a great fund of information about radiation chem-

much tedious radiation chemistry is obviated, and istry becomes available in the extensive tables of known mass spectra.

# A SURVEY OF THE RADIATION CHEMISTRY OF SOME ALIPHATIC ETHERS<sup>1</sup>

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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.

#### Introduction

The radiolysis products of aliphatic alcohols have been studied by McDonell and Newton.<sup>2</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 been summarized recently by Steacie.<sup>3</sup> Data on the thermal decomposition of dimethyl ether recently have been reconsidered by Benson.<sup>4</sup> The reactions of radicals with isopropyl ether in the liquid state have been described by Kharasch, Friedlander and Urry<sup>5</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.

#### 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 distilla-tion were discarded. The center-cut material was collected in ampoules, evacuated, and stored in a dark cupboard.

(5) M. S. Kharasch, H. N. Friedlander and W. H. Urry, J. Org. Chem., 16, 533 (1951).

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>6</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.

t-Butyl Ethers.-Methyl and ethyl t-butyl ethers were synthesized by the method of Norris and Rigby.<sup>7</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  $(>0.3 \times 10^{22} \text{ e.v./ml.})$  were made in the metal cyclotron target described by McDonell and Newton<sup>8</sup> as modified to contain 100 ml. of liquid sample. The ethers were introduced at room temperature and degassed by slowly distilling about 10% of the liquid under vacuum. These were irra-diated at an ion current of 1 to 2  $\mu$ a. with 28-Mev. helium ions impingent 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 Garri-son, Haymond and Weeks.<sup>9</sup> The ether was degassed by son, Haymond and weeks. The ether was degassed by refluxing under vacuum, <sup>10</sup> then vacuum-distilled into the target chamber and sealed off. These cells were irradiated with about 42-Mev. helium ions impingent 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 shaken rapidly during the irradiation. The vapor-phase irradiation of methyl *t*-butyl ether was made in a cell consisting of a 4 in -diam. Duray with a 56 in long with 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>11</sup> was about  $\frac{2}{3}$  the length of the target. The target was wrapped with alumi-num foil and mounted on insulators for the hear measure num 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>10</sup> Frac-tions volatile at -196, -125 and  $-80^{\circ}$  were collected and then analyzed with a Consolidated Engineering Corporation Model 21-103 mass spectrometer as described previously.<sup>2</sup>

(10) A. S. Newton, Anal. Chem., 28, 1214 (1956).

<sup>(1)</sup> Presented at the Symposium on the Radiation Chemistry of Organic Compounds, 131st meeting, American Chemical Society, Miami, April 8, 1957.

<sup>(2)</sup> W. R. McDonell and A. S. Newton, J. Am. Chem. Soc., 76, 4651 (1954).

<sup>(3)</sup> E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 2nd Ed., Vol. I, 1954, pp. 196-205.

<sup>(4)</sup> S. W. Benson, J. Chem. Phys., 25, 27 (1956).

<sup>(6)</sup> E. L. Skau, This JOURNAL, 37, 609 (1933).

<sup>(7)</sup> J. F. Norris and G. W. Rigby, J. Am. Chem. Soc., 54, 2088 (1932).

<sup>(8)</sup> W. R. McDonell and A. S. Newton, Nucleonics, 10-1, 62 (1952). (9) W. M. Garrison, H. R. Haymond and B. M. Weeks, Radiation Research, 1, 97 (1954).

<sup>(11)</sup> T. J. Thompson, Phys. Rev., 85, 765 (1952).

Ether	Source	n <sup>25</sup> D	d25/4	B.p., °C. (760 mm.)	F.p., °C.9
n-Propyl	Eastman White Label	1.3777	0.7418	89.7	-123.6 (m.p.)
	Lit. values <sup>o</sup>	1.3786d	.74394	$90.5^{d}$	-122'
		$1.3780^{\circ}$	$.7422^{\circ}$	90.5°	
n-Butyl	Baker and Adamson reagent quality	1.3968	.7638	142.2	- 95.3 (m.p.)
	Lit. values <sup><math>b</math></sup>	1.39685	.76461	141.97	- 95.37
Methyl <i>t</i> -butyl	Synthesis	1.3663	.7352	55.2	-108.5
	Lit. values <sup>a</sup>	1.3667	.7354	55.2	•••
Ethyl <i>t</i> -butyl	Synthesis	1.3731	.7353	72.9	- 97.2
	Lit. values <sup><math>a</math></sup>	1.3728	.7364	73.1	
Ethyl <i>n</i> -butyl	Eastman White Label	1.3791	.7440	92.2	formed glass
	Lit. values <sup>a</sup>	1.3798	.7447	92.3	
Isopropyl	Baker and Adamson reagent quality	1.3653	.7184	68.6	- 85.7
	Lit. values <sup>b</sup>	1.36618	.72303	68.27	- 85.89
$\mathbf{Ethyl}$	J. T. Baker Chemical Co.	1.3497	.7077	34.5	-125.5
	Lit. values <sup>e</sup>	1.34968	.7068	34.6	-123.3 metastable $-116.3$ stable

## TABLE I PROPERTIES OF ETHERS USED

<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. Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier Press, New York, N. Y., 1950, p. 346 (interpolated values for d<sup>25</sup> and n<sup>25</sup>D). <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, Eyre and Spottiswoode, London, 1953, p. 439. <sup>e</sup> Estimated accuracy of f. p. values about ±0.2°.

TABLE II

YIELDS OF SOME PRODUCTS FORMED IN THE HELIUM-ION IRRADIATION OF SOME ALIPHATIC ETHERS											
Ether		$\mathbf{E}\mathbf{thyl}$	Ethyl $n$	-butyl	n-Propyl	n-Butyl	Isopro	pyl	Methyl	<i>t</i> -butyl	Ethyl
Energy input e.v./ml. ×	10-22	0.026/	0.026/	0.31	0.40 Yield,	0.44 G molecules	0.025 <sup>f</sup> product/10	0.36 0 e.v.	0.32	0.2μah gas phase	0,33
$H_2$		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
$CH_4$		.24	.095	.104	.071	.061	.88	0.87	1.03	. 80	.77
$C_2H_2$		.091	.037	.042	.040	. 026	.015	.03	0.018	. 1 <b>2</b>	.034
$C_2H_4$		1.07	.52	. 42	.24	.14	.064	.033	.002	$\sim .05$	. 32
$C_2H_6$		0.62	.31	. 27	. 22	. 036	.142	.159	. 66	1.38	. 45
$C_{8}H_{4}^{e}$				$\sim$ .001	$\sim$ .016	$\sim$ .004	$\sim$ .011	$\sim$ .006	$\sim$ .03	0.05	$\sim .02$
$C_{8}H_{6}$		$\sim$ .01	.12	.10	. 49	.125	1.56	1.14	.037	.05	.050
$C_{3}H_{8}$		.12	. 10	. 10	. 43	.123	0.61	0.45	. 024	.10	.28
$C_4H_8$		$\sim$ .007	. 29	> .18	$\sim$ .005	$.38^{a}$	$.02^{b}$	>0.008*	. 55%	.380	.710
$C_4H_{10}$		.15	.29	> .14	$\sim$ .03	.39	.32°	$>0.142^{\circ}$	.15°	. 59°	.22ª
Total carbo	onyl	• • •		1.13	1.36	.94		$\sim 3.1$	1.85	• • •	2.47
Total hydro	oxyl			1.32	1.30	1,4		0.33	0.69°		0.62''
"Polymer"				$\sim 1.6$	$\sim 1.7$	$\sim 2.2$		$\sim 0.33$	$\sim 1.15$		~1.0
Total reduc	etion	9.50	8.09	7.11	6.98	6.64	8.90	7.80	6.93	$11.56^{h}$	7.33
Total oxida	tion		• • •	<b>2.7</b>	3.04	<b>2.04</b>	• • •	6.64	4.37	•••	5.46

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

Total Hydroxyl.—The total hydroxyl content of the irradiated ethers was determined by the method of Ogg, Porter and Willits.<sup>12</sup> The most reproducible results were obtained by sealing the irradiated ether with the acetic anhydridepyridine reagent in an ampoule and heating at 100° for a half hour. The ampoule was cooled, opened, transferred to an erlenmeyer flask with water, warmed to hydrolyze the excess acetic anhydride, and the acetic acid titrated with alcoholic sodium hydroxide. Synthetic samples of added primary and secondary alcohols gave values within 3% 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

(12) C: L. Ogg, W. L. Porter and C. O. Willits, Ind. Eng. Chem., Anal. Ed., 17, 394 (1945). 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>2</sup> The method for aldehydes (oxidation by  $Ag_2O$ ) 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-energyinput 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 diethyl *n*-butyl ether and ethyl *t*-butyl ether, methyl *n*propyl ether from *n*-propyl ether, methyl isopropyl ether from diisopropyl ether, and dimethyl ether from methyl *t*-butyl ether. Neopentane was seen as a product from the *t*-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.

#### TABLE III

PROPERTIES OF POLYMERS RESULTING FROM THE IRRADIATION OF SOME ETHERS WITH HELIUM IONS

Ether	d <sup>25</sup> 4 n <sup>25</sup> D Properties of polymer				
n-Propyl	0.901	1.4286			
$n ext{-Butyl}$	.854	1.4328			
Ethyl <i>n</i> -butyl	.893	$1.4273^{a}$			
Isopropyl	.947	1.4309			
Methyl <i>t</i> -butyl	.902	1.4242			
Ethyl <i>t</i> -butyl	.907	1.4326			

<sup>a</sup> b. p.  $\sim 280^{\circ}$ , mol. wt. = 286. (Rast method).

#### 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>2</sup>

**Unsaturated Hydrocarbons.**—In general, the distribution of hydrocarbon types is quite similar to that found for the alcohols. The ratio of *n*-carbon alkenes to *n*-carbon alkanes is quite high. This ratio is adout 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>2</sup>

Schuler and Petry<sup>13</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>14</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>15</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

#### $ROR \longrightarrow ROH + alkene$ (1)

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 *t*-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 over-all 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 results 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 sequence (2) of steps

<sup>(13)</sup> R. H. Schuler and R. C. Petry, J. Am. Chem. Soc., 78, 3954 (1956).

<sup>(14)</sup> D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **78**, 6228 (1956).

<sup>(15)</sup> E. O. Hornig and J. E. Willard, *ibid.*, **79**, 2429 (1957); R. J. Hanrahan and J. E. Willard, *ibid.*, **79**, 2434 (1957).

	Princ	IPAL PEAKS IN MA	ss Spectra o	f Ethers <sup>a</sup>		
Ethyl	Ethyl n-butyl	n-Propyl	n-Butyl	Isopropy	Methyl <i>t</i> -butyl	Ethy t-butyl
16.9	8.91	3.85	3.12	14.4	17.2	14.0
33.9	35.4	21.3	20.3	16.0	13.9	16.0
8.16	12.0	2.76	7.94	1.83	3.96	3.22
61.9	54.7	7.72	34.1	4.71R	24.47 R?	23.1
100.0R	83.1R	5.77 R	3.25R	3.63R	2.04	8 5R
8.8	10.1	100.0	4.38	50.7	26.52	12.5
32.7	8.06	1.45R + i	$\mathbf{2.47R}$	100 OR	$6.24\mathrm{R}$	2.2R
	29.4	0.80	100.0	0.26	26.72	34.5
41.3	100.0	3.07	0.46i	8.91	0.29	100.0R
2.12	4 01	16.93	1.30		100.0	0.29
23.3P	0. <b>2</b> 9i	0.71i	0.10i		4.78i	0.00
	1.49	0.07	16.0	18.2	0.02	34 25

0.83i

1.52P

. . .

TABLE IV						
PRINCIPAL	Peaks	IN	Mass	Spectra	OF	ETHE

0.00

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6.83P

. . . <sup>a</sup> R = rearrangement peak; i = isotope peak; P = parent peak.

0.07i

3.11P

#### TABLE V

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COMPARISON OF ABSOLUTE ALKENE YIELDS AND RATIO OF ALKENE TO ALKANE PRODUCED WITH NUMBER OF HYDRO-GENS ON CARBONS, BETA TO OXYGEN IN ETHERS AND ALCOHOLS

				G(alkene)
Ether	Alkyl group	$\begin{array}{l} Z = \mathrm{No.} \\ \mathrm{H's \ on} \\ \beta \text{-carbon} \end{array}$	$\frac{G(\text{Alkene})}{Z}$	$\frac{G(\text{alkane})}{\times \frac{1}{Z}}$
$\mathbf{E}\mathbf{thyl}$	$C_2H_5$	3	0.18	0.58
Ethyl <i>n</i> -butyl	$C_2H_5$	3	.16	. 56
	$C_4H_9$	<b>2</b>	.15	. 50
n-Propyl	$n-C_3H_7$	<b>2</b>	. 12	. 57
n-Butyl	n-C <sub>4</sub> H,	<b>2</b>	.10	. 49
Isopropyl	i-C <sub>3</sub> H <sub>7</sub>	6	.13	. 43
Methyl <i>t</i> -butyl	$t-C_4H_y$	9	.06	. 41
Ethyl <i>t-</i> butyl	t-C₄H <sub>9</sub>	9	.08	. 36
	$C_2H_5$	3	.11	.31ª
Alcohol (from ref. 2)				
$\mathbf{Ethyl}$	$C_2H_6$	3	0.06	0.43ª
n-Propyl	$n-C_3H_7$	2	.075	.47
Isopropyl	i-C <sub>3</sub> H <sub>7</sub>	<b>6</b> ·	.045	.51
n-Butyl	$n-C_4H_9$	<b>2</b>	.045	.37
Isobutyl	$i-C_4H_8$	1	.07	.41
sec-Butyl	$s-C_4H_9$	5	.035	.36*
t-Butyl	t-C.H.	9	. 03°	28°

<sup>a</sup> Ethane yield corrected for estimated yield from methyl radical reactions. <sup>b</sup> n-Butane yield corrected for estimated production from ethyl radicals. 'Isobutane analysis only approximate.

The principal peaks in the mass spectra of these ethers are shown in Table IV.<sup>16</sup> Except for npropyl, *n*-butyl and methyl *t*-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 also can be formed by other fragmentation processes.

0.90i

1.29P

. . .

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

$$C_{3}H_{7}OC_{3}H_{7} \longrightarrow C_{2}H_{4} + CH_{3}OC_{3}H_{7} \qquad (3)$$

0.02P

. . .

. . .

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 also can be formed by other processes. 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>13</sup> who observed more ethylene than ethane from the radiolysis of *n*-propyl iodide.

Radical Reactions.—Because of 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>5</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 radicalmolecule 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

## $R_{\cdot} + C_2H_5 \longrightarrow$

 $RH + C_2H_5OC_2H_4(R = H \text{ or alkyl})$  (4)

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

2.4i

. . .

0.00P

102

130

<sup>(16)</sup> 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.

is H, or form a high-boiling compound if the radical is another like itself. Kharasch<sup>5</sup> suggests that such radical-radical reactions result in disproportionation to give, in the case of isopropyl ether,  $\alpha$ -methylvinyl 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>17</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 *t*-butyl ether, the ethane yield appears quite high when compared to ethane from *t*-butyl alcohol. If the criterion suggested in the paper of McDonell and Newton<sup>2</sup> is applied

$$K = [CH_4] / ([H_2] / [C_2H_6])^{1/2}$$
(I)

K for methyl t-butyl ether is only about 1.2 compared to 1.96 for t-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 t-butyl ether is very high, being over half the ethane yield, while the ethane yield from ethyl tbutyl ether is less than that from methyl t-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 t-butyl ether using equation  $I_{,18} G = 0.09$ 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 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>2</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 *t*-butyl ether and the propane from ethyl t-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

$$ROC(CH_3)_3 \longrightarrow RCH_3 + CH_3COCH_3$$
 (5)

The evidence for or against such a methyl rearrangement is not conclusive. Stevenson<sup>19</sup> and

(18) Whether or not one accepts eq. I, which was derived empirically from alcohol radiolysis data,<sup>2</sup> as having any validity of application to ethers, the arithmetical relations discussed still yield the inescepable conclusion that much of the ethane and propane from methyl *i*-butyl ether and ethyl *i*-butyl ether, respectively, cannot arise from competitive radical-radical reactions.

(19) D. P. Stevenson, J. Chem. Phys., 19, 17 (1951).

Honig<sup>20</sup> have postulated a randomization and isomerization of  $C^{13}$ -labeled hydrocarbons under electron impact in the mass spectrometer, and Magat and Viallard<sup>21</sup> have postulated a rearrangement of ethyl groups in the mass spectral ionization pattern of 3,3-diethylpentane. Chapiro<sup>22</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.

1. 
$$\operatorname{ROC}(\operatorname{CH}_3)_3 \longrightarrow \operatorname{R}_{\cdot} + (\operatorname{CH}_3)_3 \operatorname{CO}_{\cdot}$$
 (6)

2. 
$$(CH_3)_3CO \longrightarrow (CH_3)_2CO + CH_3$$
 (7)

3. 
$$\mathbf{R} + \mathbf{CH}_{\mathbf{3}} \longrightarrow \mathbf{RCH}_{\mathbf{3}}$$
 (8)

Steps 7 and 8 must follow in very rapid order if the radicals R and CH<sub>3</sub> are not to be separated by diffusion. The t-butoxy ion is somewhat stable, as it occurs in the mass spectrum of di-t-butyl peroxide,<sup>23</sup> and to a small extent the t-butoxy ion occurs in the mass spectrum of ethyl t-butyl ether. The *t*-butoxy radical has been shown to exist for at least limited periods in the thermal decomposition of di-t-butyl peroxide in liquid solvents.<sup>24,25</sup> Its decomposition by reaction  $\hat{7}$  has been calculated to be endothermic by 5 kcal.<sup>24</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 t-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 t-butyl ether (Table II) 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 over-all 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 *t*-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.

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(21) M. Magat and R. Viallard, J. chim. phys., 48, 385 (1951).

<sup>(17)</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>(20)</sup> R. E. Honig, Phys. Rev., 75, 1319 (1949).

<sup>(22)</sup> A. Chapiro, *ibid.*, **53**, 806 (1956); **53**, 295 (1956).
(23) Ref. 16, Serial No. 831.

<sup>(24)</sup> J. H. Raley, F. F. Rust and W. E. Vaughan, J. Am. Chem. Soc., 70, 1336 (1948).

<sup>(25)</sup> J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 88 (1948).

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## SOME ASPECTS OF THE RADIOLYSIS OF ISOPROPYL ETHER

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Data are presented on the effects of variations in total energy input (total dose), temperature, type of radiation, added iodine, and added acetaldehyde on the radiolysis products of isopropyl ether. The changes in product yield with changes in these variables have been qualitatively interpreted in terms of a mechanism involving both radical reactions and molecular disproportionations.

#### Introduction

Recently the radiolysis products of a series of ethers were surveyed, showing the marked effect of the ether linkage in determining the reactivity of various bonds in ether molecules toward highenergy radiation.<sup>1</sup> Experiments with ethyl alcohol<sup>2</sup> have shown that if the initial product yields in radiolytic experiments are to be determined, extrapolation must be made to zero energy input, especially for those products which have low excited states or can act as radical scavengers.

The present study is an attempt to vary some of the conditions of radiolysis and an attempt at formulation of a mechanism for the radiolysis of a complex organic molecule in the liquid phase. For this purpose, isopropyl ether was chosen, as it seemed to present a favorable case for study in that the analyses did not appear impossibly difficult and the mechanisms might be simplified by the secondary linkages in the isopropyl groups.

#### Experimental

The purification of the isopropyl ether and the room temperature helium-ion irradiation techniques have been described previously.<sup>1,2</sup> The irradiations at 80° were made in glass cells wrapped in heavy aluminum foil and lacquered dull black. The cells were preheated to 80° in an oven and during the irradiation the temperature was maintained by heating with an infrared heat lamp, empirically calibrated with respect to distance and voltage to maintain the cell at 80°. This method of heating produced no interference with the beam measurement. Iodine solutions were made by weighing the proper amount of freshly sublimed iodine into a standard taper-fitted tube, attaching this to a corresponding taper on the cell, using silicone stopcock lubricant, and vacuum subliming the iodine into the cell which was cooled in a Dry Ice-bath. The lead to the taper was then sealed off, the cell pumped well, and previously degassed isopropyl ether added by vacuum distillation and sealed under vacuum. These were irradiated at room temperature (25°).

The electron irradiations were made on a 2.3-Mev. microwave electron accelerator pulsed 15 times/sec. with a pulse length of two microseconds. Because the beam was not monoenergetic and the energy distribution of the beam was not well known, the energy input was known only approximately. Yields from the electron irradiations were therefore calculated relative to hydrogen, the yield of which was assumed to be the same as for a helium-ion irradiation of the same energy input. This appears to be reasonably reliable because of the small difference in hydrogen yield between helium-ion and  $\gamma$ -ray irradiations (Table III, Figs. 1, 2). The  $\gamma$ -ray irradiations were made in a Co<sup>60</sup>-source<sup>3</sup> in 60-

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

(2) A. S. Newton and W. R. McDonell, J. Am. Chem. Soc., 78, 4554 (1956).

(3) P. Adams and R. Noller, University of California Radiation Laboratory Quarterly Report, UCRL-1959, August 1952, p. 76. ml. Pyrex ampules containing 40 to 50 ml. of deaerated ether. The dose rate was about  $2 \times 10^{6}$  R./hr.<sup>3</sup> and the source calibration was checked with a ferrous sulfate dosimeter in the same type container as used in the irradiations. The ferric ion yield in this dosimeter was assumed to be 15.6/100 e.v.<sup>4</sup> Corrections were made for the difference in  $\gamma$ -ray absorption in the dosimeter solution and the isopropyl ether.

#### **Experimental Results**

Effect of Total Energy Input.-In Fig. 1A, the observed yields  $\overline{G}$  of products formed by irradiation with helium ions at room temperature to various energy-input levels are shown.  $\bar{G}$  represents the average yield from an energy input of E = 0 to an energy input of E = E, the total amount of energy supplied the system. From this same set of data, differential yields,  $G_d$ , the yield of product at E =E, have been obtained and plotted in Fig. 1B. These differential yields were obtained by plotting the observed gross yield of each product in millimoles against energy input and measuring the slope of the resulting curves at various points. Thus, the experimental deviations of the points in Fig. 1A are averaged out in Fig. 1B. Corrections were made for differences in liquid volume by calculating for each case the yield in millimoles that would have been formed had  $\bar{G}$  and the energy input per ml. been kept as observed and the volume normalized to 100 ml. This correction was small. The relation between the two sets of curves is

$$\bar{G} = 1/E \int_0^E G_{\rm d} dE \tag{1}$$

From Fig. 1 it is obvious that there is a large effect of total-energy input on the yield of several of the radiolysis products resulting from helium-ion irradiations. In principle, these results are qualitatively understandable on the basis of radical reactions, though a detailed analysis is not feasible at the present time.

The increase in CO,  $CH_4$  and  $C_2H_6$  yields can be attributed to the action of acetaldehyde and/or acetone as radical scavengers as illustrated in reactions 2 to 6 for acetaldehyde.

$$\begin{array}{ccc} R \cdot + CH_{3}CHO \longrightarrow RH + CH_{3} \cdot + CO & (2) \\ R \cdot + CH_{3}CHO \longrightarrow RH + CH_{3}CO \cdot & (3) \\ CH_{3}CO \cdot \longrightarrow CH_{3} \cdot + CO & (4) \\ CH_{3} \cdot + M_{1} \longrightarrow CH_{4} + R_{1} \cdot & (5) \\ CH_{3} \cdot + CH_{3} \cdot \longrightarrow C_{2}H_{5} & (6) \end{array}$$

(4) C. J. Hochanadel and J. H. Ghormley, J. Chem. Phys., 21, 880 (1953).