π transition state was proposed by Cvetanović[18] in his studies of the addition of oxygen atoms to olefins, and recently Trotman-Dickenson[39] discussed the same idea in terms of steric and energetic considerations.

Acknowledgments. This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society, and by a grant from the National Science Foundation.

A Cationic Chain Reaction in the Radiolysis of Ethanol Vapor

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Abstract: During the radiolysis of ethanol vapor at 350° and higher temperatures, diethyl ether is formed by a cationic chain reaction. At 380°, $G(Et_2O)$ decreased from 62 at an ethanol pressure of 85 Torr to 2.6 at 1630 Torr. The overall activation energy of the chain mechanism was 43 ± 4 kcal/mol, independent of ethanol pressure within experimental error. The values of the rate constants of one or both of the reactions $(EtOH)_mH^+ \rightarrow Et_2O\cdot H^+\cdot(OH_2)(EtOH)_{m-2}$ (4_m) and $Et_2O\cdot H^+\cdot(OH_2)(EtOH)_{m-2} + 2EtOH \rightarrow Et_2O + H_2O + (EtOH)_mH^+$ (5_m) decreased with increasing m for $m \geq 2$. The rate of ether formation is reduced by the presence of ammonia, a proton scavenger. The vapor-phase reaction $CH_2O + C_2H_5OH \rightarrow CH_3OH + CH_3CHO$ occurs at 200–380° by a thermal mechanism that is not appreciably sensitized by radiation. The rate of the reaction is unaffected by the presence of propylene, a free radical scavenger.

In a recent communication we reported the discovery of a gas-phase cationic chain reaction that converted ethanol to ether and water during radiolysis at 350°.[2] The present article includes experimental details and new results about this system.

It has also been found that the reaction of formaldehyde with ethanol to form methanol and acetaldehyde[2] occurs by a thermal mechanism that is not appreciably sensitized by radiation.

Experimental Section

Materials. Absolute ethanol (2 l.) from Rossville Gold Shield was refluxed for approximately 4 hr in an atmosphere of nitrogen, after the addition of 3 g of 2,4-dinitrophenylhydrazine and 2 ml of concentrated sulfuric acid. The solution was then distilled on a Nester-Faust spinning band column. The middle fraction of the distillate was retained for use and was stored under vacuum in a Pyrex reservoir.

Paraformaldehyde (trioxymethylene) from Fischer Scientific Co. was used without further purification.

Sample Handling. The 300-ml cylindrical irradiation cells were cleaned with permanganic and nitric acids, followed by many rinsings with doubly distilled water. They were then baked overnight at about 500° in air and finally for 2 hr at 500° while being evacuated.

The desired amount of ethanol was measured as a liquid in a calibrated tube in a vacuum line, then distilled into the cell.

The ethanol–formaldehyde samples were prepared as follows. Paraformaldehyde was weighed into a breakseal tube and was thoroughly degassed, using liquid nitrogen as coolant. The tube was sealed off and then sealed to the sample preparation manifold of the vacuum apparatus. A known amount of ethanol was distilled into the irradiation cell. The paraformaldehyde tube and the tubing connecting it to the irradiation cell were heated with electrical tape. The seal was then broken. Paraformaldehyde on heating formed formaldehyde vapor, which then condensed into the irradiation cell.

The filled and sealed irradiation cells were placed in an electric furnace, heated to the desired temperature, and irradiated in a Gammacell-220 (Atomic Energy of Canada Ltd.). The temperature was maintained constant to within 3°. The heating and cooling times were kept constant at each temperature. The entire cycle required about 1 hr at all temperatures.

The dose rate was 8.6×10^{19} eV/(g hr), measured with ethylene and assuming $G(H_2) = 1.31 \pm 0.03$.[3,4] Sufficient ethylene was placed in the cell so that the electron density of ethylene in the dosimeter was approximately the same as that of ethanol in the samples. The dose rate in ethanol was corrected for the difference between the stopping powers of ethanol and ethylene. All radiolysis samples were given a dose of 4.3×10^{19} eV/g.

The ratiolysis products were analyzed by gas chromatography using two 4-mm i.d. columns (a) 7 ft, Polypak-1, 40–80 mesh; (b) 13 ft, the first 9 ft packed with 25% 1,2,3-tris-2-cyanoethoxypropane on Chromosorb P, and the next 4 ft packed with 10% Carbowax-4000 on Chromosorb W, acid-washed, 60–80 mesh. The gas chromatograph was an F and M Model 5750 equipped with a flame ionization detector. Calibration factors were determined with solutions of authentic products at known concentrations.

Results

(A) $2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$. Although water was observed to be a radiolysis product, its yield was not measured accurately.

1. Effect of Ethanol Pressure on the Ether Yield at 380°. The pressure was varied over the range 85–1630 Torr, which corresponded to ethanol densities from 0.096 to 1.85 g/l. The diethyl ether yield decreased from 62 to 2.6 as the pressure was increased (Figure 1).

The possibility of ether formation by normal pyrolysis or by a catalytic reaction on the vessel wall was checked by putting two ethanol samples through the same heating cycle as was used for the irradiated samples, but without irradiation. An ethanol pressure of 85 Torr was used because the ether yield in the irradiated samples was highest at the lowest pressure. No ether was detected after the heating cycle, which means

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(1) (a) Carnegie-Mellon University; (b) University of Alberta.

(2) K. M. Bansal and G. R. Freeman, *J. Amer. Chem. Soc.*, **90**, 5632 (1968).

(3) (a) R. A. Back, T. W. Woodward, and K. A. McLauchlan, *Can. J. Chem.*, **40**, 1380 (1962); (b) G. G. Meisels, *J. Chem. Phys.*, **41**, 51 (1964).

(4) W. J. Holtslander and G. R. Freeman, *Can. J. Chem.*, **45**, 1649 (1967).

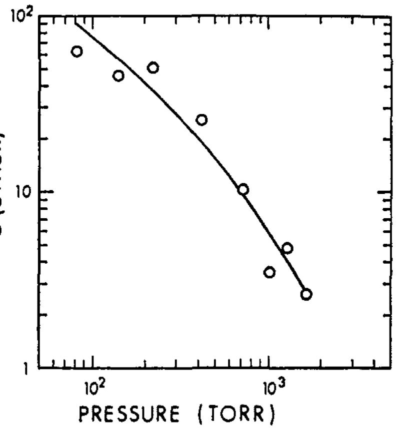

Figure 1. Effect of ethanol pressure on the radiolytic yield of diethyl ether at 380°.

that the amount of ether formed by normal pyrolysis and by wall catalysis in the irradiated samples corresponded to a G value of less than 0.1. The corresponding radiolysis yield under these conditions was $G(\text{ether}) = 62$.

2. Effect of Temperature on the Ether Yield at Constant Ethanol Density. The ether yield was measured at temperatures from 300 to 400°. Two series of experiments were done, each series at a different constant ethanol density. At an ethanol density of 0.096 g/l. G(ether) increased smoothly from 0.27 at 300° to 98 at 400°, whereas at a density of 1.85 g/l. G(ether) changed from 0.40 at 300° to only 0.77 at 360°, then increased to 6.9 at 400° (Figure 2). The results reported earlier[2] for an ethanol density of 0.66 g/l. are included in Figure 2 for comparison; G(ether) increased smoothly from 1.1 at 320° to 15.9 at 375°.

The slopes of the lines for the ethanol densities of 0.096 and 0.66 g/l. and of the high-temperature end of the line for 1.85 g/l. correspond to Arrhenius activation energies of 49, 38, and 42 kcal/mol, respectively. Thus the activation energy of the radiation-induced chain reaction that forms ether from ethanol has an activation energy of 43 ± 4 kcal/mol, independent of ethanol pressure within the experimental error.

(B) $CH_2O + C_2H_5OH \rightarrow CH_3OH + CH_3CHO$. The densities of ethanol and formaldehyde were 0.80 and 0.05 g/l., respectively, in all samples.

The apparent G values of methanol and acetaldehyde increased from about 10 at 200° to about 900 at 380°. However, when "blank" samples were put through the heating cycle without being subjected to irradiation, the same amounts of methanol and acetaldehyde were formed as had been produced in the presence of the radiation. The activation energy of the reaction was roughly 16 kcal/mol.

The addition of 3–21 mol % of propylene at 350° had a negligible effect on the yields of methanol and acetaldehyde.

Discussion

(A) $2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$. The following observations signify that ether was formed at high temperatures by a cationic chain reaction: (1) values of G(ether) up to 98, (2) negligible ether formation in the absence of radiation, (3) G(ether) was much reduced by the addition of a proton scavenger (ammonia) to the alcohol.[2]

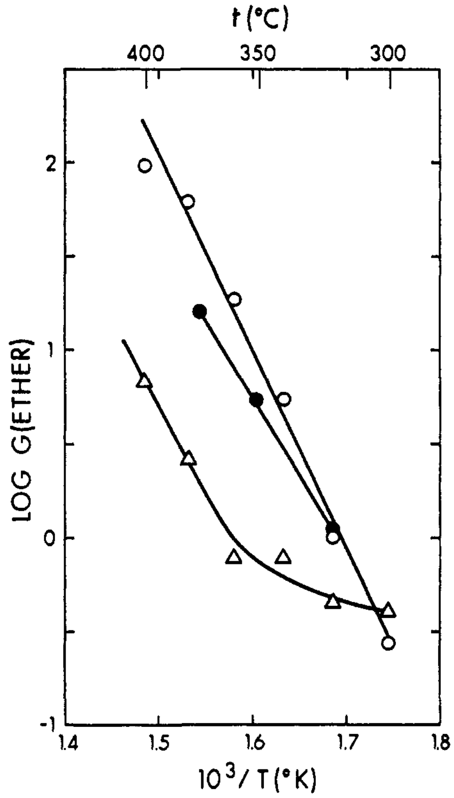

Figure 2. Arrhenius plots of the radiolytic yield of diethyl ether at different temperatures and ethanol densities. Ethanol density (g/l): ○, 0.096; ●, 0.660; △, 1.85.

The slope of a log–log plot of the ether yield against the ethanol pressure equals $n - 1$, where n is the overall order of the ether formation mechanism. The order of ether formation at 380° appears to be about 0.2 at 100 Torr and −0.5 at 1000 Torr (Figure 1). (The preliminary result in the communication[2] is here revised.)

The following mechanism is consistent with the above results.

$$\text{EtOH} \rightsquigarrow \text{EtOH}^+ + e^- \tag{1}$$

$$\text{EtOH}^+ + \text{EtOH} \longrightarrow \text{EtOH}_2^+ + \text{CH}_3\text{CHOH} \tag{2}$$

$$\text{EtOH}_2^+ + \text{EtOH} \rightleftarrows (\text{EtOH})_2\text{H}^+ \tag{3_1}$$

$$(\text{EtOH})_2\text{H}^+ + \text{EtOH} \rightleftarrows (\text{EtOH})_3\text{H}^+ \tag{3_2}$$

$$(\text{EtOH})_m\text{H}^+ + \text{EtOH} \rightleftarrows (\text{EtOH})_{m+1}\text{H}^+ \tag{3_m}$$

$$(\text{EtOH})_m\text{H}^+ \longrightarrow \text{Et}_2\text{O}\cdot\text{H}^+\cdot(\text{OH}_2)(\text{EtOH})_{m-2} \tag{4_m}$$

$$\text{Et}_2\text{O}\cdot\text{H}^+\cdot(\text{OH}_2)(\text{EtOH})_{m-2} + 2\text{EtOH} \longrightarrow \text{Et}_2\text{O} + \text{H}_2\text{O} + (\text{EtOH})_m\text{H}^+ \tag{5_m}$$

$$(\text{EtOH})_m\text{H}^+ + e^- \longrightarrow \text{neutralization} \tag{6_m}$$

The minimum value of m required for reaction 4_m is 2, in which case the product ion is $Et_2O \cdot H^+ \cdot OH_2$. Reaction 4_m is a chemical rearrangement of two molecules that are attached by a proton bridge; it is a typical acid-catalyzed reaction. (5_m) occurs in several steps involving the successive growth of the clustered ion by ethanol molecule attachment and partial dissociation by the more or less random detachment of one of the molecules from the cluster.

The proton affinity of an ether is greater than that of the parent alcohol,[5] which in turn is greater than that of water.[6] These differences are apparently due to the fact that the polarizability of an alkyl group is greater than that of a hydrogen atom. One may therefore conclude that the heats of reactions 7 and 8

$$H^+ + 2EtOH \longrightarrow (EtOH)_2H^+ \tag{7}$$

$$H^+ + H_2O + Et_2O \longrightarrow Et_2O\cdot H^+\cdot OH_2 \tag{8}$$

are approximately the same. The heat of reaction 4_m is therefore about equal to that of (9); $\Delta H_9 = -6$ kcal/mol.[7] Furthermore, (5_m) is roughly thermoneutral.

$$2EtOH \longrightarrow Et_2O + H_2O \tag{9}$$

Reactions 1-6_m comprise a refinement of the mechanism proposed earlier.[2] A steady-state treatment of these reactions indicates that if the values of the rate constants of reactions 4_m and 5_m, k_{4_m} and k_{5_m}, respectively, were independent of the value of m for $m \geq 2$, the order of ether formation would be 1.5 at very low ethanol pressures and would decrease to 0.5 at higher pressures. The order would be 0.5 at all pressures where the steady-state concentration of the monomeric ion ($m = 1$) was much smaller than the total concentration of larger ions ($m > 1$). The fact that the order of ether formation is actually less than 0.5 implies that the values of one or both of k_{4_m} and k_{5_m} decrease with increasing n for $m \geq 2$. The average value of m in the system increases with increasing ethanol pressure. It is assumed that the value of k_{6_m} is essentially independent of m.

The interpretation of the observed activation energy of ether formation requires knowledge about the influences of temperature and ethanol pressure on the distribution of m values in the equilibria (3_m). This information is not yet available, but could be obtained by high-pressure mass spectrometry.

Ammonia inhibits ether formation, probably through reactions such as

$$(EtOH)_mH^+ + NH_3 \longrightarrow (EtOH)_mNH_4^+ \tag{10_m}$$

$$\longrightarrow (EtOH)_{m-1}NH_4^+ + EtOH \tag{11_m}$$

The proton affinity of ammonia (209 ± 7 kcal/mol[8]) is greater than that of ethanol (193 ± 8 kcal/mol[6]).

The present work may be relevant to studies of the dehydration of alcohols on solid catalyst surfaces[9,10] and of the acid-catalyzed dehydration in the liquid phase.

(B) $CH_2O + C_2H_5OH \rightarrow CH_3OH + CH_3CHO$. The reaction between formaldehyde and ethanol to form methanol and acetaldehyde occurred by a thermal mechanism and was not sensitized by radiation. The rate of the reaction was not appreciably affected by the presence of propylene, a free radical scavenger, so the mechanism apparently did not involve free radicals. The overall reaction is exothermic by 4 kcal/mol.[7]

The reaction mechanism is not obvious, but it might involve the intermediate formation of ethyl hemiformal. Hemiformals form readily from formaldehyde and simple aliphatic alcohols.[11,12]

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[5] M. S. B. Munson, *J. Amer. Chem. Soc.*, 87, 2332 (1965).

[6] V. L. Tal'rose and E. L. Frankevich, *ibid.*, **80**, 2344 (1958).

[7] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

[8] G. R. Freeman, *Radiat. Res. Rev.*, **1**, 1 (1968), see Table 1.

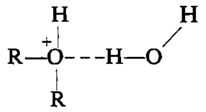
[9] H. Knözinger, *Angew. Chem., Int. Ed. Engl.*, 7, 791 (1968).

[10] H. Knözinger, A. Scheglila, and A. M. Watson, *J. Phys. Chem.*, 72, 2770 (1968).

[11] J. F. Walker, "Formaldehyde," 3rd ed, American Chemical Society Monograph Series, Reinhold, New York, N. Y., 1964, p 264.

[12] Note Added in Proof. Preliminary results of M. Yoshida and P. Kebarle (private communication) indicate that under our ranges of temperature and pressure $(EtOH)_2H^+$ and $(EtOH)_3H^+$ comprise at least 99% of the total ions. The only equilibrium that need be considered is therefore (3_2).

The most probable configuration of the transition state of reaction 4_2 would form an initial product ion that contained a weak hydrogen bond



rather than the much stronger ion–dipole bond $R_2OH^+\cdots OH_2$. Thus reaction 4_2 is probably endothermic by 20–30 kcal/mol, which would explain a large portion of the observed activation energy of 43 ± 4 kcal/mol. (4_2) might be better written as in our original communication.[2]

$$(EtOH)_2H^+ \longrightarrow Et_2OH^+ + H_2O \tag{4_2}$$

(5_2) would then involve the steps

$$\begin{gathered} Et_2OH^+ + EtOH \longrightarrow Et_2O\cdot H^+\cdot(EtOH) \\ Et_2O\cdot H^+\cdot(EtOH) + EtOH \rightleftarrows Et_2O\cdot H^+\cdot(EtOH)_2 \\ Et_2O\cdot H^+\cdot(EtOH)_2 \longrightarrow Et_2O + (EtOH)_2H^+ \end{gathered} \tag{5_2}$$