in Table II; the appended errors are average deviations from the mean value.

Internal Consistency of the Results.—Procedural deficiencies are frequently reflected in the several X values for a given series of experiments being in improper relationship to each other. Where the acetic acid is burned, as in series A, the X values should be related as

$$2X_B + X_C = 3X_D \qquad (7)$$

for that series, with the X's multiplied by 10^6 for convenience, we calculate: (21706 ± 8) + (10621 ± 2) = (32327 ± 8), while the value observed is (32328 ± 6).

Where the acetic acid is degraded, the X values are related as

$$X_A + X_M + X_C = 3X_D \qquad (8)$$

For the results obtained in the series B experiments we compute: (10902 ± 15) + (10741 ± 2) + (10630 ± 2) = (32273 ± 15), the observed value being (32328 ± 6). This discrepancy is believed to be due largely to the erratic results for carboxyl carbon in the acetic acid degradation. The data from the series C experiments are much more consistent; we calculate: (10919 ± 5) + (10723 ± 3) + (10609 ± 2) = (32251 ± 6), and observed (32259 ± 15).

Average Values for k_4/k_3.—Average values of $100[(k_4/k_3) - 1]$ calculated with equations 5 and 6 are given in Table III; the results from our series A are compared with those of Lindsay, Bourns and Thode[2] in which dry combustion procedures were employed. The mean value obtained from the former is 2.91 ± 0.08; that from the latter is 2.53 ± 0.27.

TABLE III

AVERAGE VALUES OF $100[(k_4/k_3) - 1]$ CALCULATED ON TWO BASES

	CO_2 basis eq. 5	HAc basis eq. 6
L, B and T	2.87 ± 0.36	2.20 ± 0.21
Series A	2.92 ± .04	2.90 ± .13

The most accurate results for the isotope effect should come from the series C experiments. In Table IV are given values of $100[(k_4/k_3) - 1]$ calculated with equation 4. The mean value obtained is 2.92 ± 0.05. If the calculation is based on average X values, a procedure which emphasizes the experimental error in the degradation, a value 2.92 ± 0.07 is found.

TABLE IV

VALUES FOR $100[(k_4/k_3) - 1]$ CALCULATED BY EQ. 4 FOR SERIES C

Run No.	X_C	X_A	$100[(k_4/k_3) - 1]$
9	10610	10926	2.98 ± 0.03
10	10608	10914	2.88 ± .03
11	10608	10917	2.91 ± .03
		Av.	2.92 ± .05

Discussion

Bigeleisen[11] has concluded that k_4/k_3 is temperature independent, which requires that its value for the C^{13} case at hand be 1.0198. The mean of all results obtained at 138° by Lindsay, Bourns and Thode[2] is 1.0253 ± 0.0027, carbon isotope homogeneity of the malonic acid being demonstrated. Our results at 140°, with the effect of carbon isotope inhomogeneity eliminated through the use of acetic acid degradation, are $k_4/k_3 = 1.0292 \pm 0.0007$. It is interesting to note that an interpretation of related experiments in quinoline medium[12] leads to a prediction of $k_4/k_3 = 1.0284 \pm 0.0012$ at 140°.

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(11) J. Bigeleisen, *J. Phys. Chem.*, **56**, 823 (1952).

(12) P. E. Yankwich and R. L. Belford, THIS JOURNAL, **76**, 3067 (1954).

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The Radiation Chemistry of the Aliphatic Alcohols[1,2]

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The products formed in the irradiation of the liquid, air-free alcohols, methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *s*-butyl, *t*-butyl, *n*-octyl and *n*-decyl, with 28 Mev. helium ions have been determined. The reduced products were hydrogen and saturated hydrocarbons with a total $G_{(\text{reduction})}$ of 7 to 8 equivalents per 100 e.v. in all cases. The oxidized products were aldehydes and glycols from primary alcohols, aldehydes, ketones and glycols from secondary alcohols and ketones with minor amounts of glycol from tertiary alcohols. Carbon monoxide and water were formed in all cases. The products are consistent with the principal bond rupture at the carbinol carbon atom, with the reactivity of such carbinol bonded groups exhibiting the order H > C_2H_5 > CH_3 in the alcohols studied. The mechanism of formation of some of the products has been discussed.

Introduction

Knowledge of the influence of structural and functional factors on the radiolytic behavior of organic compounds is necessary both for the development of a theoretical basis for the radiation chemistry of organic compounds and the uses of radiation chemistry in organic synthesis. Few systematic studies of the radiation chemistry of generic groups of pure compounds have been made. Lind and Bardwell[3] using α-particles, studied the saturated hydrocarbon gases methane to butane, and Honig and Sheppard[4] using both α-particles and deuterons

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(1) Much of the work presented here is from the University of California Radiation Laboratory Report UCRL-1378 (June 1951) by W. R. McDonell (declassified Ph.D. thesis).

(2) Presented in part at the Los Angeles Meeting of the American Chemical Society (March 1953).

(3) S. C. Lind and D. C. Bardwell, THIS JOURNAL, **48**, 2335 (1926).

(4) R. E. Honig and C. W. Sheppard, *J. Phys. Chem.*, **50**, 119 (1946).

have characterized the effects of these radiations on the simple saturated hydrocarbons, methane and butane. Schoepfle and Fellows[5] surveyed the effects of cathode rays on an extensive list of hydrocarbons, measuring gas production. Burton and his co-workers[6] have studied the aromatic hydrocarbons. The only detailed investigation of a generic group of pure oxygenated compounds is the work on organic acids in connection with American Petroleum Institute project 43C.[7] These studies showed the influence of the highly electronegative carboxyl group resulting in a marked reaction specificity toward decarboxylation.

The purpose of the present investigation has been to extend research on the effects of structural and functional variations to the radiolytic behavior of other groups of organic compounds. As an initial step in this program, the products formed in the radiolysis of a series of alcohols have been determined. The only previous work on the behavior of alcohols with ionizing radiations is that of McLennan and Patrick[8] who reported the cathode ray bombardment of methyl and ethyl alcohol vapors. The products contained hydrogen, carbon monoxide, carbon dioxide, methane and in the case of ethyl alcohol, ethane. In the non-gaseous products, formaldehyde and acetaldehyde were found, the methyl alcohol favoring formaldehyde and the ethyl alcohol favoring acetaldehyde. Patat and Hock[9] studied the photolysis of methyl and ethyl alcohol vapors, the products being hydrogen, aldehyde and carbon monoxide. Recently Phibbs and Darwent[10] investigated the mercury sensitized photolysis of methyl alcohol vapor. The products at low temperatures were principally hydrogen and ethylene glycol. Formaldehyde production became important only above 400°, showing its formation to be a high activation energy process.

Experimental

The alcohols used were reagent grade, further dried and purified by refluxing over calcium oxide for several days followed by distillation through a 25-plate adiabatic column at a reflux ratio of about 15 to 1. The middle third of product from this distillation, with a boiling range of less than 0.2°, was used for the bombardment. The mass spectrum of each alcohol was periodically checked during the distillation and no change in pattern coefficients was found to occur.

For bombardment, about 110 ml. of the alcohol was added to the liquid chamber of a cyclotron target which has been described elsewhere.[11] The alcohol and target were then deaerated by careful evacuation at room temperature. Several ml. of alcohol was distilled from the target in this process, the amount distilled depending on the volatility of the alcohol. All bombardments were thus performed in "dry" alcohol in the absence of air. Bombardments were made with helium ions on the Crocker Laboratory 60-inch cyclotron. Integrated beam current measurements made during the bombardment are believed accurate to about 1%. The cyclotron beam energy varied slightly during the period of this work and the energy used for each bombardment was that from the latest determination of the range in aluminum foils. Corrections were made for energy loss in the aluminum and copper target windows, their gold platings, and the air space, according to the calculated energy loss curves of Aron, Hoffman and Williams[12] to obtain the energy of the helium ions impingent on the liquid. The windows served to degrade the energy of the beam from the 38 to 40 Mev. with which they emerged from the cyclotron to 26 to 29 Mev. on entering the liquid. Beam energy measurements are believed accurate to about 2%. A standard bombardment of 2 μah. yielded sufficient products to make analyses of products in the liquid phase possible. Since only 2 to 3% of the alcohol was chemically altered by this bombardment secondary processes are considered negligible. During bombardment the target was water cooled to approximately 16°. The temperature rise in the bulk of the liquid was not over 2 or 3°, but measurements of the temperature immediately adjacent to the window where beam absorption occurred were not possible. In the case of *t*-butyl alcohol, melting point 25.5°, the cooling water was heated to approximately 30° to maintain the alcohol liquid during degassing and bombardment. After bombardment the products formed lowered the melting point sufficiently to keep the alcohol liquid. The rate of irradiation was maintained as constant as possible at 3 μa. beam current and in no case was the current allowed to exceed 4 μa.

After irradiation one of four procedures was used for handling the products formed. When the analysis for the liquid phase products was of prime interest, the target was simply opened to an evacuated volume-calibrated manometric system, the pressure and temperature were recorded for calculation of a "total gas yield" and a sample of the gas was taken. This sample was then directly analyzed with a mass spectrometer (gas treatment I) or roughly fractionated by pumping with an automatic Toepler pump through traps at −80 and −196° into a gas buret, obtaining successive fractions volatile at −196°, volatile at −80° and volatile at room temperature (gas treatment II). Treatment II allowed the determination of more minor components than treatment I, but both treatments yielded low results in those components such as butanes and butenes, which are appreciably soluble in alcohols.

For analyses in which the gaseous products were of prime interest, the gases were pumped with an automatic Toepler pump through traps at −30, −80, −111 (carbon disulfide slush bath) and −196° into a gas buret. By promoting traps, successive samples volatile at −196, −111, −80 and −30° were obtained. Up to one-third the alcohol was distilled into the traps during this process and this distillate was later added to the liquid phase.

In two cases, ethyl and *n*-butyl alcohols, complete distillations of the target materials were run by introducing the target gases and vapors at the bottom of an evacuated 24-inch Heli-grid packed semimicro Podbielniak column. The condenser was run at −70° and the gases were pumped through the column, then a trap at −196° and into the gas buret. A second fraction was taken with the trap temperature at −80°, and the distillate in the trap was then collected as a third fraction. The entire target contents were then added to the still pot and fractionated at atmospheric pressure, with a condenser temperature of −30° and a reflux ratio of 100 to 1. The distillate was collected in 0.2-ml. fractions until the mass spectrometer pattern of the distillate was that of the pure alcohol. The bulk liquid was then distilled using water cooling and a 25 to 1 reflux ratio and the last 10 ml. again was collected in small fractions. The pot residue of about 3 ml. was molecularly distilled. The final residue is referred to as "polymer" though it was severely contaminated with stopcock grease from the above operations. The first liquid fractions from *n*-butyl alcohol could not be accurately analyzed from the mass spectrometer records in terms of compounds for which calibrations were available, but maximum limits could be set on the occur-

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[5] C. S. Schoepfle and C. H. Fellows, *Ind. Eng. Chem.*, **23**, 1396 (1931).

[6] T. J. Sworski and M. Burton, THIS JOURNAL, **73**, 3790 (1951); T. J. Sworski, R. R. Hentz and M. Burton, *ibid.*, **73**, 1998 (1951); R. R. Hentz and M. Burton, *ibid.*, **73**, 552 (1951).

[7] W. L. Whitehead, C. Goodman and I. A. Breger, *J. chim. phys.*, **48**, 184 (1951); C. W. Sheppard and V. L. Burton, THIS JOURNAL, **68**, 1636 (1946); I. A. Breger and V. L. Burton, *ibid.*, **68**, 1639 (1946); V. L. Burton, *ibid.*, **71**, 4117 (1949).

[8] J. C. McLennan and W. L. Patrick, *Can. J. Research*, **5**, 470 (1931).

[9] F. Patat and H. Hock, *Z. Elektrochem.*, **41**, 1194 (1935).

[10] M. K. Phibbs and B. deB. Darwent, *J. Chem. Phys.*, **18**, 495 (1950).

[11] W. R. McDonell and A. S. Newton, *Nucleonics*, **10**, 62 (1952).

[12] W. A. Aron, B. G. Hoffman and F. C. Williams, U. S. Atomic Energy Commission Unclassified Document AECU-663, Second Revision (1949). Technical Information Service, Oak Ridge, Tennessee (May 28, 1951).

rence of certain expected products such as *n*-propyl *n*-butyl ether by this technique.

The gaseous and liquid fractions so collected were analyzed according to well established procedures using a Consolidated Engineering Corporation Analytical mass spectrometer, Model 21-102, later converted to Model 21-103. Mass spectrometer calibrations were performed with the purest material available, using Phillips Research grade hydrocarbons and Eastman White Label oxygenated compounds, repurified where doubt existed as to their purity. Some calibrating materials such as mixed ethers and dimethyl[13] and diethyl peroxides were synthesized according to established procedures.

Liquid Analyses.—The liquid fraction in the target, combined with that in the traps, was chemically analyzed as follows.

Water was determined by the Karl Fischer method[14] using an electrometric end-point. The interference of carbonyl compounds in this titration cited by Mitchell and Smith apparently did not occur with the concentrations present in the bombarded alcohols. The use of hydrogen cyanide to complex the carbonyl groups prior to titration gave results identical within the precision of the titration to those obtained without its use. In general, cyanide complexing of the carbonyl compounds was not used. Blank determinations of water were made on the original alcohol in all cases.

Total carbonyl content of the irradiated liquid was determined by the hydroxylamine hydrochloride titration method of Bryant and Smith.[15] Checks on the method using acetaldehyde, formaldehyde and acetone standards in alcohols gave results with a maximum deviation of 1% from the added values.

Total aldehydes were determined by the silver oxide oxidation method of Mitchell and Smith.[16] Standards of formaldehyde, acetaldehyde and acetone in alcohols gave results within 5% of the added values of the aldehydes, though in irradiated solutions the values found were sometimes lower than those obtained independently by the dimedone procedure described below. Therefore, the values obtained by silver oxide oxidation are considered only semi-quantitative.

Acetaldehyde and formaldehyde were determined using the dimedone (5,5-dimethylcyclohexanedione-1,3) precipitation method of Yoe and Reid,[17] modified to include the acetaldehyde–formaldehyde separation of Vorländer, Ihle and Volkholz.[18] The aldehydes were precipitated with dimedone under buffered conditions. This precipitate was then dehydrated with sulfuric acid, the acetaldehyde derivative forming a non-acidic anhydride, insoluble in sodium carbonate solution in which the formaldehyde derivative dissolved. The formaldehyde derivative was then reprecipitated from the sodium carbonate filtrate by addition of acid and the two fractions determined gravimetrically. This method gave results within 2% of the added values on standard solutions of acetaldehyde and formaldehyde in ethyl alcohol, when corrected for the solubility of the acetaldehyde derivative. In the presence of higher aldehydes, the method failed, probably because the higher aldehyde derivatives were only partially dehydrated, ruining both the formaldehyde and higher aldehyde determinations.

Ketones were taken as the difference of the total carbonyl and aldehyde determinations, the latter by the dimedone procedure where it was applicable.

Total glycols and total high boiling hydroxyl components in the irradiated liquids were determined by a modification of the method of Shaefer.[19] The alcohol solution was distilled with an intermediate boiling solvent, specifically pyridine, and the hydroxyl content of the high boiling components determined by acetylation with acetic anhydride in the resulting pyridine solution. In practice, to avoid polymerization of the aldehydes present, which formed a dark brown solution and interfered with the phenolphthalein endpoint in the titration of acetic acid, a pre-distillation step using excess of the pure alcohol or added dioxane was made, ridding the solution of the bulk of the aldehydes before adding the pyridine. While the method of Shaefer, which utilized a 3 M solution of acetic anhydride in pyridine, gave essentially quantitative results on alcohol solutions of ethylene glycol, propylene glycol, trimethylene glycol and 1,4-butanediol, it was found necessary to increase the acetic anhydride–pyridine ratio considerably to get reliable results with 1,3-butanediol and 2,3-butanediol. This was done by adding 1 ml. of pure acetic anhydride to the 5 ml. of pyridine solution resulting from distillation. The method fails with compounds where the hydroxyl group is attached to a tertiary carbon atom and it is also limited to those alcohols boiling well below pyridine. For higher boiling alcohols, 2,3-lutidine was used as an intermediate solvent. This formed no azeotropes with the glycols tested and replaced pyridine as the acetylation catalyst. The lutidine technique was used with butyl alcohols. It failed with *n*-propyl alcohol solutions for unknown reasons, giving erratic values less than the vicinal glycol present and less than that obtained with pyridine.

Vicinal glycols were determined by the method of Siggia[20] using the periodic acid reduction equivalence. This method gave results within 3% of the added values on ethylene glycol, propylene glycol and 2,3-butanediol in alcohol solutions in the presence of acetaldehyde and formaldehyde. The method was further extended in those cases in which the glycol components were oxidized to formaldehyde, acetaldehyde and acetone by determining the oxidation products resulting from the periodic acid treatment, using a modification of the dimedone procedure previously outlined. In this way the formaldehyde and acetaldehyde equivalents in the original glycol were determined directly after subtraction of formaldehyde and acetaldehyde originally present in the bombarded alcohol. Ketonic equivalents were taken as the difference between the aldehyde equivalents in the glycol and the total vicinal glycol yield.

Other products were less satisfactorily determined. Acids were a very small component and determined by direct titration with alcoholic sodium hydroxide. In early bombardments, esters were shown to be negligibly small by saponification equivalent and thereafter were not generally determined. Dialkyl peroxides were shown to be present in small amounts in irradiated methyl and ethyl alcohols, where, due to their high volatility, they could be determined with the mass spectrometer and must be presumed also present in the other alcohols. A satisfactory chemical method for their determination in this type mixture was not found. No satisfactory general method for unsaturated compounds in the liquid state was found. Ethers were not determined except as they were detected in the mass spectrometer analyses of gas and liquid fractions. Hydrocarbons above butane were not determined quantitatively with the procedure used for separation of the gases.

Experimental Results

In Tables I and II are presented the radiolysis products observed in the helium ion bombardment of the alcohols studied. The yield figures given are the weighted averages of several bombardments with the exception of *n*-octyl and *n*-decyl alcohols where only single bombardments were performed. The yields are expressed in terms of G, the molecules formed of the product specified per 100 e.v. energy input into the liquid. The probable errors on this figure have been estimated considering the reproducibility of the bombardments, the reliability of the beam and beam energy measurement, and tests of the analytical methods on synthetic samples. No account has been taken of possible variations due to temperature, rate of bombardment or total bombardment given, which effects have not been studied.

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(13) The authors wish to thank Professor R. E. Brinton, Department of Chemistry, University of California, Davis, for an authentic sample of dimethyl peroxide.

(14) J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

(15) W. M. D. Bryant and D. M. Smith, THIS JOURNAL, **57**, 57 (1935).

(16) J. Mitchell and D. M. Smith, *Anal. Chem.*, **22**, 746 (1950).

(17) J. H. Yoe and L. C. Reid, *Ind. Eng. Chem., Anal. Ed.*, **13**, 238 (1941).

(18) D. Vorländer, C. Ihle and H. Volkholz, *Z. anal. Chem.*, **77**, 321 (1929).

(19) W. E. Shaefer, *Ind. Eng. Chem., Anal. Ed.*, **9**, 449 (1937).

(20) S. Siggia, "Quantitative Organic Analyses via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 8.

TABLE I

YIELDS OF PRODUCTS FORMED IN THE HELIUM ION BOMBARDMENT OF ALCOHOLS

In units of *G*(molecules of the product specified/100 e.v.)

	Methyl alcohol	Ethyl alcohol	*n*-Propyl alcohol	Isopropyl alcohol	*n*-Butyl alcohol	Isobutyl alcohol	*s*-Butyl alcohol	*t*-Butyl alcohol	*n*-Octyl alcohol	*n*-Decyl alcohol
H_2	3.46 ± 0.05	3.46 ± 0.05	2.80 ± 0.10	2.71 ± 0.05	3.59 ± 0.05	2.77 ± 0.05	2.61 ± 0.05	1.24 ± 0.03	3.48 ± 0.03	3.47 ± 0.03
CO	0.23 ± .01	0.11 ± .01	0.100 ± .005	0.083 ± .005	0.066 ± .005	0.100 ± .005	0.060 ± .005	0.046 ± .002	0.052 ± .005	0.044 ± 0.005
CO_2	.002 ± .001	<0.002	...	...	...	...	...	...	...	...
CH_4	.36 ± .01	.43 ± 0.02	.067 ± .003	1.14 ± .05	.055 ± .002	.142 ± .005	.37 ± .01	1.60 ± .10	.022 ± .002	.018 ± .002
C_2H_2	...	.040 ± .005	.035 ± .003	0.019 ± .002	.027 ± .003	.013 ± .003	.050 ± .005	0.014 ± .003	~0.009	~0.012
C_2H_4	...	.17 ± .01	.30 ± .01	.022 ± .002	.090 ± .005	.022 ± .003	.38 ± .02	.091 ± .010	~ .029	~ .049
C_2H_6	.014 ± .001	.17 ± .01	.54 ± .01	.17 ± .01	.035 ± .001	.017 ± .003	.86 ± .02	.52 ± .03	~ .021	~ .036
C_3H_6	...	.003 ± .001	.140 ± .003	.27 ± .01	.21 ± .01	.81 ± .02	.051 ± .005	.020 ± .005	~ .009	~ .011
C_3H_8	...	.025 ± .005	.145 ± .005	.088 ± .005	.46 ± .01	.65 ± .02	.110 ± .010	.017 ± .005	~ .018	~ .030
C_4H_8(1)	...	<0.001	.010 ± .002	...	...	...	0.053	...	...	...
C_4H_8(2)	...	...	...	...	...	...	.126	...	...	...
i-C_4H_8	...	...	...	~0.007	...	.067 ± .005	...	.27 ± .03	...	...
Total butene	...	...	...	...	.093 ± .005	...	.179 ± .005	...	> .004	> .007
n-C_4H_{10}	...	<0.010	0.10 ± .02	...	.124 ± .010	...	.216 ± .010	...	> .008	> .014
i-C_4H_{10}	...	...	...	~0.04	...	.162 ± .010	...	.11 ± .02	...	...
Total gas	4.48	4.47	3.86	4.35	4.26	3.99	4.51	3.48	3.68	3.63
Acid	0.011 ± 0.002	0.012 ± 0.002	0.012 ± 0.002	0.005 ± 0.001	0.012 ± 0.001	0.05 ± 0.01	0.026 ± 0.004	0.003 ± 0.001	0.011	0.008
H_2O	.93 ± .03	0.81 ± .05	0.93 ± .05	0.89 ± .03	0.63 ± .03	0.63 ± .05	0.58 ± .03	1.00 ± .03	.43	.31
Total carbonyl	1.66 ± .04	2.10 ± .10	2.05 ± .05	2.96 ± .10	1.52 ± .05	1.65 ± .05	2.95 ± .05	2.78 ± .20	.87	.76
Aldehyde	1.4 ± .1	2.2 ± .2	2.14 ± .15	...	1.5 ± .1	1.70 ± .10	1.83 ± .10	...	.7	1.0
HCHO	1.67 ± .05	0.30 ± .02	...	0.00 ± .05	...	...	...	0.00 ± .05	...	...
CH_3CHO	0.00 ± .05	1.71 ± .10	...	0.94 ± .05	...	...	...	0.09 ± .05	...	...
Ketone	0.0 ± .1	0.00 ± .10	...	2.02 ± .10	0.0 ± .1	0.00 ± .10	1.12 ± .10	2.78 ± .20	...	...
Total glycol	1.60 ± .10	1.00 ± .05	1.16 ± .05?	0.40 ± .05	...	.87 ± .05	>0.2	0.10 ± .05?	...	...
vic-Glycol	1.75 ± .05	1.05 ± .05	0.85 ± .05	.39 ± .03	0.92 ± .05	.88 ± .03	0.56 ± .04	.10 ± .05	0.56	0.51
$-CH_2OH$	3.48 ± .07	0.30 ± .03	...	.035 ± .010	...	...	...	.12 ± .02	...	...
$-CH(CH_3)OH$	0.00 ± .05	1.75 ± .10	...	.29 ± .010	...	...	...	.0 ± .02	...	...
$-C(CH_3)_2OH$	.00 ± .05	0.00 ± .10	...	.48 ± .10	...	...	...	.08 ± .04	...	...
Non-*vic*-glycol	.00 ± .10	0.00 ± .10	0.6?	.00 ± .05	...	.00 ± .05	...	.00 ± .05	...	...
"Polymer"	...	<0.06	...	...	<0.2	...	...	...	...	...
Equiv. reduction	7.67	8.19	7.30	8.30	8.53	7.47	8.33	6.97	7.10	7.14
Equiv. oxidation	7.64	6.86	6.32	7.11	5.26	5.69	7.46	6.01	3.13	2.78

The figures for total gas yield represent the amount of gas observed when the target was opened to a calibrated manometric system, no correction being made for solubility of components or vapor pressure of the alcohol. The total oxidation and reduction equivalents have been calculated on the basis of the yield of each product multiplied by the number of electrons transferred in forming that product from the original alcohol, using the usual method of giving oxygen an oxidation number of −2 (except in peroxides) and hydrogen +1.

In a closed system there are two simple checks that can be made on the adequacy of the analytical procedures, these being an oxidation–reduction balance and a stoichiometric atom balance. Since the reduced products consist of hydrogen and saturated hydrocarbons which, through the butyl alcohols, are reliably determined, the total reduction observed represents an almost complete measure of the oxidation–reduction which has occurred in the system. In octyl and decyl alcohols, lack of data on higher hydrocarbons makes the reduction equivalents given low by as much as $G = 0.4$ equivalent. An atom balance made by writing stoichiometric equations for the formation of various products observed shows unaccounted hydrogen and water. Since the equations were written limiting the amount of alcohol by the carbon found in the products, the unaccounted hydrogen is approximately equivalent to the undetected oxidation in each case. Table III lists the unaccounted hydrogen and water and undetected oxidation equivalents for the alcohols studied.

The water discrepancy exists even in methyl alcohol where oxidation and reduction balance quite closely. Possible undetected products such as higher alcohols, ethers, acetals and polymers which might contribute to the water yield can each be eliminated as the

TABLE II

MISCELLANEOUS MINOR PRODUCTS FORMED IN THE HELIUM ION IRRADIATION OF LIQUID ALCOHOLS

Alcohol	Product	Yield, *G*, molecules product/100 e.v.
Methyl	CH_3OCH_3	>0.032
	CH_3OOCH_3	> .003
	$CH_2(OCH_3)_2$	> .008
Ethyl	$CH_3C{\equiv}CH$(?)	trace
	$CH_3OC_2H_5$	0.09 ± 0.02
	$C_2H_5OC_2H_5$	.05 ± .01
	CH_3OH	.06 ± .01
	$CH_2{=}CHOC_2H_5$(?)	~ .005
	$C_2H_5OOC_2H_5$	.008 ± .001
n-Propyl	$CH_3C{\equiv}CH$(?)	trace
	$C_5H_{10} + C_5H_{12}$	> .02
Isopropyl	$CH_3OCH(CH_3)_2$	> .008
n-Butyl	C_4H_6 (butadiene?)	~ .003
	C_5H_{12}	> .01
	C_6H_{14}	> .005
	$C_3H_7OC_4H_9$	< .08
	$C_4H_9OC_4H_9$	< .07
t-Butyl	$CH_3C{\equiv}CH$(?)	.009 ± .002
	$C(CH_3)_4$	> .05
	$CH_3OC(CH_3)_3$	> .002
n-Octyl	C_5H_{10}	> .001
	C_5H_{12}	> .002
n-Decyl	C_5H_{10}	> .001
	C_5H_{12}	> .003

TABLE III

DISCREPANCY IN HYDROGEN, WATER AND TOTAL OXIDATION IN STOICHIOMETRY OF ALCOHOL RADIOLYSIS PRODUCTS

Alcohol	*G*, water unaccounted	*G*, hydrogen unaccounted	*G*, equiv. oxidation undetected
Methyl	0.5	0.0	0.0
Ethyl	.5	.7	1.3
n-Propyl	.7	.6	1.0
Isopropyl	.5	.6	1.2
n-Butyl	.5	1.6	3.3
Isobutyl	.5	0.9	1.8
s-Butyl	.2	0.5	0.9
t-Butyl	.6	0.5	1.0
n-Octyl	.4	2.0	4.1
n-Decyl	.3	2.1	4.4

major source of the excess water, though any or all of such products could contribute. In those cases where such products could be detected, they were not found in nearly the required amount, or the corresponding hydrocarbon co-products were in low yields.

The unaccounted hydrogen and undetected oxidation became larger the larger the molecule bombarded. In higher alcohols, the formation of unsaturated alcohols could conceivably occur, but this assumption breaks down in the case of ethyl alcohol where the product would be detected as acetaldehyde. The yield of dialkyl peroxide was shown to be low in methyl and ethyl alcohols, eliminating this type compound as a major co-product of the excess hydrogen.

Discussion

In the following discussion, it has been assumed that the initial events in the radiolysis process follow the Eyring, Hirschfelder and Taylor mechanism recently summarized by Burton.[21] The initial events involving ionization, excitation and ion recombination will not be further discussed in this paper.

General Correlations.—The observed yields of products are equivalent to 7–10 molecules of alcohol reactant per 100 e.v. energy input and are consistent with a yield of about one molecule of alcohol reactant per excitation or ionization.[22] These yields do not exclude radical–molecule reactions rapidly terminated by radical–radical reactions, but do exclude long chain processes.

Of the various bonds in the alcohol molecules, those involving the carbinol carbon atom are the most reactive. The yields of hydrocarbons from ruptures at the carbinol carbon atom are preponderant, and not so from lack of other bonding positions available for reaction. The principal hydrocarbons produced from the alcohols are methane from ethyl, isopropyl and *t*-butyl alcohols, ethane from *n*-propyl alcohol, propane from *n*-butyl and isobutyl alcohols and both methane and ethane from *s*-butyl alcohol. The yield of methane from isopropyl alcohol is eight times the yield of methane from isobutyl alcohol, though the number of available methyl groups is the same in each case. As shown in Fig. 1, the $n - 1$ carbon hydrocarbons from *n*-carbon primary alcohols are in greatest yield.

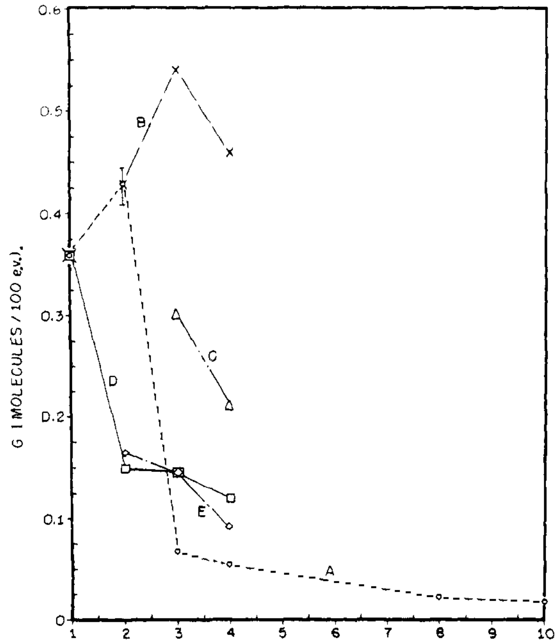

Fig. 1.—Yields of hydrocarbons in irradiated normal primary alcohols: A, (O) methane; B, (X), saturated hydrocarbon of *n*-1 chain length; C, (Δ), ethylenic hydrocarbon of *n*-1 chain length; D, (□), saturated hydrocarbon of *n*-chain length; E, (◇), ethylenic hydrocarbon of *n*-chain length.

The yields of glycols illustrate the same principle, though the data are not as reliable in this

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[21] M. Burton, "Annual Review of Physical Chemistry," G. K. Rollefson, Editor, Vol. I, Annual Reviews, Inc., Stanford, California, 1950, p. 117.

[22] U. Fano, "Symposium on Radiobiology," J. J. Nickson, Editor, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 18.

case. Within fairly large experimental errors, only vicinal glycols are formed in the radiolysis of alcohols.

The yield of hydrogen is almost constant in the normal alcohols except for a marked decrease at *n*-propyl alcohol, the only odd carbon alcohol irradiated. Water shows a corresponding discrepancy and this may represent an even–odd effect in the radiolysis.

The decrease in yield of hydrocarbons from the normal alcohols with increasing chain length and the corresponding decrease in yield of aldehydes and glycol products while the hydrogen yield remains essentially constant, suggest a possible falling off of the reaction at bonds of the carbinol carbon in favor of reactions at bonds elsewhere in the molecule. This might be described as a non-functional production of hydrogen and unidentified co-products, probably unsaturated. It is conceivable that such a change in reactivity is a necessary consequence of the fact that the radiolysis was carried out in the liquid state with heavily ionizing particles. If every molecule in a track volume were excited by the passage of the helium ions, then the number of molecules excited would vary as a direct function of the molecular density, falling off for the higher alcohols. The density of molecular excitation in the track of an ionizing particle is not known precisely for liquid systems, but estimates based on Lea's[23] calculations of ion distribution in α-particle tracks indicate such a saturation density to be unlikely by at least an order of magnitude. If the yields of oxygenated product were equivalent to a totality of reactant molecules in a densely activated volume, hence dependent on their size, then the excess hydrogen in the higher alcohols would of necessity be derived from the same molecules as the oxygenated products. This implies the formation of unsaturated glycols and aldehydes. No satisfactory method for determining such unsaturation was found, but unless evidence of the dense molecular excitation required is found, the concept of simultaneous but independent chemical events at different locales in the same molecule cannot be regarded favorably.[24]

Of the various groups attached to the carbinol carbon atom, the low yield of *n* carbon hydrocarbons from *n* carbon alcohols compared to products resulting from reactions of hydrogen or alkyl groups on the carbinol carbon atom shows the hydroxyl group to be comparatively unreactive. The low yields of ethers and peroxides (where these could be determined) substantiates this conclusion.

Comparative Reactivity of Groups.—A comparison of yields of products formed by rupture of bonds between the carbinol carbon atom and hydrogen, methyl and ethyl groups, respectively, shows the relative reactivity of these groups to be in the order H > C_2H_5 > CH_3, in the alcohols studied. In Table IV the yields expected for equal reactivity of carbinol bonded groups and the observed yields are compared for products resulting from the reaction of these respective bonds. It is seen that in all cases where hydrogen–carbinol and methyl–carbinol bonds are compared, the products resulting from hydrogen–carbinol bonds are in excess of that expected for equal reactivity. However, when methyl–carbinol and ethyl–carbinol bonds are compared using the yields of methane and ethane from *s*-butyl alcohol, the ethane is greatly in excess. Even considering that some ethane can arise from methyl radical combinations, the ethyl–carbinol bond is the more reactive. The ratio of ketone to aldehyde in *s*-butyl alcohol (the ketone identified was methyl ethyl ketone though traces of acetone might not have been detected in the gas phase) is about as expected and this may be ascribed to the comparatively high reactivity of the ethyl group leading to relatively more aldehyde than found in isopropyl alcohol.

TABLE IV

COMPARISON OF RATIOS OF PRODUCTS EXPECTED FOR EQUAL REACTIVITY OF BONDS TO THE CARBINOL CARBON ATOM TO THE RATIOS FOUND

Alcohol	Product ratio	Carbinol bonding groups	Ratio expected for equal bond reactivity	Ratio found
C_2H_5OH	$\frac{CH_3CHO}{HCHO}$	H/CH_3	2	5.7
	$\frac{CH_3CHOH}{CH_2OH}$[b]	H/CH_3	2	5.8
$(CH_3)_2CHOH$	$\frac{(CH_3)_2CO}{CH_3CHO}$	H/CH_3	0.5	2.15
	$\frac{(CH_3)_2COH}{CH_3CHOH}$[b]	H/CH_3	0.5	1.75
$(CH_3)(C_2H_5)CHOH$	$\frac{CH_4}{C_2H_6}$	CH_3/C_2H_5	1[a]	0.44
	$\frac{\text{ketone}}{\text{aldehyde}}$	$H/C_2H_5 + CH_3$	0.5	0.6

[a] Ignoring contribution of methyl radicals to ethane production. If this is considered a slightly smaller ratio will be expected. [b] Groups shown are $^1/_2$ of glycol molecules.

Effect of Structure.—The series methyl, ethyl, isopropyl and *t*-butyl alcohols affords a means of comparing the effect of alkyl substitution on the comparative reactivity of bonds to the carbinol carbon atom. In Fig. 2 the yields of some products derived from reactions at methyl–carbinol bonds and hydrogen–carbinol bonds divided by the number of such bonds, respectively, have been plotted for this series of alcohols. The yield of methane (plus twice ethane) per methyl–carbinol bond increases through the series ethyl, isopropyl, *t*-butyl showing an apparent increased reactivity per bond as an increasing number of methyls are substituted. The same behavior is noted for the carbonyl products. The yield per bond of glycol products derived from these type bonds decreases with increasing substitution but the decrease does not compensate the increase in carbonyl products and the over-all net effect is an apparent increase in the reactivity of both types of bonds with increasing methyl substitution on the carbinol carbon atom. The over-all yield of glycol and carbonyl products from these bonds remained about constant in spite of the apparent increase in reactivity per bond since, as was shown in the previous section, the methyl–carbinol bonds which are being substituted are comparatively less reactive than the hydrogen–carbinol bonds they are replacing.

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(23) D. E. Lea, "Action of Radiations on Living Cells," Cambridge University Press, London, 1946, p. 23.

(24) R. L. Platzman, ref. 22, p. 103.

Radical Reactions.—Kharasch, Rowe and Urry[25] have investigated the reactions of methyl radicals derived from the thermal decomposition of acetyl peroxide in several alcohols including isopropyl and *t*-butyl. They found no ethane among the products and from this one can conclude the reaction of a methyl radical with an alcohol to form ethane to be a reaction of high activation energy. Thus the ethane found among the radiolysis products of isopropyl and *t*-butyl alcohol must be formed either by the reaction of two methyl radicals or by the reaction of "hot" methyl radicals with the alcohol. The ethane from isopropyl and *t*-butyl alcohols cannot arise from molecular rearrangement, for this would lead to the production of formaldehyde from isopropyl alcohol and acetaldehyde from *t*-butyl alcohol, and these products were not found from these respective sources.

Both the methyl–methyl radical reaction and the "hot" methyl alcohol reaction (if both occur) must occur in the primary track or in spurs. Otherwise the radicals will rapidly become thermalized by collision and diluted by diffusion so conditions much like those in Kharasch's experiment would prevail and no ethane would be formed. From the data at hand no unambiguous decision as to the relative importance of the radical–radical and radical–molecule reactions can be made. It can be shown, however, that the yields of hydrogen, methane and ethane are consistent with a radical mechanism for formation of a major portion of all these products. For a radical mechanism the following kinetic equations can be written.

$$H + CH_3 \longrightarrow CH_4;\ R_{(CH_4)} = k_1(CH_3)(H) \qquad (1)$$

$$CH_3 + CH_3 \longrightarrow C_2H_6;\ R_{(C_2H_6)} = k_2(CH_3)^2 \qquad (2)$$

$$H + H \longrightarrow H_2;\ R_{(H_2)} = k_3(H)^2 \qquad (3)$$

Eliminating the radical concentrations one can write

$$\frac{R_{(CH_4)}}{R^{1/2}_{(C_2H_6)} \times R^{1/2}_{(H_2)}} = \frac{k_1}{k^{1/2}_3 \times k^{1/2}_2} = K_1 \qquad (4)$$

In a competitive system the yields of products are proportional to their rates of formation so the *G* values of the yields of hydrogen, methane or ethane can be substituted for their rates of formation. The results in Table V of calculating K_1 for methyl, isopropyl and *t*-butyl alcohols show that while the values of K_1 differ by more than the experimental error, they are reasonably constant considering the methane yield has varied by a factor of 4.4, ethane by 37, and hydrogen by 2.8 in the series of alcohols. Any process producing molecular hydrogen would cause the observed value of K_1 to be too low. Such processes are the rearrangement of an excited molecule of methyl alcohol to form hydrogen and formaldehyde; or the formation of hydrogen and acetone from an excited isopropyl alcohol molecule. These reactions have been proposed as the primary steps in the photolysis of these alcohols.[26] On the other hand processes in which methane is formed by a molecular rearrangement, *e.g.*, the formation of methane and acetone by rearrangement of an excited *t*-butyl alcohol molecule, or methane and acetaldehyde from an excited isopropyl alcohol molecule, would cause the observed value of K_1 to be too high. It would thus appear that K_1 for a pure radical reaction should lie somewhere between 1.63 and 1.99 for helium ion irradiations in the energy range used (~28 Mev.).[27]

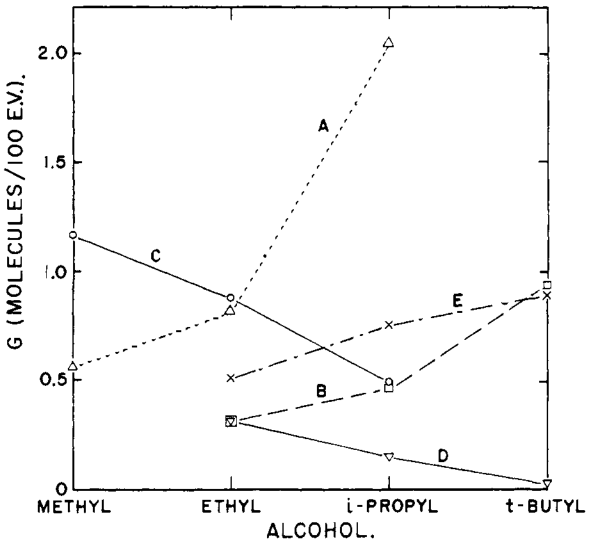

Fig. 2.—Yields of methane, glycol and carbonyl products from methyl, ethyl, isopropyl and *t*-butyl alcohols: A, (△), carbonyl products from hydrogen–carbinol bonds, per hydrogen–carbinol bond; B, (□), carbonyl products from methyl–carbinol bonds, per such bond; C, (⊙), glycol equivalents from hydrogen–carbinol bonds, per bond; D, (▽), glycol equivalents from methyl–carbinol bonds, per bond; E, (X), methane twice ethane per methyl–carbinol bond (ethyl alcohol point corrected for estimated separate yield of ethane).

TABLE V

VALUES OF K_1 FOR EQUATION 4 FOR METHYL, ISOPROPYL AND *t*-BUTYL ALCOHOLS

Compound	$G_{(CH_4)}{}^2$	$G_{(C_2H_6)}$	$G_{(H_2)}$	K_1
CH_3OH	0.36	0.014	3.46	1.63
$(CH_3)_2CHOH$	1.14	0.17	2.71	1.68
$(CH_3)_3COH$	1.60	0.52	1.24	1.99

Carbonyl and Glycol Formation.—Phibbs and Darwent[10] have proposed a radical mechanism for the formation of ethylene glycol and formaldehyde in the mercury activated photolysis of methyl alcohol. The formation of formaldehyde by a radical decomposition was shown to be a reaction of high activation energy compared to glycol formation. The data on glycol and carbonyl products formed from the radiolysis of alcohols are consistent with such a mechanism though other high energy processes such as direct rearrangements may contribute to the carbonyl products. Except for methanol, the number of RCHOH and CH_2OH radicals resulting in glycol and carbonyl products, respectively, are

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[25] M. S. Kharasch, J. L. Rowe and W. H. Urry, *J. Org. Chem.*, **16**, 905 (1951).

[26] G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939, pp. 219–220.

[27] Calculation of K_1 for the radiolysis products of methyl iodide irradiated with X-rays by R. H. Schuler and R. C. Petry, THIS JOURNAL, **75**, 3792 (1953), gave a value of about 1.9 using *G*-values as corrected by Schuler. These authors proposed a different explanation for ethane production in this case.

very roughly equal for all the normal primary alcohols, indicating about equal probability for dissociation and association of these radicals. The relative yield of glycol is much higher from methyl alcohol despite the possible direct formation of formaldehyde and hydrogen by rearrangement.

The decreased yield of glycols from secondary and tertiary alcohols can be attributed to either a lowering of the activation energy for decomposition into carbonyl compounds or a steric hindrance effect preventing reaction of these radicals to form glycols.

***n*-Carbon Hydrocarbons.**—Saturated and ethylenic hydrocarbons derivable from the same radical, except those of *n*-carbons from *n*-carbon alcohols, are formed in the ratio of about two to one, implying the radical R has about twice the probability of picking up a hydrogen radical as dissociating (other reactions being neglected). On the other hand, the yield of ethylenic hydrocarbons of *n*-carbons is equal to or greater than the *n*-carbon saturated hydrocarbons from most alcohols. This suggests an additional mechanism to be operative for the formation of the ethylenic hydrocarbons in this case. Such a mechanism is provided by a molecular rearrangement as illustrated by the following net reaction in ethyl alcohol.

$$CH_3CH_2OH \rightsquigarrow C_2H_4 + H_2O$$

The yields of such *n*-carbon ethylenic hydrocarbons are found to be roughly proportional to the number of hydrogens on carbon atoms beta to the hydroxyl group of the alcohol. As shown in Table VI, the respective yields of such hydrocarbons divided by the number of hydrogens on beta carbon atoms vary from 0.030 to 0.070 while the number of hydrogens in beta carbons has varied from 1 for isobutyl alcohol to 9 for *t*-butyl alcohol. The variation in the ratio also follows roughly the yield of *n*-carbon saturated hydrocarbons as shown in the last column of Table VI where the ratio of C_nH_{2n} hydrocarbons per hydrogen on beta carbon atoms to C_nH_{2n+2} hydrocarbons is seen to be reasonably constant. The interaction of hydroxyl groups with hydrogen atoms on beta carbon atoms is the accepted mechanism for the catalytic dehydration of alcohols.[28] Considering the possible production of such ethylenic hydrocarbons by radical decomposition of *n*-carbon radicals, as well as structural factors which might influence the yield, the agreement is sufficient to show the rearrangement to be important for the formation of this type hydrocarbon. It accounts only for a small part of the total water yield.

TABLE VI

COMPARISON OF YIELDS OF C_nH_{2n} AND C_nH_{2n+2} HYDROCARBONS FROM *n*-CARBON ALCOHOLS

Alcohol	GC_nH_{2n}	$H\beta C$	$GC_nH_{2n}/H_{\beta C}$	GC_nH_{2n+2}	$\frac{G(C_nH_{2n})/H_{\beta C}}{G(C_nH_{2n+2})}$
Ethyl	0.17	3	0.057	~0.13[a]	~2.3
n-Propyl	.14	2	.070	.145	2.05
Isopropyl	.27	6	.045	.088	1.95
n-Butyl	.093	2	.046	.124	2.7
Isobutyl	.067	1	.067	.162	2.4
s-Butyl	.179	5	.036	~ .10[b]	~2.8
t-Butyl	.27	9	.030	.011[c]	~3.3

[a] Corrected for estimated production of ethane from reaction of methyl radicals. [b] Corrected for estimated formation of C_4H_{10} by reaction of ethyl radicals. [c] Isobutane in *t*-butyl alcohol only approximate due to interference of acetone in mass spectrometer analysis of gas fraction analyzed.

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(28) W. G. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Company, London, 1936, p. 109.