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Radiolysis of Diethyl Ether. I. Liquid Phase¹

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Edmonton, Alberta, Canada. Received November 20, 1964

The G values of the major products of the γ -radiolysis of liquid diethyl ether at 25° and a dose of 10^{20} e.v./g. are as follows: hydrogen, 3.4; 2,3-diethoxybutane, 2.6; ethanol, 2.1; ethane, 1.3; ethylene, 0.8; ethyl vinyl ether, 1.1 (at 8×10^{20} e.v./g.); ethyl *sec*-butyl ether, 0.7; $G(-C_2H_5OC_2H_5) = 11.3$. The yields of most of the products were independent of dose over the range studied. However, $G(C_2H_4)$ decreased from 1.1 at 8×10^{18} e.v./g. to 0.6 at 3.9×10^{20} e.v./g. The value of $G(H_2)$ decreased from an extrapolated value of 3.7 at zero dose to a steady value of 3.4 at doses greater than 4×10^{19} e.v./g. Ethyl vinyl ether, 1,3-pentadiene, and benzene inhibit the formation of all of the products except CO ($G = 0.07$). The reaction mechanism is discussed. The approximate yields of three kinetically distinguishable sources of hydrogen were $G(e^-_{solv}, \text{free ion}) = 0.3$, $G(\text{scavengeable } H_2) = 1.4$, and $G(\text{unscavengeable } H_2) = 2.0$. The relative probabilities, per bond, of cleavage of the various types of bond are C-O ($G = 1.6$) \gg C-H ($G = 0.34$) $>$ C-C ($G = 0.28$). The value of the ratio of the steady-state concentration of $CH_3CHOC_2H_5$ radicals to that of $\dot{C}H_2CH_2OC_2H_5$ radicals in liquid ether during radiolysis was about 40 to 1.

Introduction

The He^{+2} ion radiolysis of liquid diethyl ether and of several other aliphatic ethers have been investigated.^{2,3} The γ -radiolysis of diethyl ether⁴ and of diisopropyl ether⁵ have also been studied. However, only the gaseous products of these reactions were analyzed.

(1) This work received financial assistance from the National Research Council of Canada.

(2) A. S. Newton, *J. Phys. Chem.*, **61**, 1485 (1957).

(3) A. S. Newton, *ibid.*, **61**, 1490 (1957).

(4) G. E. Adams, J. H. Baxendale, and R. D. Sedgwick, *ibid.*, **63**, 854 (1959).

Evidence pointed to the selectivity of C-O bond rupture.^{2,3}

The present work included the measurement of the gaseous and liquid product yields as functions of dose and additive concentration. Further information has been obtained concerning the reaction mechanism and the reactivities of the various bonds.

Experimental

Materials. Spectrograde ethyl ether from Eastman Organic Chemicals Co. was stored in a vacuum system. The radiolysis product yields were the same whether or not the ether was stored over sodium wire. No impurities could be detected in the ether by gas chromatography (g.c.) on the following four columns: silicone grease, Ucon LB-1800X, di-2-ethyl hexyl sebacate, and tetraethylene glycol dimethyl ether, each on Chromosorb W. Thus, any given impurity concentration was less than 0.01%.

Eastman Organic ethyl vinyl ether was purified by g.c. The total concentration of impurities in the resulting liquid was <1%.

1,3-Pentadiene (Columbia Organic Chemicals Co.) was distilled before use. The remaining impurities were in the C_5 region and totaled about 5%.

Phillips research grade benzene was used as received.

2,3-Diethoxybutane was prepared by Moore's method⁵ and was distilled before use (impurities <3%). 1,4-Diethoxybutane was obtained from K and K Laboratories, Inc. The 1,3 isomer could not be obtained.

Sample Preparation, Irradiation, and Analysis. The ether was vaporized into a known volume to a desired pressure, then condensed into an irradiation cell. Additives were measured similarly. The pressures used

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

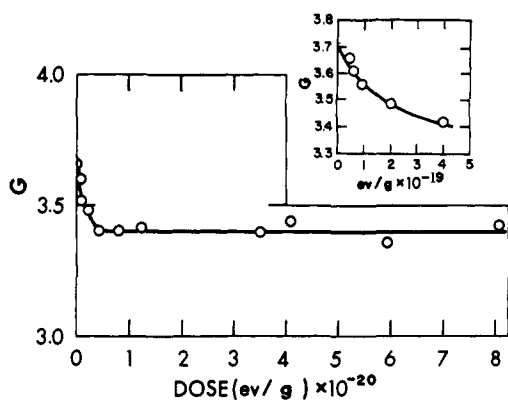


Figure 1. Dose dependence of $G(\text{H}_2)$.

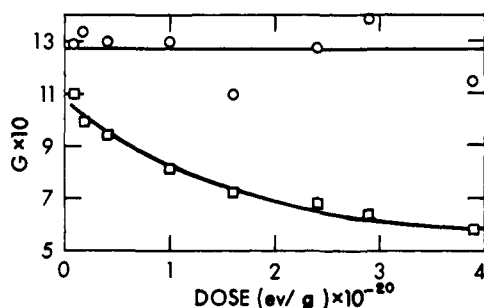


Figure 2. Dose dependence of C_2H_6 and C_2H_4 yields: \circ , C_2H_6 ; \square , C_2H_4 .

were low enough that deviations of the vapors from ideal gas behavior were less than 1%. The cell was either a Pyrex tube (15-mm. diameter) that contained 1–2 ml. of liquid and 2–3 ml. of vapor or a thin-walled bulb (12-mm. diameter) that contained 0.1–0.3 ml. of liquid.

The Co^{60} γ -irradiation dose rate was 6×10^{19} e.v./g. hr. The temperature was $25 \pm 3^\circ$.

The small bulbs were broken open in the g.c. system directly in the carrier gas stream and were used for the analysis of all the gaseous products except hydrogen.

Hydrogen, along with methane and carbon monoxide, was separated from 2-ml. samples by distillation through traps at -196° . The total amount of the gas fraction was measured in a Toepler–McLeod apparatus, and the composition of the fraction was determined by g.c. or by mass spectrometry.

Formaldehyde was analyzed by a chromotropic acid method.⁶ The method was slightly modified because ether is not very soluble in water. The formaldehyde was extracted from the ether by breaking a 0.3-ml. sample in a thin-walled bulb under the surface of 3 ml. of water in a test tube, shaking, then allowing the ether to evaporate.

The other liquid products were analyzed by g.c. Acetaldehyde was successfully measured using a 2.5-m. column of di-2-ethyl hexyl sebacate on Chromosorb W at 25° , with helium carrier gas.

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

(6) J. M. Ramaradha and G. R. Freeman, *Can. J. Chem.*, **39**, 1836 (1961).

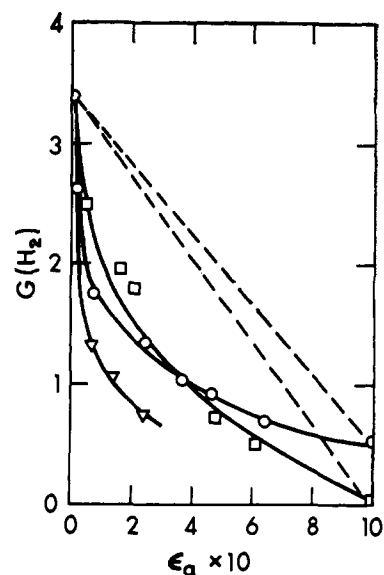


Figure 3. Effects of additives on $G(\text{H}_2)$ (dose given in parentheses as 10^{19} e.v./g.): \square , benzene (7); \circ , ethyl vinyl ether (7); ∇ , 1,3-pentadiene (35). (ϵ_a = electron fraction of additive.)

Results

Pure Diethyl Ether. The value of $G(\text{H}_2)$ decreased rapidly from 3.7 (extrapolated value) at zero dose to a steady value of 3.4 at doses greater than 4×10^{19} e.v./g. (Figure 1).

The ethylene yield decreased with dose over the entire range studied (0.1 – 4×10^{20} e.v./g.), whereas the ethane yield was essentially independent of dose (Figure 2).

The yields of all other products were independent of dose within the region investigated. The G values of the major products are presented in Table I, and those of the minor products in Table II.

Table I. G Values of Major Products

Compound	G	Dose range, e.v./g. $\times 10^{-20}$
Hydrogen	3.7 ± 0.1 (G_i)	0
	3.41 ± 0.02	0.4–8.0
2,3-Diethoxybutane	2.63 ± 0.23	1.0–5.5
Ethanol	2.13 ± 0.20	0.5–5.5
Ethane	1.27 ± 0.17	0.08–3.9
Ethylene	1.1 to 0.6	0.08–3.9
Ethyl vinyl ether	1.1 ± 0.1	8–23
Ethyl <i>sec</i> -butyl ether	0.74 ± 0.03	0.3–5.5

The 2,3-diethoxybutane appeared as two overlapping peaks of approximately equal area. The two peaks were probably due to the *meso* and *dl* forms of the compound. *meso*- and *dl*-2,3-butanediol were produced during the radiolysis of ethanol, and these diastereoisomers also appeared as two overlapping peaks.⁷

Ether-Additive Solutions. The effects of ethyl vinyl ether, benzene, and 1,3-pentadiene on the product yields were determined.

(7) J. J. J. Myron and G. R. Freeman, *ibid.*, **43**, 381 (1965).

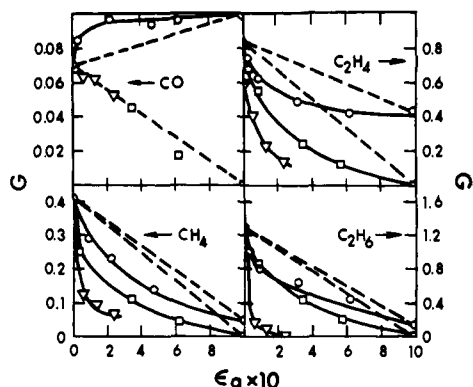


Figure 4. Effects of additives on some gaseous products (dose given in parentheses as 10^{19} e.v./g.): \square , benzene (7); \circ , ethyl vinyl ether (7); ∇ , 1,3-pentadiene (35). (ϵ_a = electron fraction of additive.)

The effects of the additives on the hydrogen yield are shown in Figure 3. Each of the additives inhibits the formation of hydrogen although 1,3-pentadiene is the most effective inhibitor of the three. The dashed lines in Figures 3–5 indicate the yields that would be expected if each component of a solution did not interfere with the formation of radiolytic products from the other.

Table II. G Values of Minor Products

Compound	G	Dose range, e.v./g. $\times 10^{-20}$
Methane	0.41 ± 0.03	0.7–3.6
Acetaldehyde	0.18 ± 0.03	3–5
Acetal	0.14 ± 0.03	3–10
1,2-Diethoxypropane	~ 0.09	4–17
1,2-Diethoxyethane	0.08 ± 0.03	1–3
Propane	0.078 ± 0.004	0.4–2.9
Diethoxymethane	0.075 ± 0.007	3–10
Ethyl isopropyl ether	0.074 ± 0.003	1.5–3.5
Carbon monoxide	0.07 ± 0.01	0.7–3.6
Ethyl <i>n</i> -propyl ether	0.059 ± 0.003	0.8–2.3
Butane	0.053 ± 0.005	0.4–2.9
Ethyl <i>n</i> -butyl ether	0.031 ± 0.004	3–10
Acetylene	0.013 ± 0.001	0.4–2.9
Formaldehyde	0.0	3
Unknown 1 (1,3-diethoxybutane?)	~ 0.09	4–17
Unknown 2 (dimer?)	~ 0.16	4–17

The carbon monoxide yield was unaffected by benzene or pentadiene but was enhanced by ethyl vinyl ether (Figure 4A). The yields of methane, ethane, ethylene, ethanol, ethyl *sec*-butyl ether, and 2,3-diethoxybutane were inhibited in varying degrees by the three additives, but pentadiene was always the most effective (Figures 4 and 5).

Discussion

Pure Ether. Material Balance. A mass balance of all of the products observed at a dose of 10^{20} e.v./g. was done since the yields of most of the products could not be measured at lower doses. The reaction products add up to an empirical formula of $C_{4.00}H_{10.04}O_{0.97}$. The good balance indicates that most of the

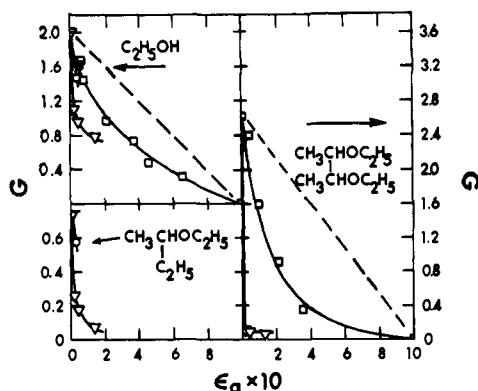
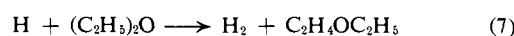
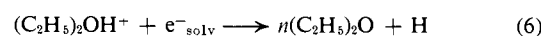
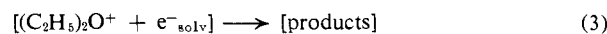
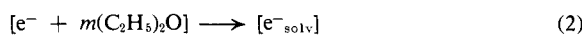
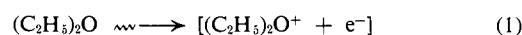


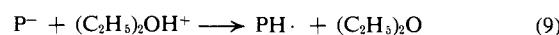
Figure 5. Effects of additives on liquid products (dose given in parentheses as 10^{19} e.v./g.): \square , benzene (7); \circ , ethyl vinyl ether (7); ∇ , 1,3-pentadiene (100). (ϵ_a = electron fraction of additive.)

products have been measured. The total rate of ether decomposition corresponded to $G(-C_4H_{10}O) = 11.3$.

Dose Dependence of Product Yields. As shown in Figures 1 and 2, there is no correlation between the dose dependence of the hydrogen and ethylene yields. The change in the hydrogen yield ($\Delta G = 0.3$) might be due to the scavenging of "free solvated electrons" by a radiolysis product. This was the cause of the dose dependence of the hydrogen yield from ethanol at low doses.⁷ The value of $G(\text{free } e^-_{\text{solv}}) = 0.3$ is consistent with the radiation-induced conductance of diethyl ether.⁸ The following is a possible mechanism for this portion of the reaction. The brackets indicate that the entities are within a spur.



The reason for suggesting that reactions 2 and 3 occur in the spur will be discussed in a later paper.⁸ Whether or not reaction 5 takes place in the spur does not influence the present discussion. As the dose absorbed increases, the concentration of products increases, and some of the products, such as the aldehydes and perhaps ethyl vinyl ether, will compete with the positive ions for the solvated electrons.



Thus, reactions 6 and 7 will be replaced by reactions 8 and 9, and the hydrogen yield will decrease. The decrease in $G(C_2H_4)$ with increasing dose is probably due to the reaction



where R is a free radical.

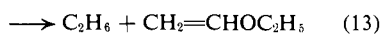
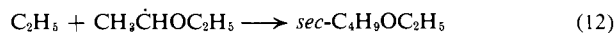
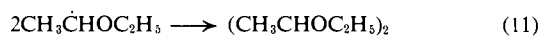
The Effects of Additives of the Product Yields. The effects of additives were studied at doses that were sufficiently high ($> 4 \times 10^{19}$ e.v./g.) that reaction 8 was occurring to the exclusion of reaction 6. The remaining

(8) G. R. Freeman and J. M. Fayadh, to be published.

portion of the hydrogen yield ($G = 3.4$) is formed from scavengeable and unscavengeable species. Kinetic analysis of the hydrogen yields from the ethyl vinyl ether solutions was done⁹ using mechanisms analogous to those reported in an earlier paper.¹⁰ The unscavengeable yield was found to be $G(\text{H}_2)_{\text{uns}} = 2.0 \pm 0.5$, whereas the scavengeable yield was $G(\text{H}_2)_{\text{sc}} = 1.4 \pm 0.5$. Adams and co-workers¹¹ found $G(\text{H}_2)_{\text{uns}} = 2.1$ and $G(\text{H}_2)_{\text{sc}} = 1.3$ for the γ -radiolysis of diethyl ether, using benzoquinone as inhibitor.

Low concentrations of 1,3-pentadiene were roughly ten times as efficient as benzene in inhibiting hydrogen and methane formation. The value of the ratio of the methyl affinity of 1,3-pentadiene to that of benzene in alkane solution is about 3000,^{12,13} and it seems unlikely that this value would be reduced 300-fold by changing the solvent from alkane to ether. It therefore appears that benzene affects the product yields mainly by an activation-transfer process.

The results from the pentadiene solutions indicate that most of the 2,3-diethoxybutane, ethyl *sec*-butyl ether, and ethane were scavengeable. These products were probably formed by the following free-radical reactions.



The small amount of butane (Table II) would be formed by

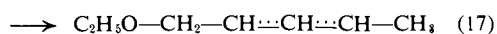
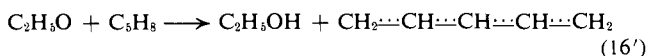


Further evidence that reactions 11, 12, and 15 occur is manifested by the value of the ratio $G(\textit{sec}\text{-C}_4\text{H}_9\text{OC}_2\text{H}_5)/[G(\text{C}_4\text{H}_{10}) \times G((\text{CH}_3\text{CHOC}_2\text{H}_5)_2)]^{1/2} = 2.0$. This is roughly the value that would be expected if the products were formed by the suggested free-radical combination reactions.¹⁴

Only about half of the ethanol is scavengeable, but this has several possible explanations among which it is not yet possible to choose. Part of the ethanol is probably formed by the reaction



where XH is a molecule or a free radical. However, reaction 16 could not be completely inhibited by 1,3-pentadiene because alkoxy radicals have a strong tendency to abstract from as well as to add to olefins.¹⁵



Part of the ethanol might also be formed by the reaction

(9) M. K. M. Ng, Ph.D. Thesis, University of Alberta, 1964.

(10) A. Singh and G. R. Freeman, *Can. J. Chem.*, **42**, 1877 (1964).

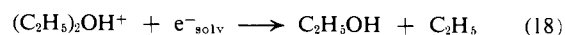
(11) G. E. Adams, J. H. Baxendale, and R. D. Sedgwick, *J. Phys. Chem.*, **63**, 854 (1959).

(12) A. Razbenbach and M. Szwarc, *Proc. Roy. Soc. (London)*, **A251**, 394 (1959).

(13) M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954).

(14) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 105 (1961). The "expected" value of 2 for the ratio involves assumptions about the relative values of the disproportionation to combination ratios of the radicals which do not seem unreasonable as a first approximation.

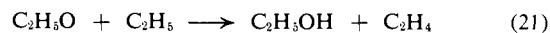
(15) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).



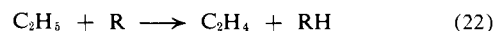
Only a half or less of the ethanol is formed by the unimolecular decomposition of ether because the ethylene yield is half or less of the ethanol yield (Figures 4 and



5). Reaction 19 could not be distinguished from reactions 20 and 21 occurring in a spur



The inhibition of the ethylene yield by pentadiene is probably due to interference with the reaction



although part of it might also be due to activation-transfer reactions.

The increased yield of carbon monoxide when ethyl vinyl ether was added to diethyl ether is evidence that activation transfer occurred from the latter to the former.

The Relative Probabilities of Cleaving the Various Types of Bonds. The product yields obtained at a dose of 10²⁰ e.v./g. will be used in this part of the discussion because the yields of some of the products could not be measured at lower doses.

The probability of primary cleavage of a C-H bond, per bond, is proportional to $G(\text{H}_2)/10 = 0.34$. The relative probabilities, per bond, of cleavage of the various types of bond are C-O ($G = 1.6$) \gg C-H ($G = 0.34$) $>$ C-C ($G = 0.28$)¹⁶. The probability of C-O cleavage is much greater than that of any other type of bond in the molecule. This coincides with the lowest bond dissociation energy in the molecule: $D(\text{C}_2\text{H}_5-\text{OC}_2\text{H}_5) = 77$ kcal./mole¹⁵; $D(\text{C}_2\text{H}_5\text{OCH}(\text{CH}_3)-\text{H}) = 94$ kcal./mole¹⁷; $D(\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2-\text{H}) \approx 99$ kcal./mole¹⁸⁻²⁰; $D(\text{C}_2\text{H}_5\text{OCH}_2-\text{CH}_3) \approx 85$ kcal./mole.¹⁸⁻²⁰ It also appears that electronic excitation energy in ether concentrates in the oxygen atom,²¹ and this might favor cleavage of bonds to the oxygen.

The C-H bonds rupture more frequently than the C-C bonds in spite of the fact that the former have a higher dissociation energy than do the latter. This can be partly explained by the cage effect. Methyl radicals are larger in size than are hydrogen atoms and so will undergo more recombination in the liquid cages.



The net amount of C-O bond cleavage would be less affected by the cage effect because alkoxy radicals are more likely to disproportionate with alkyl radicals than to combine with them.²²

The Relative Reactivities of the Methylene and Methyl Groups in Ether. The net amount of abstraction of hydrogen from the methylene group is much greater than that from the methyl group. The yield of 2,3-

(16) Relative $G(\text{C}-\text{C}) = 1/2G(\text{CH}_4 + \text{C}_2\text{H}_6 + \text{C}_2\text{H}_5\text{OCH}(\text{CH}_3)_2)$.

(17) C. Walling, *J. Phys. Chem.*, **64**, 166 (1960).

(18) Walling¹⁷ suggested that the ethoxy group and the methyl group have the same resonance stabilization effect, so these dissociation energies have been taken as equal to the corresponding dissociation energies in propane.^{19,20}

(19) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1958, p. 270 ff.

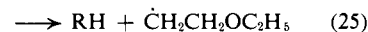
(20) L. A. Erede, *J. Phys. Chem.*, **65**, 2262 (1961).

(21) G. J. Hernandez, *J. Chem. Phys.*, **39**, 1355 (1963).

(22) J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley and Sons, New York, N. Y., 1964, p. 184.

diethoxybutane (2,3-dimer) was 2.57 units, that of the 1,3-dimer was ≤ 0.09 units, and the 1,4-dimer was not observed. Similarly, $G(\text{ethyl } \textit{sec}\text{-butyl ether}) = 0.74$ and $G(\text{ethyl } \textit{n}\text{-butyl ether}) = 0.03$. There is some doubt about the exact yields of the minor products, but the results indicate that the value of the ratio of the steady-state concentration of $\text{CH}_3\dot{\text{C}}\text{HOC}_2\text{H}_5$ to that of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{OC}_2\text{H}_5$ was about 40 to 1. If this difference is

attributed to the difference in the activation energies of the two abstraction reactions



then $\Delta E = (E_{25} - E_{24}) = 2.4$ kcal./mole. This is in good agreement with the corresponding value $\Delta E = 2.7$ kcal./mole in the ethanol system.⁷

Radiolysis of Diethyl Ether. II. Deuterium-Substituted Ethers in the Gas and Liquid Phases¹

Mark K. M. Ng and Gordon R. Freeman

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. Received December 5, 1964

The G values of the major products of the γ -radiolysis of diethyl ether vapor at 25° and a dose of 3×10^{20} e.v./g. are: hydrogen, 6.4; 2,3-diethoxybutane, 2.4; ethylene, 2.1; acetaldehyde, 1.4; methane, 1.3; ethyl isopropyl ether, 1.0; formaldehyde, 0.9; ethyl *sec*-butyl ether, 0.8; ethanol, 0.7; $G(-\text{C}_2\text{H}_5\text{OC}_2\text{H}_5) = 11.2$, based on the carbon in the measured products; $G(\text{excess } \text{H}_2 \text{ in products}) = 1.7$. The yields of acetaldehyde and ethyl vinyl ether ($G = 0.4$ at 19×10^{20} e.v./g.) decreased with increasing dose. The value of $G(-\text{ether})$ in the vapor phase is nearly the same as that in the liquid phase, although the product distribution is quite different in the two phases. Ether molecules, on the average, break into smaller fragments in the gas than in the liquid phase radiolysis. For the reactions $\text{R} + \text{M} \xrightarrow{k_a} \text{RH} + \text{R}'$ and $\text{R} + \text{R} \xrightarrow{k_c} \text{R}_2$, k_a/k_c is smaller in the vapor than in the liquid phase. Comparison of the product yields from the radiolysis of $(\text{C}_2\text{H}_5)_2\text{O}$, $(\text{CD}_3\text{CH}_2)_2\text{O}$, $(\text{CH}_3\text{CD}_2)_2\text{O}$, and $(\text{C}_2\text{D}_5)_2\text{O}$ showed that $\alpha\text{-C-H}$ bond cleavage was most important in hydrogen and methane formation, and $\beta\text{-C-H}$ cleavage was most important in ethylene formation although both types of cleavage made significant contributions to the formation of all three products.

Introduction

The γ -radiolysis of liquid diethyl ether was reported earlier.² The present article describes a brief study of the γ -radiolysis of the ether in the gas phase and also reports the influence of phase on the hydrogen-deuterium content of some of the gaseous products from various deuterium-substituted diethyl ethers.

Baxendale and Gilbert³ found the values $G(\text{H}_2) = 6.75 \pm 0.05$ and $G(\text{CH}_4) = 3.55 \pm 0.15$ for the γ -radiolysis of diethyl ether vapor. The yields of the other products were not measured. The conditions of the experiments were 116°, 140 and 470 mm. pressure,

(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) J. H. Baxendale and G. P. Gilbert, *Discussions Faraday Soc.*, **36**, 186 (1963).

dose rate = 3×10^{17} e.v./g. hr. (N_2O dosimetry), dose $\approx 10^{18}$ e.v./g.

Experimental

Most of the materials and procedures were described earlier.² Only new materials and techniques will be described here.

Three deuterated ethers were obtained from Merck Sharp and Dohme of Canada Ltd: $(\text{C}_2\text{D}_5)_2\text{O}$ (ether- d_{10}); $(\text{CD}_3\text{CH}_2)_2\text{O}$ (ether- $\beta\text{-}d_6$); $(\text{CH}_3\text{CD}_2)_2\text{O}$ (ether- $\alpha\text{-}d_4$). The isotopic impurities of the ethers were measured by n.m.r. analysis and are listed in Table I.

Table I. Isotopic Impurities in the Deuterated Ethers

Ether	Impurity	Atom % ^a
$(\text{CD}_3\text{CD}_2)_2\text{O}$	$\alpha\text{-H}$	9.0
	$\beta\text{-H}$	0.6
$(\text{CD}_3\text{CH}_2)_2\text{O}$	$\alpha\text{-D}$	25
	$\beta\text{-H}$	18
$(\text{CH}_3\text{CD}_2)_2\text{O}$	$\alpha\text{-H}$	4.2
	$\beta\text{-D}$	4.3

^a For example, $100(\alpha\text{-H})/(\alpha\text{-H} + \alpha\text{-D})$ is the atom % of H impurity in the α position.

The gas phase radiolysis cells were 500-ml. Pyrex bulbs with break-seals. Each cell contained about 0.7 g. (0.5 atm.) of sample. The irradiation temperature was $25 \pm 3^\circ$, and the dose rate was 6×10^{19} e.v./g. hr. Unless otherwise stated, the liquid and the vapor samples received a dose of 3.5×10^{20} e.v./g.

Liquid phase dosimetry was done with the Fricke dosimeter. Vapor phase dosimetry was done with ethylene, using $G(\text{H}_2) = 1.28$.⁴ Sufficient ethylene was placed in the bulb that the electron density of ethylene was approximately the same as that of ether in the ether samples.

The products were analyzed by the same techniques as those reported in the previous paper,² except that the gaseous products were analyzed by mass spectrom-

(4) R. A. Back, T. W. Woodward, and K. A. McLaughlan, *Can. J. Chem.*, **40**, 1380 (1962).