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A SURVEY OF THE RADIATION CHEMISTRY OF SOME ALIPHATIC ETHERS

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Amos S. Newton

February 19, 1957

Printed for the U.S. Atomic Energy Commission

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University of California, Berkeley, California

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ABSTRACT

The products resulting from the irradiation of seven liquid aliphatic ethers with helium ions have been determined. Correlation between the ethers and comparison with previous alcohol radiolysis data show the alkyl-oxygen bond to be most susceptible to rupture. The total G value for reduction equivalent of 7 to 10 is in the same range as previous results with alcohols. A postulated rearrangement of the ethers to an alkene and an alcohol is shown to follow the number of hydrogens on carbon atoms beta to the oxygen. Possible mechanisms for the formation of certain other products are discussed.

A SURVEY OF THE RADIATION CHEMISTRY OF  
SOME ALIPHATIC ETHERS<sup>a</sup>

Amos S. Newton  
Radiation Laboratory  
University of California, Berkeley, California  
February 19, 1957

INTRODUCTION

The radiolysis products of aliphatic alcohols have been studied by McDonnell and Newton.<sup>1</sup> It was shown that the principal products arise from reactions occurring at bonds between alkyl groups of hydrogen and the carbinol carbon atom. This was further evidence for the specificity of radiolytic reactivity. In order to develop a theoretical basis for such specificity of radiolytic reactivity a considerable body of data for compounds containing various functional groups and of various structural types is needed. Therefore the work has now been extended to cover some selected aliphatic ethers.

No previous studies of the radiation chemistry of pure ethers has been made nor have studies been possible on the direct photolysis of pure ethers. The studies on various ethers by thermal decomposition and studies on the decomposition of ethers in the presence of photochemically produced radicals have recently been summarized by Steacie.<sup>2</sup> Data on the thermal decomposition of dimethyl ether have recently been reconsidered by Benson.<sup>3</sup> The reactions of radicals with isopropyl ether in the liquid state have been described by Kharasch, Friedlander, and Urry<sup>4</sup> for radicals from the thermal decomposition of acetyl peroxide. These previous studies are related to the radiolysis of ethers as they give information about the reactions of free radicals with the substrate ether molecules under various conditions.

(a) Presented at the Symposium on the Radiation Chemistry of Organic Compounds, 131st meeting, American Chemical Society, Miami, April 8, 1957.

## EXPERIMENTAL

Purification of ethers. Reagent grade commercial or purified synthetic ethers were refluxed with sodium under an atmosphere of argon for 2 to 3 days, then distilled under argon through a 15-plate adiabatic column at a reflux ratio of about 20 to 1. The first and last quarters of this distillation were discarded. The center-cut material was collected in ampoules, evacuated, and stored in a dark cupboard. Samples taken periodically during the distillation were checked for constancy of refractive index and mass-spectrometer pattern coefficients. No variations larger than experimental error were found in the center-cut material. The density and freezing (or melting) point were determined on a sample taken about the middle of the distillation. The freezing point was determined in an apparatus similar to that described by Skau.<sup>5</sup> In those cases where the freezing point could not be determined because of excessive supercooling, the melting point is given, except for ethyl n-butyl ether, which could not be crystallized. The properties of the purified ethers are shown in Table I.

Tert-Butyl ethers. Methyl and ethyl tert-butyl ethers were synthesized by the method of Morris and Rigby.<sup>6</sup> After the initial purification according to these authors, the ethers were further purified by distillation from sodium as described above.

Irradiation procedures. Irradiations of higher energy input ( $> 0.3 \times 10^{22}$  ev/ml) were made in the metal cyclotron target described by McDonnell and Newton<sup>7</sup> as modified to contain 100 ml of liquid sample. The ethers were introduced at room temperature and degassed by slowly distilling about 10 percent of the liquid under vacuum. These were irradiated at an ion current of 1 to 2  $\mu$ a with 28-Mev helium ions impinging on the liquid. The bulk temperature of the liquid was 16 to 20°. Lower-energy-input irradiations were made in evacuated glass cells of the type described by Garrison, Haymond, and Weeks.<sup>8</sup> The ether was degassed by refluxing under vacuum,<sup>9</sup> then vacuum-distilled into the target chamber and sealed off. These cells were irradiated with about 42-Mev helium ions impinging on the liquid at currents of 0.1 to 0.2  $\mu$ a. The temperature was 25° to 30° and was roughly controlled by an air blast against the target, which was rapidly shaken during the irradiation. The vapor-phase irradiation

of methyl tert-butyl ether was made in a cell consisting of a 4-in.-diam. Pyrex tube 56 in. long with a thin ( $30 \text{ mg/cm}^2$ ) glass window in one end and a liquid reservoir sealed onto the other end. This was irradiated on the cyclotron using a beam external to the magnetic field. The calculated helium-ion range, using the stopping-power correlation derived by Thompson,<sup>10</sup> was about  $2/3$  the length of the target. The target was wrapped with aluminum foil and mounted on insulators for the beam measurement.

Gaseous products. Gaseous and low-boiling products were determined by draining the target liquid into an evacuated system and refluxing the target liquid under vacuum while pumping with an automatic Toepler pump.<sup>9</sup> Fractions volatile at  $-196^\circ$ ,  $-125^\circ$ , and  $-80^\circ$  were collected and then analyzed with a Consolidated Engineering Corporation Model 21-103 mass spectrometer as described previously.<sup>1</sup>

Total hydroxyl. The total hydroxyl content of the irradiated ethers was determined by the method of Ogg, Porter, and Willits.<sup>11</sup> The most reproducible results were obtained by sealing the irradiated ether with the acetic anhydride - pyridine reagent in an ampoule and heating at  $100^\circ$  for a half hour. The ampoule was cooled, opened, transferred to an Erlemeyer flask with water, warmed to hydrolyze the excess acetic anhydride, and the acetic acid titrated with alcohol sodium hydroxide. Synthetic samples of added primary and secondary alcohols gave values within 3 percent of the added values.

Polymer was determined by vacuum evaporation of the ether at room temperature, finally pumping at a few microns pressure. The values are only approximate, as some of the "polymer" may evaporate in this process or some ether may be left dissolved in the residue. "Polymer" is thus an approximate measure of the total high-boiling materials present.

Total carbonyl was determined as described previously.<sup>1</sup> The method for aldehydes (oxidation by  $\text{Ag}_2\text{O}$ ) gave very erratic results on ether solutions of aldehydes and ketones. Thus no separation of aldehydes and ketones was made though this would have been desirable in some cases.



## EXPERIMENTAL RESULTS

The radiolysis products of the ethers are shown in Table II. Only those products are listed which could be determined by the methods outlined. Liquid-phase analyses on samples from low-energy-input bombardments were not satisfactory because of the low concentration of products. Water yields were checked on the irradiated ethers but the yields, if any, were very low and the results erratic.

Several products were identified as present in the gas phase but not determined quantitatively. These have not been listed in Table II. For example, methyl ethyl ether was formed from diethyl and ethyl n-butyl ethers, diethyl ether from ethyl n-butyl ether and ethyl tert-butyl ether, methyl n-propyl ether from n-propyl ether, methyl isopropyl ether from diisopropyl ether, and dimethyl ether from methyl tert-butyl ether. Neopentane was seen as a product from the tert-butyl ethers. These products are in low yield. The amounts detected did not indicate large changes in yield with changes in total energy input, so it may be assumed that they are primary products.

The total oxidation-reduction equivalents given do not include any contribution from the "polymer," as the compounds formed have not been identified. Some properties of the "polymer" from various ethers are listed in Table III. These properties are to be interpreted as indicative only of the direction of change and not as the property of a pure compound. No vicinal glycols were found in any of the polymers.

## DISCUSSION

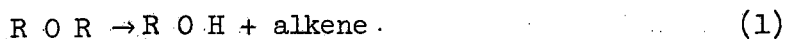
General correlations. Even from a cursory survey of the yields of hydrocarbons from the various ethers, it is evident that those formed in greatest yields are those resulting from rupture of the alkyl-oxygen bond. The total hydrocarbons resulting from bond ruptures at other carbon atoms are lower than those from the alkyl-oxygen bond by about a factor of two. This is in contrast to the alcohols, where the alkyl-oxygen bond was relatively less reactive than bonds to the carbinol carbon atom by about the same factor.

As in the alcohols, the yield of hydrogen is a maximum for ethers containing normal alkyl groups and decreases with increasing branching of the alkyl groups. The hydrocarbon yields are greatest for ethers containing branched alkyl groups and least for those containing normal alkyl groups.

The total reduction equivalent yield from liquid ethers is on the same order of magnitude ( G red. = 7 to 10 ) as for the alcohols.<sup>1</sup>

Unsaturated hydrocarbons. In general, the distribution of hydrocarbon types is quite similar to that found for the alcohols.<sup>1</sup> The ratio of n-carbon alkenes to n-carbon alkanes is quite high. This ratio is about one for the normal alkyl groups and increases with increasing branching of the alkyl group. This is as expected for a molecular disproportionation involving a rearrangement with hydrogen on a beta carbon atom, as previously postulated for the alcohols.<sup>1</sup>

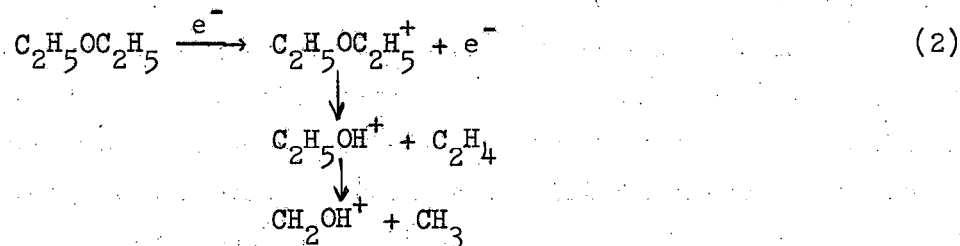
Schuler and Petry<sup>12</sup> have observed a similar excess of alkene over alkane in the x-ray radiolysis of ethyl iodide, n-propyl iodide, and isopropyl iodide, and suggests a disproportionation reaction as a mechanism for alkene formation. Bunbury, Williams, and Hamill<sup>13</sup> have found a similar high yield of alkene in the photolysis of ethyl iodide, and have postulated a diffusion-controlled disproportionation of radicals to account for the excess ethylene. Hanrahan and Willard and Hornig and Willard<sup>14</sup> have also observed the excess alkene from various alkyl iodides and have suggested a disproportion mechanism involving a molecular rearrangement with hydrogen atoms on the beta carbon atom. For ethers, this arrangement can be written:



Comparison of the yields of such alkenes from the various ethers and alcohols in Table V shows the absolute yield of alkene per hydrogen on beta carbon atoms to be fairly constant for the ethers, though low for the tertiary butyl ethers. The absolute yield per hydrogen on beta carbon atoms in alcohols is only about half that of the ethers. This is not unexpected because in alcohols the overall reactivity of the carbon-oxygen bond is low compared to other bonds at the carbinol carbon atom, and this competition must reduce the alkene yield. To eliminate such competition from the comparison, a better correlation is the ratio of alkene to alkane,

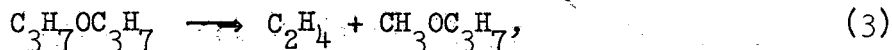
which represents a comparison of the rearrangement with other reactions (assumed as radical reactions) at the carbon-oxygen bond. The ratios of alkene per hydrogen atom on beta carbons to the corresponding alkanes are reasonably consistent considering the variety of compounds compared and the variations of the number of such hydrogen atoms from one to nine. If either product is produced by another mechanism the ratio will suffer. The ratio also suffers directly as the uncertainties in the determination of such alkenes and alkanes.

Such rearrangements as postulated in Eq. (1) are consistent with the rearrangements occurring in the mass-spectrometer ionization patterns of many of these ethers. For example, with diethyl ether the largest peak in mass spectrum is mass 31, which probably arises from the following sequence of steps:



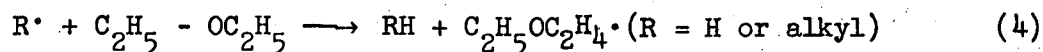
The principal peaks in the mass spectra of these ethers are shown in Table IV.<sup>15</sup> Except for n-propyl, n-butyl, and methyl tert-butyl ethers, all have large rearrangement peaks consistent with the type of mechanism outlined above for formation of alkenes. Difficulties with the use of mass-spectral data in attempting to predict such molecular rearrangement are: first, rearrangements can occur in neutral excited molecules as well as in the molecule ion; and, second, in any fragmentation process it has not been possible to predict with certainty which group will carry the charge, and thus a rearrangement in the ion might not be obvious. For example, in Eq. (2) above, if the methyl group had carried the final charge the arrangement would not have been obvious, since methyl ions can also be formed by other fragmentation processes.

From the higher ethers, other rearrangements are possible, e.g., from n-propyl ether the rearrangement,



can occur and would explain the ethylene yield being higher than the ethane yield from this compound. Methyl propyl ether was identified in the heavier gas fractions from this irradiation, but was not measured quantitatively. Such rearrangement does not occur to any extent in the ions as observed in the mass-spectrometer pattern of the normal ethers, and the products can also be formed by other processes, though these involve high-activation-energy reactions. Thus the evidence is not clear on this rearrangement. A possible correlation with alkyl halides is found in the data of Schuler and Petry,<sup>12</sup> who observed more ethylene than ethane from the radiolysis of n-propyl iodide.

Radical reactions. Due to the lack of identification of the "polymer" components, it is not possible at this time to formulate a complete mechanism for reactions occurring either in the primary track or in the bulk of the solution. From the results of Kharasch, Friedlander, and Urry<sup>4</sup> on the reactions of radicals with isopropyl ether, it does not appear likely that more than a small fraction of the observed yields of higher hydrocarbons can be formed in the bulk of the solution. Therefore, products such as propane and butane from ethyl ether, which cannot be formed from a radical-molecule reaction by hydrogen abstraction, must be formed principally in the tracks and spurs. The "polymer" and a large part of the hydrogen probably arise in the bulk of the solution from radical-molecule reactions, as illustrated with ethyl ether:



Since the resulting radical cannot react with another substrate ether molecule, it can only react with another radical to form a higher ether if the radical is alkyl, regenerate the ether if the radical is H, or form a high-boiling compound if the radical is another like itself. Kharasch<sup>4</sup> suggests that such radical-radical reactions result in disproportionation to give, in the case of isopropyl ether, alpha methyl-vinyl isopropyl ether. This latter compound would be expected to react further with radicals, though some should appear as a product. No evidence for such

disproportionation was found in the radiolysis experiments,<sup>a</sup> but the products might not have been observed by our analytical methods. This author suggests that the radical combination is more stable in the liquid at room temperature than was the case in Kharasch's experiment to yield a substituted glycol diether, in at least a good fraction of such collisions, leading to "polymer".

From methyl tert-butyl ether, the ethane yield appears quite high when compared to ethane from tert-butyl alcohol. If the criterion suggested in the paper of McDonnell and Newton<sup>1</sup> is applied,

$$K = \frac{|\text{CH}_4|}{[|\text{H}_2| \cdot |\text{C}_2\text{H}_6|]^{1/2}}, \quad \text{I}$$

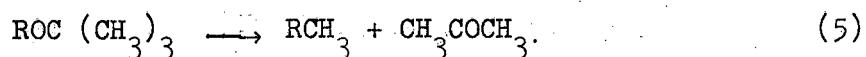
K for methyl tert-butyl ether is only about 1.2 compared to 1.96 for tert-butyl alcohol. If a K of 1.7 to 1.9 is applied, one finds that the ethane yield is expected to be only about 0.22, compared to a value found of 0.66. Similarly the propane yield from ethyl tert-butyl ether is very high, being over half the ethane yield, while the ethane yield from ethyl tert-butyl ether is less than that from methyl tert-butyl ether even though some ethane from the former compound must be formed from ethyl radicals as well as from methyl radical combinations. If one calculates the ethane formed from methyl radicals in ethyl tert-butyl ether using equation I,<sup>b</sup>  $G = 0.09$  of ethane results from methyl radicals, leaving 0.34 to arise from ethyl radicals. This value from ethyl radicals,  $G = 0.34$ , is about half the yield of ethane

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<sup>a</sup>Titration of the residual liquid from several ethers with bromine shows a bromine absorption about equivalent to the hydrogen formed. It is not certain that only double bonds are reacting in such a titration. Gas chromatograms of the residual liquid show unidentified peaks which have not been identified from the mass spectrum of the material collected from such peaks.

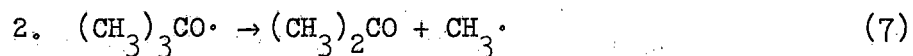
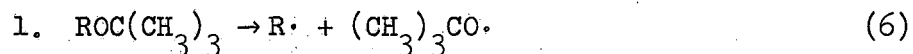
<sup>b</sup>Whether or not one accepts equation I, which was derived empirically from alcohol radiolysis data,<sup>1</sup> as having any validity of application to ethers, the arithmetical relations discussed still yield the inescapable conclusion that much of the ethane and propane from methyl tert-butyl ether and ethyl tert-butyl ether respectively cannot arise from competitive radical-radical reactions.

from ethyl ether, which is consistent with the distribution of ethyl groups. The yield of propane of  $G = 0.28$  is almost three times that found from sec-butyl alcohol.<sup>1</sup> It is also proportionately much larger than the yield of n-butane,  $G = 0.026$ , which product probably results from reactions of two ethyl radicals. Therefore it is necessary to conclude that much of the ethane from methyl tert-butyl ether and the propane from ethyl tert-butyl ether cannot be formed by competitive radical-radical reactions. One explanation of these high values for ethane and propane in these two respective ethers is the formation of such products by a methyl rearrangement, which can be written:



The evidence for or against such a methyl rearrangement is not conclusive. Stevenson<sup>16</sup> and Honig<sup>17</sup> have postulated a randomization and isomerization of  $\text{C}^{13}$ -labelled hydrocarbons under electron impact in the mass spectrometer, and Magat and Viallard<sup>18</sup> have postulated a rearrangement of ethyl groups in the mass spectral ionization pattern of 3,3, diethyl pentane. Chapiro<sup>19</sup> has postulated a methyl rearrangement to explain the degradation of polyisobutylene and polymethyl methacrylate.

The same effective result can be achieved by a kinetic mechanism outlined in the sequence of steps in Eq. 6, 7, and 8. Such a mechanism has the added advantage that the principle of microscopic reversibility is preserved.



Steps 7 and 8 must follow in very rapid order if the radicals R and  $\text{CH}_3$  are not to be separated by diffusion. The tert-butoxy ion is somewhat stable, as it occurs in the mass spectrum of di-tert-butyl peroxide,<sup>20</sup> and to a small extent the t-butoxy ion occurs in the mass spectrum of ethyl tert-butyl ether. The tert-butoxy radical has been shown to exist for at least limited periods in the thermal decomposition of di-tert-butyl peroxide in

liquid solvents.<sup>21,22</sup> Its decomposition by reaction (7) has been calculated to be endothermic by 5 kcal.<sup>21</sup> There is no necessary reason to suppose the reactions in the above sequence involve the same excitation states as the thermal process. In order for reactions (6), (7), and (8) to occur in the sequence outlined, the tert-butoxy radical would have to dissociate immediately and leave the radicals R and CH<sub>3</sub> close enough together to make the probability of reaction high.

The increased yield of ethane in the gas-phase irradiation of methyl tert-butyl ether (Table I) does not prove or disprove the above mechanism. It does show the existence of many radicals which, in the gas phase, are uncaged and which therefore contact fewer molecules of substrate. Thus, in the gas phase, it is expected that radical-radical reactions should be increased and radical-molecule reactions decreased, yielding relatively more ethane and less methane. Back reactions are also decreased, resulting in an increase in overall yields. A surprising result is the large increase in isobutane yield. This is coupled with an almost equally high yield of neopentane. Thus the back reaction of tert-butyl radicals and methoxy radicals in the liquid state must be quite large. The total reduction equivalent in the vapor phase is about 1.7 times that in the liquid phase, a result also indicative of a large back reaction in the liquid phase.

#### ACKNOWLEDGMENTS

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Table I  
Properties of Ethers Used

Ether	Source	$n_D^{25}$	$d_{25/4}$	B.P. ° 760 mm Hg	F.P. ° <sup>g</sup>
n-Propyl	Eastman White Label	1.3777	0.7418	89.7°	-123.6° (m.p.)
	Literature values <sup>c</sup>	1.3786 <sup>d</sup> 1.3780 <sup>c</sup>	0.7439 <sup>d</sup> 0.7422 <sup>c</sup>	90.5 <sup>d</sup> 90.5 <sup>c</sup>	-122 <sup>f</sup>
n-Butyl	Baker and Adamson reagent quality	1.3968	0.7638	142.2	-95.3 (m.p.)
	Literature values <sup>b</sup>	1.39685	0.76461	141.97	-95.37
Methyl tert-butyl	Synthesis	1.3663	0.7352	55.2	-108.5
	Literature values <sup>a</sup>	1.3667	0.7354	55.2	--
Ethyl tert-butyl	Synthesis	1.3731	0.7353	72.9	-97.2
	Literature values <sup>a</sup>	1.3728	0.7364	73.1	--
Ethyl n-butyl	Eastman White Label	1.3791	0.7440	92.2	formed glass
	Literature values <sup>a</sup>	1.3798	0.7447	92.3	--
Iso propyl	Baker and Adamson reagent quality	1.3653	0.7184	68.6	-85.7
	Literature values <sup>b</sup>	1.36618	0.72303	68.27	-85.89
Ethyl	J.T. Baker Chemical Company	1.3497	0.7077	34.5	-125.5
	Literature values <sup>e</sup>	1.34968	0.7068	34.6	-123.3 metastable -116.3 stable

<sup>a</sup>J. F. Norris and G. W. Rigby, J. Am. Chem. Soc. 54, 2097 (1932).

<sup>b</sup>R. R. Dreisbach and R. A. Martin, Ind. Eng. Chem. 41, 2875 (1949).

<sup>c</sup>J. Timmerans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Press, New York, 1950, p. 346 (Interpolated values for  $d^{25}$  and  $n_D^{25}$ ).

<sup>d</sup>A. I. Vogel, J. Chem. Soc. (London), 616 (1948).

<sup>e</sup>R. R. Dreisbach, "Physico-Properties of Chemical Substances," Serial No. 17.2. Dow Chemical Co., Midland, Michigan.

<sup>f</sup>Heilbron, Dict. of Organic Compounds, Vol. II, p. 439, Egge and Spottiswode, London (1953).

<sup>g</sup>Estimated accuracy of F. P. values about  $\pm 0.2^\circ$ .



Table II

## Yields of Some Products Formed in the Helium-Ion Irradiation of Some Aliphatic Ethers

Ether	Ethyl	Ethyl n-Butyl	n-Propyl	n-Butyl	Isopropyl	Methyl t-Butyl	Ethyl			
	0.026 <sup>g</sup>	0.026 <sup>g</sup>	0.31	0.40	0.44	0.025 <sup>g</sup>	0.36	0.32	0.33	
Energy input ev/ml x 10 <sup>-22</sup>	Yield, G. molecules product/100ev.									
	0.2μah gas phase									
H <sub>2</sub>	3.62	3.25	2.94	2.74	2.71	2.50	2.28	1.55	1.84	1.96
CO	0.127	0.070	0.087	0.104	0.055	0.071	0.082	0.144	0.43	0.099
CH <sub>4</sub>	0.24	0.095	0.104	0.071	0.061	0.88	0.87	1.03	0.80	0.77
C <sub>2</sub> H <sub>2</sub>	0.091	0.037	0.042	0.040	0.026	0.015	0.03	0.018	0.12	0.034
C <sub>2</sub> H <sub>4</sub>	1.07	0.52	0.42	0.24	0.14	0.064	0.033	0.002	<0.05	0.32
C <sub>2</sub> H <sub>6</sub>	0.62	0.31	0.27	0.22	0.036	0.142	0.159	0.66	1.38	0.45
C <sub>3</sub> H <sub>4</sub> (e)	--	--	~0.001	~0.016	~0.004	~0.011	~0.006	~0.03	0.05	~0.02
C <sub>3</sub> H <sub>6</sub>	~0.01	0.12	0.10	0.49	0.125	1.56	1.14	0.037	0.05	0.050
C <sub>3</sub> H <sub>8</sub>	0.12	0.10	0.10	0.43	0.123	0.61	0.45	0.024	0.10	0.28
C <sub>4</sub> H <sub>8</sub>	~0.007	0.29	>0.18	~0.005	0.38 <sup>a</sup>	0.02 <sup>b</sup>	>0.008 <sup>b</sup>	0.55 <sup>b</sup>	0.38 <sup>b</sup>	0.71 <sup>b</sup>
C <sub>4</sub> H <sub>10</sub>	0.15	0.29	>0.14	~0.03	0.39	0.32 <sup>c</sup>	>0.142 <sup>c</sup>	0.15 <sup>c</sup>	0.59 <sup>c</sup>	0.22 <sup>d</sup>
Total carbonyl	--	--	1.13	1.36	0.94	--	~3.1	1.85	--	2.47
Total hydroxyl	--	--	1.32	1.30	1.4	--	0.33	0.69 <sup>h</sup>	--	0.62 <sup>h</sup>
"Polymer"	--	--	~1.6	~1.7	~2.2	--	~0.33	~1.15	--	~1.0
Total reduction	9.50	8.09	7.11	6.98	6.64	8.90	7.80	6.93	11.56 <sup>j</sup>	7.33
Total oxidation	--	--	2.7	3.04	2.04	--	6.64	4.37	--	5.46

a. Mixture of about 67% butene-1 and 33% butene-2; b. All isobutene; c. All isobutane; d. 11.7% n-butane 88.3% isobutane; e. Have not distinguished methyl acetylene from propadiene; g. Bombardment in glass cell; h. t-Butyl alcohol not measured by the technique used; j. Includes neopentane yield of G = 0.57.

Table III

Properties of polymers resulting from the irradiation  
of some ethers with helium ions.

Ether	$d_4^{25}$	$n_D^{25}$
Properties of Polymer		
n-Propyl	0.901	1.4286
n-Butyl	0.854	1.4328
Ethyl n-Butyl	0.893	1.4273(a)
iso-Propyl	0.947	1.4309
Methyl tert-Butyl	0.902	1.4242
Ethyl tert-Butyl	0.907	1.4326

(a) BP =  $\sim 280^\circ$ , MW = 286 (Rast method)

Table IV

Principal peaks in mass spectra of ethers.

<u>M/e</u>	<u>Ethyl</u>	<u>Ethyl n-Butyl</u>	<u>n-Propyl</u>	<u>n-Butyl</u>	<u>iso-Propyl</u>	<u>Methyl tert-Butyl</u>	<u>Ethyl tert-Butyl</u>
15	16.9	8.91	3.85	3.12	14.4	17.2	14.0
27	33.9	35.4	21.3	20.3	16.0	13.9	16.0
28	8.16	12.0	2.76	7.94	1.83	3.96	3.22
29	61.9	54.7	7.72	34.1	4.71R	24.47R?	23.1
31	<u>100.0R</u>	83.1R	5.77R	3.25R	3.63R	2.04	8.5R
43	8.8	10.1	<u>100.0</u>	4.38	50.7	26.52	12.5
45	32.7	8.06	1.45R+i	2.47R	<u>100.0R</u>	6.24R	2.2R
57	--	29.4	0.80	<u>100.0</u>	0.26	26.72	34.5
59	41.3	<u>100.0</u>	3.07	0.46i	8.91	0.29	<u>100.0R</u>
73	2.12	4.01	16.93	1.30	--	<u>100.0</u>	0.29
74	23.3P	0.29i	0.71i	0.10i	--	4.78i	0.00
87	--	1.49	0.07	16.0	18.2	0.02	34.25
88	--	0.07i	0.00	0.83i	0.90i	0.02P	2.4i
102	--	3.11P	6.83P	--	1.29P	--	0.00P
130	--	--	--	1.52P	--	--	--

R = rearrangement peak.

i = isotope peak.

P = parent peak.

Table V

Comparison of absolute alkene yields and ratio of alkene to alkane produced with number of hydrogens on carbons, beta to oxygen in ethers and alcohols.

Ether	Alkyl Group	Z-No. H's on $\beta$ -carbon	$\frac{G(\text{Alkene})}{Z}$	$\frac{G(\text{alkene})}{G(\text{alkane})} \cdot \frac{1}{Z}$
Ethyl	$C_2H_5$	3	0.18	0.58
Ethyl n-Butyl	$C_2H_5$	3	0.16	0.56
	$C_4H_9$	2	0.15	0.50
n-Propyl	n- $C_3H_7$	2	0.12	0.57
n-Butyl	n- $C_4H_9$	2	0.10	0.49
Isopropyl	i- $C_3H_7$	6	0.13	0.43
Methyl tert-Butyl	t- $C_4H_9$	9	0.06	0.41
Ethyl tert-Butyl	t- $C_4H_9$	9	0.08	0.36
	$C_2H_5$	3	0.11	0.31 <sup>(a)</sup>
<u>Alcohol (from Ref. 1)</u>				
Ethyl	$C_2H_5$	3	0.06	0.43 <sup>(a)</sup>
n-Propyl	n- $C_3H_7$	2	0.075	0.47
Isopropyl	i- $C_3H_7$	6	0.045	0.51
n-Butyl	n- $C_4H_9$	2	0.045	0.37
Isobutyl	i- $C_4H_9$	1	0.07	0.41
sec-Butyl	s- $C_4H_9$	5	0.035	0.36 <sup>(b)</sup>
tert-Butyl	t- $C_4H_9$	9	0.03 <sup>(c)</sup>	0.28 <sup>(c)</sup>

(a) Ethane yield corrected for estimated yield from methyl radical reactions.

(b) n-Butane yield corrected for estimated production from ethyl radicals.

(c) Isobutane analysis only approximate.

## REFERENCES

1. W. R. McDonell and A. S. Newton, J. Am. Chem. Soc. 76, 4651 (1954).
2. E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, 2nd Ed. Vol. I, 1954, pp. 196-205.
3. S. W. Benson, J. Chem. Phys. 25, 27 (1956).
4. M. S. Kharasch, H. N. Friedlander, and W. H. Urry, J. Org. Chem. 16, 533 (1951).
5. E. L. Skau, J. Phys. Chem. 37, 609 (1933).
6. J. F. Norris and G. W. Rigby, J. Am. Chem. Soc. 54, 2088 (1932).
7. W. R. McDonell and A. S. Newton, Nucleonics 10-1, 62 (1952).
8. W. M. Garrison, H. R. Haymond, and B. M. Weeks, Radiation Research 1, 97 (1954).
9. A. S. Newton, Anal. Chem. 28, 1214 (1956).
10. T. J. Thompson, Phys. Rev. 85, 765 (1952).
11. C. L. Ogg, W. L. Porter, and C. O. Willits, Ind. Eng. Chem., Anal. Ed. 17, 394 (1945).
12. R. H. Schuler and R. C. Petry, J. Am. Chem. Soc. 78, 3954 (1956).
13. D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, J. Am. Chem. Soc. 78, 6228 (1956).
14. E. O. Hornig and J. E. Willard; and R. J. Hanrahan and J. E. Willard, private communication. (In press, J. Am. Chem. Soc., 1957).
15. The complete mass spectral patterns for most of these ethers are recorded in "Catalog of Mass Spectral Data," API Project 44, Carnegie Institute of Technology, Pittsburgh. F. D. Rossini, Editor, Serial Nos. 321, 327, 372, 804, 818, and 830.
16. D. P. Stevenson, J. Chem. Phys. 19, 17 (1951).
17. R. E. Honig, Phys. Rev. 75, 1319 (1949).
18. M. Magat and R. Viallard, J. chimie phys. 48, 385 (1951).
19. A. Chapiro, J. chimie phys. 53, 306 (1956); 53, 295 (1956).
20. Ref. 12, Serial No. 831.
21. J. H. Raley, F. F. Rust, and W. E. Vaughan, J. Am. Chem. Soc. 70, 1336 (1948).
22. J. H. Raley, F. F. Rust, and W. E. Vaughan, J. Am. Chem. Soc. 70, 88 (1948).