carbon monoxide is 19 ± 1 kcal/mol between 200 and 400°.

The large yields of ethylene formed at high temperatures (Figure 3) indicate that it also was formed by a chain reaction, with an overall activation energy of 18 ± 2 kcal/mol over the temperature range from 257 to 403°. The stoichiometric equation was no doubt (3).[3] The product ethanol was not measured, due to

$$C_2H_5OC_2H_5 \longrightarrow C_2H_5OH + C_2H_4 \qquad (3)$$

analytical difficulties.

Hydrogen was not a chain product: $G(H_2) \approx 5$ at 257 and 307°, equal to the nonchain yield.[2]

To illustrate the relative magnitudes of the different reaction chains, the G values of the corresponding pairs of products at 300° are listed in Table III. The activation energies of the chains are also given for this temperature.

Table III. Radiation-Induced Pyrolysis of Diethyl Ether at 300°. G Values and Activation Energies of Formation of Chain Products[a]

Product pair	G_{chain}	E_a, kcal/mol
$CH_3CHO + C_2H_6$	660	11 ± 1
$CH_4 + CO$	31	19 ± 1
$C_2H_4\ (+C_2H_5OH)$	14	18 ± 2

[a] Ether density = 0.78 g/l. (1.05×10^{-5} mol/cm^3); dose = 1.6×10^{19} eV/g.

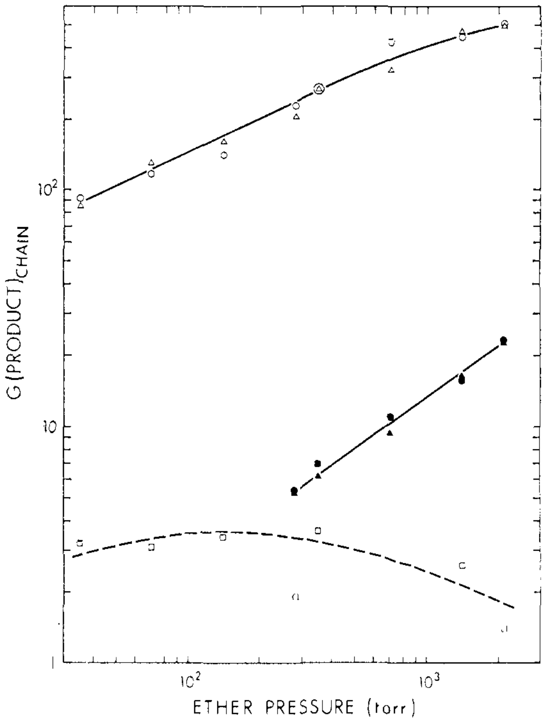

Figure 4. Yields of chain reactions as functions of ether pressure at 257°: ○, $G(CH_3CHO + CO)$ – 2.4; △, $G(C_2H_6)$ – 0.4; ●, $G(CH_4)$ – 3.0; ▲, $G(CO)$ – 1.0; □, $G(C_2H_4)$ – 2.7; 100 Torr ≡ 3.02×10^{-6} mol/cm^3.

Effect of Pressure at 257°. The pressure was varied from 35 to 2100 Torr by placing from 0.04 to 0.24 g of ether into bulbs that had volumes of from 50 to 500 cm^3. The samples were given a dose of 1.6×10^{19} eV/g.

The butane G value was 6.0 ± 0.3, independent of pressure up to 700 Torr, and decreased to 5.0 at 2100 Torr.

The G values of ethane, acetaldehyde, methane, and carbon monoxide increased with increasing pressure (Figure 4). The nonchain yields of ethane and acetaldehyde were negligible under the present conditions and the chain yields at low ether pressures increased according to expression i. The slope of the curve decreased at high pressures. The nonchain yields of

$$G(C_2H_6)_{chain} \approx G(CH_3CHO + CO)_{chain} \propto [\text{ether}]^{0.5} \qquad \text{(i)}$$

methane and carbon monoxide were independent of pressure,[2] but the chain yields increased according to

$$G(CH_4)_{chain} \approx G(CO)_{chain} \propto [\text{ether}]^{0.72} \qquad \text{(ii)}$$

The nonchain yield of ethylene was independent of pressure.[2] The chain yields were small at this temperature, and the relative precision of their measurement decreased with increasing ether pressure because the fractional content of ethylene in the products decreased (Figure 4). The G value was roughly independent of pressure. The dashed curve in Figure 4 was drawn with the shape expected from the mechanism proposed in the Discussion section. At 350 Torr the approximate result is

$$G(C_2H_4)_{chain} \propto [\text{ether}]^{-0.15 \pm 0.15} \qquad \text{(iii)}$$

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[3] G. R. Freeman, *Proc. Roy. Soc., Ser. A*, **245**, 75 (1958).

Effect of Surface/Volume Ratio. To determine whether the different sizes of reaction bulbs used in the pressure study affected the results, 70 Torr of ether was irradiated at 257° in a bulb of each volume, *i.e.* 50, 100, 250, and 500 ml. Although the surface/volume ratio changed 2.2-fold, the measured product yields were the same in all bulbs within experimental error.

Effect of Dose. Samples of ether at 348 Torr were given doses in the range from 2×10^{18} to 1.3×10^{20} eV/g at 257°. The yields of all the products except carbon monoxide and methane were independent of the dose: $G(C_2H_6) \approx G(CH_3CHO) \approx 270 \pm 10$, $G(n\text{-}C_4H_{10}) = 5.7 \pm 0.1$, $G(C_2H_4) = 5.3 \pm 0.6$. However, G(CO) and $G(CH_4)$ increased linearly with dose, as shown in Figure 5; the intercepts at zero dose correspond to the nonchain yields.

Discussion

1. $C_2H_5OC_2H_5 \rightarrow CH_3CHO + C_2H_6$

(a) Mechanism. The present results substantiate the free-radical mechanism that was proposed earlier,[2] namely

$$C_2H_5OC_2H_5 \rightsquigarrow R + R' \tag{4}$$

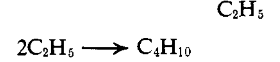
$$R + C_2H_5OC_2H_5 \longrightarrow RH + CH_3\dot{C}HOC_2H_5 \tag{5}$$

$$R' + C_2H_5OC_2H_5 \longrightarrow R'H + CH_3\dot{C}HOC_2H_5 \tag{6}$$

$$CH_3\dot{C}HOC_2H_5 \longrightarrow CH_3CHO + C_2H_5 \tag{7}$$

$$C_2H_5 + C_2H_5OC_2H_5 \longrightarrow C_2H_6 + CH_3\dot{C}HOC_2H_5 \tag{8}$$

$$2CH_3\dot{C}HOC_2H_5 \longrightarrow (CH_3CHOC_2H_5)_2 \tag{9}$$



$$CH_3\dot{C}HOC_2H_5 + C_2H_5 \longrightarrow CH_3\underset{\underset{C_2H_5}{|}}{C}HOC_2H_5 \tag{10}$$

$$2C_2H_5 \longrightarrow C_4H_{10} \tag{11}$$

where R and R′ are radicals.

Reaction 4 is first order,[2] although it involves several steps. The steps include excitation and ionization of the molecules by the radiation, decomposition of excited molecules, ion–molecule reactions, ion neutralization, and so on. One may write

$$\text{rate of (4)} = \mathbf{k}_4[\text{ether}] = 10^{-2}DG(\text{R}) \tag{iv}$$

where D is the absorbed dose rate [eV/(cm^3 sec)] and G(R) is the 100-eV yield of R. However, in the present system

$$\begin{aligned} D &= 5.2 \times 10^{17} \quad \text{eV/(g min)} \\ &= 1.07 \times 10^{-6}\,[\text{ether}] \quad \text{eV/(cm}^3\text{ sec)} \end{aligned} \tag{v}$$

where [ether] is expressed in molecules/cm^3. From eq iv and v one obtains

$$\begin{aligned} \mathbf{k}_4 &= 1.07 \times 10^{-8}G(\text{R}) \quad \text{sec}^{-1} \\ &\approx 6 \times 10^{-8} \quad \text{sec}^{-1} \end{aligned} \tag{vi}$$

since $G(\text{R}) = 6$ in the present system. The value of $\mathbf{k}_4$ is proportional to the radiation beam intensity, to the energy absorption coefficient of the ether molecule, and to the probability of occurrence of (4) per unit of energy absorbed. It should be emphasized that $\mathbf{k}_4$ is not a normal rate constant, and that its value is dependent upon the specific radiation source used, among other things. For this reason $\mathbf{k}_4$ is written in boldface.

Reactions 5–11 are elementary and their rate constants are written as, for example, k_7.

The disproportionation counterparts of reactions 9–11 also occur, but $k_{\text{disproportionation}}/k_{\text{combination}} \leq 0.14$ in each case.[2] Whenever one of reactions 9–11 is mentioned in this discussion, the inclusion of the appropriate disproportionation reaction is taken as understood.

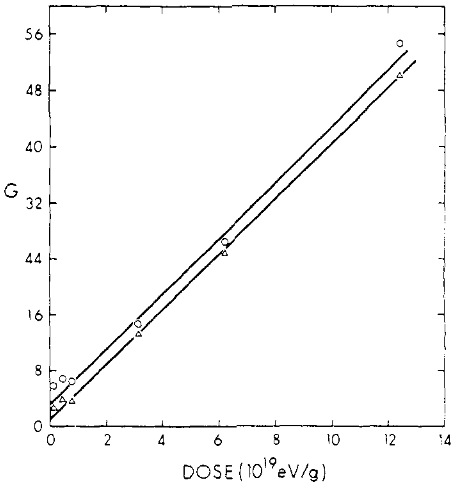


Figure 5. Dose dependence of the carbon monoxide and methane yields at 257° in 348 Torr of ether: O, CH_4; Δ, CO.

(b) Order of Formation of Ethane and Acetaldehyde. The only chain termination product measured in the present experiments was n-butane; the products of the other termination reactions were reported as functions of temperature and pressure in ref 2. At ether concentrations $\leq 10^{-5}$ mol/cm^3 and temperatures above about 180°, the main chain termination product was n-butane (Figure 2 and ref 2), so termination occurred mainly by reaction 11. Under these circumstances, one expects at steady state

$$\text{d}[C_2H_6]/\text{d}t = \text{d}[CH_3CHO]/\text{d}t = k_8(\mathbf{k}_4/k_{11})^{0.5}[\text{ether}]^{1.5} \tag{vii}$$

Thus ethane and acetaldehyde formation should be 1.5 order with respect to ether concentration. Now

$$G(C_2H_6) = (\text{d}[C_2H_6]/\text{d}t)/10^{-2}D \tag{viii}$$

From eq v, vii, and viii one obtains

$$G(C_2H_6) = \frac{k_8}{1.07 \times 10^{-8}}\left(\frac{\mathbf{k}_4}{k_{11}}\right)^{0.5}[\text{ether}]^{0.5} \tag{ix}$$

The plot of log $G(C_2H_6)$ against log [ether] at 257°, shown in Figure 4, has a slope of 0.5 at low pressures, in agreement with eq ix.

From eq vii and ix one may generalize that when the order of formation of product P is n, a plot of log G(P) against log [ether] has a slope equal to $n - 1$.

At ether pressures of several hundred Torr and temperatures between about 100 and 140°, the main chain termination reaction was (10).[2] Under these conditions, one finds the formation of ethane and acetaldehyde to be first order with respect to ether concentration.[2] The value of $G(C_2H_6)_{\text{chain}}$ is given by eq x and that of $G(CH_3CHO)_{\text{chain}}$ is given by (xi), where $b = 4k_7k_8/\mathbf{k}_4k_{10}$.

$$G(C_2H_6)_{\text{chain}} = (G(\text{R})/2)\{-1 + (1 + b)^{0.5}\} \tag{x}$$

$$G(CH_3CHO)_{\text{chain}} = G(\text{R})b/[2\{-1 + (1 + b)^{0.5}\}] \tag{xi}$$

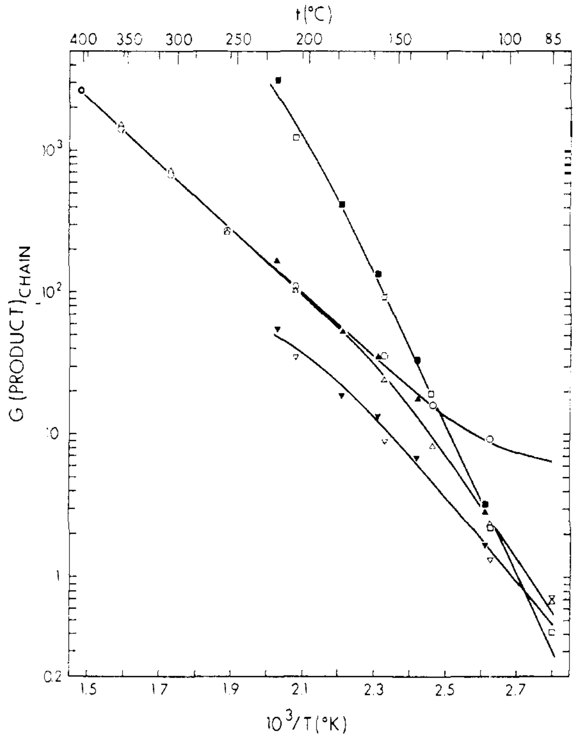


Figure 6. Arrhenius plots of various functions, *F*. *F*: ○, $G(\mathrm{CH_3CHO + CO})_{\mathrm{chain}}$; Δ, $G(\mathrm{C_2H_6})_{\mathrm{chain}}$; ∇, $[\{(G(\mathrm{C_2H_6})_{\mathrm{ch}}/3) + 1\}^2 - 1]^{0.5}$; □, $[k_8\{[\mathrm{ether}]G(\mathrm{C_4H_{10}})/(9 \times 10^6)\}^{0.5} + 1]^2 - 1$. The results from ref 2 (filled points, ether concentration = 1.56×10^{-5} mol/cm^3) have been normalized to an ether concentration of 1.05×10^{-5} mol/cm^3, with the aid of eq vii–xiv and appropriate interpolations. The acetaldehyde and ethane yields at 357 and 403° have been corrected to remove the influence of thermal initiation (see text). The curve through the $G(\mathrm{CH_3CHO + CO})_{\mathrm{chain}}$ points was calculated relative to the $G(\mathrm{C_2H_6})_{\mathrm{chain}}$ curve, using eq x and xi.

If the rate consant of reaction 7 had been in its pressure-dependent region, the order of ethane and acetaldehyde formation would have been greater than 1.0 at the temperature where the rate of reaction 10 was at its maximum. The order was in fact 1.0,[2] and it is concluded that k_7 was at or near the high-pressure limit under the experimental conditions used in both the earlier[2] and present work.

(c) **Order of Formation of *n*-Butane.** At temperatures higher than 200°, the rate of butane formation is approximately equal to the rate of the chain initiation reaction, which is first order with respect to ether concentration.

$$\mathrm{d}[\mathrm{C_4H_{10}}]/\mathrm{d}t = k_{11}[\mathrm{C_2H_5}]^2 \approx \mathbf{k}_4[\mathrm{ether}] \qquad \text{(xii)}$$

One therefore expects $G(\mathrm{C_4H_{10}})$ to be independent of ether pressure, as observed at 257°.

At lower temperatures where chain termination is mainly by (10) one has

$$\mathrm{d}[\mathrm{C_4H_{10}}]/\mathrm{d}t = (\mathbf{k}_4{}^2 k_{11}/4k_8{}^2)\,\{-1 + (1 + b)^{0.5}\}^2 \qquad \text{(xiii)}$$

and

$$G(\mathrm{C_4H_{10}}) = (G(\mathrm{R})\mathbf{k}_4 k_{11}/4k_8{}^2) \times \{-1 + (1 + b)^{0.5}\}^2[\mathrm{ether}]^{-1} \qquad \text{(xiv)}$$

Equation xiv shows that at under appropriate conditions the butane yield is inversely proportional to the ether concentration. This behavior was observed at 140° at ether pressures in the vicinity of 600 Torr.[2] At lower temperatures it would occur at lower pressures.

(d) **Reaction Rate Parameters.** Taking the activation energies of reactions 4, 9, 10, and 11 as zero, and $k_9 = k_{10} = k_{11} = 10^{14}$ cm^3/(mol sec),[4] the frequency factors and activation energies of reactions 7 and 8 can be obtained from the results in Figure 2. The experimental results from ref 2 are included in the kinetic analysis for purposes of comparison.

To facilitate the treatment of the data, the yields from ref 2 were normalized to the ether concentration (1.05×10^{-5} mol/cm^3) used in the present experiments, and the contribution of thermal initiation at $t > 350°$ was removed (Figure 6). The pressure normalization was done with the aid of eq vii–xiv and appropriate interpolations. The correction for thermal initiation was made by multiplying the measured yields at 350 and 400° by $(G(\mathrm{C_4H_{10}})/6)^{0.5}$, where 6 is the maximum butane yield that results from the radiation-induced reactions.

At temperatures above 200° the formation of ethane and acetaldehyde is approximately 1.5 order; the appropriate rate equations are vii and ix. From the slope of the Arrhenius plot of the yields of these products at $t > 200°$ (Figure 6) we calculate the activation energy $E_8 = 10.5 \pm 0.5$ kcal/mol.

The value of $G(\mathrm{C_2H_6})$ is 700 at 307° when the ether concentration is 1.05×10^{-5} mol/cm^3 (Figure 6). Substitution of these quantities and the values of $\mathbf{k}_4$ and k_{11} into eq ix gives $k_8 = 9.4 \times 10^7$ cm^3/(mol sec) at 307°. We therefore obtain

$$\log k_8\,[\mathrm{cm^3/(mol\ sec)}] = (11.9 \pm 0.2) - (10{,}500 \pm 500)/2.3RT \qquad \text{(xv)}$$

The first-order rate equation (x) can be rearranged to

$$\left[\left\{\frac{2G(\mathrm{C_2H_6})}{G(\mathrm{R})} + 1\right\}^2 - 1\right]^{0.5} = \left(\frac{4k_7k_8}{\mathbf{k}_4 k_{10}}\right)^{0.5} \qquad \text{(xvi)}$$

An Arrhenius plot of the left-hand side of (xvi) is given in Figure 6. The 0.5 power of the functions in eq xvi was used simply to separate the points of the different plots in Figure 6. One can deduce from information in ref 2 and in the present article that for an ether concentration of 1.05×10^{-5} mol/cm^3 the order of ethane formation was 1.0 at about 115°. The slope of the Arrhenius plot of (xvi), taken at 115°, gives $0.5(E_7 + E_8) = 13.3 \pm 0.9$ kcal/mol; therefore, $E_7 = 16 \pm 2$ kcal/mol.

A value of E_7 can also be deduced from the butane yields. When ethane formation is first order $G(\mathrm{C_4H_{10}})$ is given by eq xiv, which can be rearranged to

$$\left[2k_8\left\{\frac{[\mathrm{ether}]G(\mathrm{C_4H_{10}})}{\mathbf{k}_4 k_{11} G(\mathrm{R})}\right\}^{0.5} + 1\right]^2 - 1 = \frac{4k_7k_8}{\mathbf{k}_4 k_{10}} \qquad \text{(xvii)}$$

An Arrhenius plot of the left side of (xvii) is shown in Figure 6. The slope in the region of 115° gives $(E_7 + E_8) = 24.4 \pm 0.9$ kcal/mol whence $E_7 = 14 \pm 1$ kcal/mol.

We conclude that $E_7 = 16 \pm 2$ kcal/mol.

At 115° the value of the left side of eq xvi is 2.1 and that of k_8 is 1.0×10^6 cm^3/(mol sec); using $\mathbf{k}_4 = 6 \times 10^{-8}$ sec^{-1} and $k_{10} = 10^{14}$ cm^3/(mol sec), one

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(4) A. F. Trotman-Dickenson, *Advan. Free-Radical Chem.*, 1, (1965).

Table IV. Reaction Rate Parameters

Reaction	t, °C	Log A[a]	E_a, kcal/mol	Ref	ΔH_{th},[b] kcal/mol
(7) $CH_3\dot{C}HOC_2H_5 \rightarrow CH_3CHO + C_2H_5$	110 ± 30	9.7 ± 1.1[c]	16 ± 2	*d*	5
	110 ± 30		19	2	
	163 ± 18	13.7 ± 1[e]	23.5 ± 2	5	
	590 ± 30	13	30	6, *f*	
(8) $C_2H_5 + C_2H_5OC_2H_5 \rightarrow C_2H_6 + CH_3\dot{C}HOC_2H_5$	300 ± 100	11.9 ± 0.2	10.5 ± 0.5	*d*	−5
	220		9	2	
	590 ± 30	11	10	6, *f*	
(12) $CH_3 + C_2H_5OC_2H_5 \rightarrow CH_4 + CH_3\dot{C}HOC_2H_5$	163 ± 18	12.3 ± 0.3[g]	9.75 ± 0.5	5	−11
	590 ± 30	11	10	6, *f*	
(13) $C_2H_5 + CH_3CHO \rightarrow C_2H_6 + CH_3\dot{C}O$	300 ± 100	12.1 ± 0.6	8.5 ± 1.5	*d*	−10
(15) $C_2H_5 + C_2H_5CHO \rightarrow C_2H_6 + C_2H_5\dot{C}O$	280 ± 230	11.1	5.9	4	−10
(16) $CH_3 + CH_3CHO \rightarrow CH_4 + CH_3\dot{C}O$	147 ± 28	11.9	7.6	4	−16
(20) $\dot{C}H_2CH_2OC_2H_5 \rightarrow C_2H_4 + C_2H_5O$	330 ± 77		22 ± 4	*d*	21

[a] The units of A are sec^{-1} for unimolecular and cm^3 mol^{-1} sec^{-1} for bimolecular reactions. All values of A and E_a refer to pressures in the vicinity of 10^2–10^3 Torr. [b] Heat of reaction, calculated from thermodynamic data in the following references and taking $D(C_2H_5OCH_2\text{-}CH_2\text{–}H) = 98$ and $D(C_2H_5OCH(CH_3)\text{–}H) = 93$ kcal/mol: S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [c] Near to infinite pressure values A_∞ and E_∞. [d] Present work. Reported errors in kinetics and most other fields refer to precision, not to accuracy. [e] Calculated from data in ref 5, from which it can be estimated that at 165° the mean lifetime of the radicals with respect to combination was 4 × 10^{-3} sec and k_7 = 100 sec^{-1}. Long and Skirrow[5] stated that log A_7 = 13 would be a reasonable value, but did not calculate it from their results. The value log A_7 = 10.9 quoted in ref 7 and attributed to ref 5 is in error. [f] A and E were not measured, but were listed as values that were consistent with the overall activation energy and reaction order of ether pyrolysis. [g] Misprinted as 12.0 ± 0.3 in the abstract of ref 5.

obtains k_7 = 7 sec^{-1} from (xvi). Therefore

$$\log k_7\,(\text{sec}^{-1}) = (9.7 \pm 1.1) - (16{,}000 \pm 2{,}000)/2.3RT \qquad \text{(xviii)}$$

Equation xviii is also derivable from (xvii) and the butane yields.

The present values of frequency factors and activation energies are compared with earlier estimates[2,5,6] in Table IV. There is reasonable agreement between the several reported values of A_8 and E_8, which are similar to those of A_{12} and E_{12}, respectively.

$$CH_3 + C_2H_5OC_2H_5 \longrightarrow CH_4 + CH_3\dot{C}HOC_2H_5 \qquad (12)$$

However, there is great disparity among the reported values of A_7 and E_7. The values of E_7 and E_8 in ref 2 were taken from estimated slopes at the two ends of a curve, and were therefore crude. The curve was extended in both directions with the present work; the required slopes are no longer at the extremities and are much more reliable.

Long and Skirrow[5] reported E_7 = 23.5 ± 2.0 kcal/mol, and data in their paper can be used to estimate that k_7 = 100 sec^{-1} at 165°. These two quantities imply that log A_7 = 13.7 (Table IV). Estimated values of rate constants are usually more accurate than those of frequency factors and activation energies. Reduction of Long and Skirrow's value of E_7 to 16 kcal/mol would reduce their value of log A_7 to 9.9, in agreement with our result.

Laidler and McKenney's work was done at 560–620°.[6] They did not measure A_7 and E_7, but gave values that were consistent with their results (Table IV). Reduction of their E_7 from 30 to 16 kcal/mol would reduce their log A_7 from 13 to 9.5, also in agreement with our value. On the other hand, reduction of E_7 from 30 to 23.5 kcal/mol would reduce log A_7 from 13 to 11.4, which is not consistent with Long and Skirrow's results.

The values $A_7 = 10^{(9.7\pm1.1)}$ sec^{-1} and E_7 = 16 ± 2 kcal/mol are near the high-pressure limits, because k_7 was in or near the pressure-independent region in the present work. The frequency factor is lower than most other reported values for radical decompositions.[7] Further study of this type of reaction is warranted.

The curve through the acetaldehyde points in Figure 6 was calculated relative to the ethane curve, using eq x and xi. The agreement between the calculated and experimental results supports the above conclusions.

2. $CH_3CHO \rightarrow CH_4 + CO$. (a) Mechanism. The chain decomposition of the product acetaldehyde was negligible at $t < 200°$ in the present system (Figure 3). The chain mechanism is therefore mainly composed of the following reactions.

$$C_2H_5 + CH_3CHO \longrightarrow C_2H_6 + CH_3\dot{C}O \qquad (13)$$

$$CH_3\dot{C}O \longrightarrow CH_3 + CO \qquad (14)$$

$$CH_3 + C_2H_5OC_2H_5 \longrightarrow CH_4 + CH_3\dot{C}HOC_2H_5 \qquad (12)$$

$$CH_3\dot{C}HOC_2H_5 \longrightarrow CH_3CHO + C_2H_5 \qquad (7)$$

$$2C_2H_5 \longrightarrow C_4H_{10} \qquad (11)$$

The chain is initiated by (4). Steady-state treatment gives

$$d[CO]/dt = d[CH_4]/dt = k_{13}(\mathbf{k}_4/k_{11})^{0.5}[CH_3CHO][\text{ether}]^{0.5} \qquad \text{(xix)}$$

and

$$G(CO)_{\text{chain}} = G(CH_4)_{\text{chain}} = \frac{k_{13}G(R)}{(\mathbf{k}_4 k_{11})^{0.5}}\frac{[CH_3CHO]}{[\text{ether}]^{0.5}} \qquad \text{(xx)}$$

The linear increase in yield with increasing dose shown in Figure 5 is consistent with eq xx combined with the fact that the acetaldehyde yield was essentially independent of dose; the fraction of the acetaldehyde that decomposed was small.

At 257° the average slope of a plot of log $G(CH_3CHO)$ against log (ether pressure) between 300 and 2100 Torr was 0.37. The time-averaged concentration of alde-

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(5) J. Long and G. Skirrow, *Trans. Faraday Soc.*, **58**, 1043 (1962)

(6) K. J. Laidler, and D. J. McKenney, *Proc. Roy. Soc., Ser. A*, **278**, 505. (1964)

(7) J. A. Kerr and A. C. Lloyd, *Quart. Rev., Chem. Soc.*, **22**, 549 (1968).

hyde present in samples during the experiments therefore increased as $[\text{ether}]^{1.37}$. The fact that the exponent of the ether concentration was 1.37 rather than 1.5 was mainly due to a contribution of reaction 10 to chain termination at these pressures. The value 1.37 also requires that the exponent of [ether] in eq xix be 0.37 instead of 0.5. We therefore expect

$$d[CO]/dt = d[CH_4]/dt \propto [CH_3CHO][\text{ether}]^{0.37} \propto [\text{ether}]^{1.37}[\text{ether}]^{0.37} = [\text{ether}]^{1.74} \qquad \text{(xxi)}$$

and

$$G(CO)_{\text{chain}} = G(CH_4)_{\text{chain}} \propto [\text{ether}]^{0.74} \qquad \text{(xxii)}$$

which agrees with the observed $[\text{ether}]^{0.7}$, shown in Figure 4.

(b) Reaction Rate Parameters. When the ether concentration was 1.05×10^{-5} mol/cm^3 at 257°, the average concentration of acetaldehyde during an experiment was 2.4×10^{-8} mol/cm^3 and $G(CO)_{\text{chain}}$ was 6.5 (Figure 4) From eq xx we obtain $k_{13} = 4 \times 10^8$ cm^3/(mol sec) at 257°.

The activation energy of carbon monoxide and methane formation was 19 ± 1 kcal/mol (Figure 3). It is equal to the activation energy of acetaldehyde formation plus E_{13}. Thus $E_{13} = 8.5 \pm 1.5$ kcal/mol and

$$\log k_{13} = (12.1 \pm 0.6) - (8500 \pm 1500)/2.3RT \qquad \text{(xxiii)}$$

For purposes of comparison, the activation energies of the similar reactions 15 and 16 were reported to be

$$C_2H_5 + C_2H_5CHO \longrightarrow C_2H_6 + C_2H_5\dot{C}O \qquad (15)$$

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3\dot{C}O \qquad (16)$$

5.9 and 7.6 kcal/mol,[4] respectively, with corresponding frequency factors of $10^{11.1}$ and $10^{11.9}$ cm/(mol sec)[4] (Table IV). The parameters of (15) are probably not really lower than those of (16), so the reported values should be considered to be equal within experimental error. Our work favors the higher values.

3. $C_2H_5OC_2H_5 \rightarrow C_2H_5OH + C_2H_4$. (a) Mechanism. The chain yield of ethylene increased from 1 to 6% of the ethane yield as the temperature was increased from 257 to 403°. The ethylene mechanism made only a small contribution to the steady-state distribution of radicals in the system under our conditions.

The chain was initiated by (4) and terminated mainly by (11). The mechanism can be represented as follows.

$$C_2H_5OC_2H_5 \rightsquigarrow 2R \qquad \text{(4a)}$$

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

$$R + C_2H_5OC_2H_5 \longrightarrow RH + \dot{C}H_2CH_2OC_2H_5 \qquad (18)$$

$$\dot{C}H_2CH_2OC_2H_5 + C_2H_5OC_2H_5 \longrightarrow C_2H_5OC_2H_5 + CH_3\dot{C}HOC_2H_5 \qquad (19)$$

$$CH_3\dot{C}HOC_2H_5 \longrightarrow CH_3CHO + R \qquad \text{(7a)}$$

$$\dot{C}H_2CH_2OC_2H_5 \longrightarrow C_2H_4 + R \qquad (20)$$

$$2R \longrightarrow R_2 \qquad \text{(11a)}$$

where R is mostly C_2H_5, with a small amount of C_2H_5O from (20).

The steady-state rate of ethylene formation is

$$\frac{d[C_2H_4]}{dt} = \frac{k_{18}k_{20}}{k_{19}[\text{ether}] + k_{20}}\left(\frac{k_{4a}}{k_{11a}}\right)^{0.5}[\text{ether}]^{1.5} \qquad \text{(xxiv)}$$

and

$$G(C_2H_4) = \frac{k_{18}k_{20}G(2R)}{(k_{19}[\text{ether}] + k_{20})(k_{4a}k_{11a})^{0.5}}[\text{ether}]^{0.5} \qquad \text{(xxv)}$$

where $G(2R) = 6$ for reaction 4a.

The reverse of (19) was negligible in our system because of the speed with which the $CH_3\dot{C}HOC_2H_5$ radicals decomposed at temperatures above 200°. Assuming that $k_{19} \approx k_8$, reaction 21 was also unimportant. The radical mean lifetime with respect to combination was about 130 msec when the ether concentration was 1×10^{-5} mol/cm^3, whereas the mean lifetime with respect to (19) was about 3 msec at 257° and shorter at higher temperatures.

$$C_2H_5 + \dot{C}H_2CH_2OC_2H_5 \longrightarrow n\text{-}C_4H_9OC_2H_5 \qquad (21)$$

According to eq xxiv the order of ethylene formation should vary from 1.5 at low pressures to 0.5 at high pressures. The line dashed through the ethylene yields in Figure 4 has the form of (xxv).

Long and Skirrow[5] found that ethylene was a negligible product in their system, so reaction 20 was also negligible. They then apparently assumed that (22) did not occur either. However, they did not report looking for *n*-propyl ethyl ether that might have been formed by (23) under their reaction conditions. It is possible that their values of A_{12} and E_{12} and ours of A_8 and E_8 actually correspond to weighted averages of the parameters for reactions 12 + 22 and 8 + 18, respectively.

$$CH_3 + C_2H_5OC_2H_5 \longrightarrow CH_4 + \dot{C}H_2CH_2OC_2H_5 \qquad (22)$$

$$CH_3 + \dot{C}H_2CH_2OC_2H_5 \longrightarrow CH_3CH_2CH_2OC_2H_5 \qquad (23)$$

(b) Reaction Rate Parameters. There are insufficient data to permit the estimation of the parameters of k_{18}, k_{19}, and k_{20}. However, if one assumes that $E_{18} \approx 12$ and $E_{19} \approx 10$ kcal/mol, the observed activation energy of ethylene formation (18 ± 2 kcal/mol under our conditions) and the results in Figure 4 indicate that $E_{20} \approx 22 \pm 4$ kcal/mol.

Equation xxiv implies that the activation energy of ethylene formation should vary from E_{18} at low ether concentrations and high temperatures, where the order is 1.5, to $(E_{18} + E_{20} - E_{19})$ at high ether concentrations and low temperatures, where the order is 0.5.

Further progress toward the understanding of the mechanism of the pyrolysis of diethyl ether requires knowledge of the rate parameters of (18), (19), and (20).

4. Entropy and Energy of Activation for Radical Decompositions. The entropy of activation of a unimolecular gas-phase reaction is given by eq xxvi.[8] Thus at temperatures near 400°K the activation entropy

$$\Delta S^{\ddagger} = 2.30R\left(\log A - \log \frac{2.72kT}{h}\right) \qquad \text{(xxvi)}$$

$\Delta S^{\ddagger} = 4.6(\log A - 13.3)$, from which we obtain $\Delta S_7^{\ddagger} = -17 \pm 5$ cal/(deg mol) for the decomposition of the $CH_3\dot{C}HOC_2H_5$ radical. At first sight this large negative value seems surprising. It is linked with an activation energy that is 11 kcal/mol greater than the thermodynamically estimated endothermic heat of reaction ΔH_{th} (Table IV).

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[8] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, Chapter 5.

The pressure-independent (infinite pressure) values of A and E_a should be used in calculations of and comparisons with thermodynamic quantities. The pressure-dependent (low pressure) values of A and E_a are lower in magnitude. It would be helpful to keep this in mind during the following discussion, because many workers did not attempt to determine whether or not their reaction rates were measured in the pressure-independent region.

Kerr and Lloyd have tabulated rate parameters and thermodynamic data for many radical decompositions.[7] Entropies of activation can be estimated from eq xxvi, with the reservations expressed in the preceding paragraph. From the data in Kerr and Lloyd's table we note that, for the decomposition of a large radical RM· into a smaller radical R· and a molecule M that contains a multiple bond, there is a correlation between

$$\mathrm{RM\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{M} \qquad (24)$$

the identity of R· and the rate parameters A_{24} and E_{24}. When R· is a hydrogen atom, (24) has an activation energy that is within 2 kcal/mol of the thermodynamically calculated endothermic heat of reaction, and the entropy of activation is usually slightly positive [1–4 cal/(deg mol)]. In the cases where the estimated values of $\Delta S_{24}^{\ddagger}$ were negative for R· = H, the reported activation energies were lower than ΔH_{th}; these activation energies are therefore probably lower than the infinite-pressure values, and the corresponding values of A and $\Delta S^{\ddagger}$ would also be low. Increasing $(E_a - \Delta H_{\mathrm{th}})$ to 1 kcal/mol would make $\Delta S^{\ddagger}$ positive in all cases.

When R· is a methyl or ethyl radical the quantity $(E_a - \Delta H_{\mathrm{th}})$ is usually 2–10 kcal/mol and the apparent values of $\Delta S_{24}^{\ddagger}$ are mostly zero or negative.

One cannot have enough confidence in the reported data to know whether the above correlations are significant. However, the most thoroughly studied reactions of these types appear to be (25) and (26),[7] for which $(E_{25} - \Delta H_{25}) = 2$ kcal/mol, $\Delta S_{25}^{\ddagger} = +4$ cal/(deg mol), $(E_{26} - \Delta H_{26}) = 2$ kcal/mol, and $\Delta S_{26}^{\ddagger} = -14$ cal/(deg mol).

$$\mathrm{C_2H_5} \longrightarrow \mathrm{C_2H_4} + \mathrm{H} \qquad (25)$$

$$\mathrm{CH_3CO} \longrightarrow \mathrm{CH_3} + \mathrm{CO} \qquad (26)$$

Our results imply that $(E_7 - \Delta H_7) = 11$ kcal/mol and $\Delta S_7^{\ddagger} = -17$ cal/(deg mol), whereas the corresponding values from the work of Long and Skirrow[5] are 19 kcal/mol and +2 cal/(deg mol). The latter values appear to be too high for that type of reaction.

Reaction between Deuterium and Cyclic Olefins on Platinum/Alumina in the Liquid Phase

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Abstract: This paper reports the results of reaction in the liquid phase between deuterium and cyclopentene, cyclohexene, cycloheptene, cyclooctene, bicyclo[3.3.0]-2-octene, and 1-hexene on platinum/alumina. Runs involved the solvents: none, tetrahydrofuran (THF), THF + D_2O, CH_3COOD, CH_3OD, $(CH_3)_3COD$, and ethanolamine-d_3 + CH_3OD. The exchange reaction, H* + ROD = D* + ROH, proceeds rather rapidly, thus considerably increasing (D*/H*) over the low value which obtains during runs with no solvent or with THF. The increased (D*/H*) facilitates interpretation of the isotopic distributions of the cycloalkanes which are formed. These distributions can now be seen closely to resemble those found in exchange of each cycloalkane with deuterium on platinum, a result which strongly supports the view that exchange of alkanes and hydrogenation of alkenes are closely interlinked mechanistically. The isotopic distributions of cycloalkanes formed in exchanging solvents indicate that there are at least two sets of surface sites. One is characterized by large (D*/H*), some simple addition hydrogenation, all or most of the exchange–addition hydrogenation leading to ane-d_3, ane-d_4, . . ., and a substantial rate of H* + ROD = D* + ROH. The second set involves only or mainly simple addition hydrogenation, formation of exchanged olefin, and a relatively small rate of H* + ROD = D* + ROH. There are differences among the solvents; CH_3COOD gives much the most exchange–addition hydrogenation, ethanolamine gives much the most simple addition hydrogenation.

If one replaces hydrogen by deuterium and analyzes the products mass spectrometrically, one adds considerably to the information about the hydrogenation of olefins on group VIII metals.[1,2] It becomes evident that the reaction is an *exchange–addition* hydrogenation rather than a simple addition hydrogenation; that is, the addition of deuterium atoms to the original double bond is accompanied by exchange of hydrogen atoms of the hydrocarbon. Thus, product alkane is represented not only by alkane-d_2 but also by -d_3, -d_4, and even higher. In terms of the classical Horiuti–Polanyi mechanism of Scheme I,[3] hydro-

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(1) J. Turkevich, F. Bonner, D. O. Schissler, and A. P. Irsa, *Discuss. Faraday Soc.*, 8, 352 (1950).

(2) G. C. Bond, "Catalysis by Metals," Academic Press, London, 1962, Chapter 11.

(3) R. L. Burwell, Jr., *Accounts Chem. Res.*, 2, 289 (1969). It has been