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Berkeley, California

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ABSTRACT

The yields of primary chemical products of the irradiation of methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, n-octyl, and n-decyl alcohols with 27 Mev helium ions have been determined. The major products detected were hydrogen, hydrocarbons, carbonyl compounds, glycols, and water. Their respective structures and yields establish that the radiolysis products of the simple alcohols result principally from reactions which involve those groups bonded to the carbon of the functional carbinol group.

Methanol yielded hydrogen, formaldehyde, ethylene glycol, and water in major amounts, and smaller quantities of carbon monoxide, methane, and ethane. The primary alcohols yielded principally hydrogen, the aldehyde corresponding to the alcohol irradiated, the vicinal glycol formed by combination of radical fragments of the alcohol after elimination of a hydrogen atom attached to the carbon of the carbinol group, water, and smaller amounts of hydrocarbons, mainly the n-1 hydrocarbon from the n-carbon alcohol, formaldehyde, and ethylene glycol. A decreasing yield of detected oxidized product compared to reduced product with increasing length of the alkyl chain of the normal alcohol indicated an increasing yield of undetermined oxidized product, probably olefinic unsaturation in the alkyl chain, and demonstrated that the functional reactant tendency decreases with increasing size

of the normal alcohol, while the non-functional tendencies increase. The secondary alcohols yielded hydrogen, increasing amounts of the hydrocarbons resulting from combination of the groups attached to the carbinol carbon, ketones, the aldehyde derived from oxidative elimination of a carbinol alkyl group, a decreasing amount of glycol, all vicinal, and water. The tertiary alcohol yielded hydrogen, major quantities of the appropriate hydrocarbons, ketones, water, and only small amounts of glycol products.

The radiolytic reactions are not chain reactions.

A résumé of analytical procedures, a stoichiometrical correlation of product yields, and a discussion of possible mechanisms for the reactions has been given.

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I. INTRODUCTION

The study of the extranuclear chemical effects of ionizing radiation on material substances is known as radiation chemistry. A systematic investigation of the field requires its subdivision into categories involving variation of several general conditions, important among them being the nature of the radiation employed and the state and composition of the substance irradiated. With respect to this last condition, the study of radiolytic phenomena in pure organic compounds, of the effects of organic chemical structure, particularly functional activity, on the nature and yield of radiolysis products, may be considered as fundamental to some more complicated systems. As a part of such a study this research has been concerned with the chemical products of the high energy particulate irradiation of aliphatic alcohols, its principal object being to investigate the possibility in radiolysis of the selective and characteristic reactivity manifested in low energy functional chemical phenomena.

The published research involving the effects of functional activity on radiolytic reaction has been largely confined to hydrocarbons, saturated and unsaturated aliphatic, and aromatic, and to organic acids. Isolated instances of the ionizing irradiation of several other type compounds, such as amines and alcohols have been reported but with no systematic investigation of the functional group they

represent. The considerable investigation of the irradiation products of organic substances in aqueous solution,[1,2] are of an essentially different nature, being concerned primarily with the chemical effects on the organic solute, of the activated species, or radicals, formed by irradiation of the water. The many researches done on inorganic substances, especially water and simple gases, are of general and theoretical interest, but will not be of concern here. General reviews by Lind,[3] of the early work, and of that more recent, by Burton[4] and Dainton,[5] afford detailed consideration and reference.

One of the earliest studies of the action of ionizing radiation on a functional organic category was that of Lind and Bardwell[6] who studied the chemical action of alpha particles on the simple saturated hydrocarbons up to and including butane. They found rather generally that hydrogen and methane in a ratio 5 to 1 were eliminated to give higher hydrocarbon products; on extended irradiation, up to those heavy enough to be liquid and solid. No unsaturation was found in the gaseous product, but the condensed components exhibited it extensively, suggesting to them that any unsaturated gas which formed immediately condensed. Honig and Sheppard,[7] substantiated these results by alpha and deuteron bombardment of methane and n-butane. They obtained yields of the various gaseous hydrocarbon products as a function of the extent of bombardment, showing the intermediate build-up of both condensation (higher) and degradation (lower) hydrocarbon products, all saturated, with their eventual conversion to non-gaseous condensates and hydrogen. The liquid products obtained gave evidence of the presence of olefin and cyclic components.

Schoepfle and Fellows[8] measured and partially analyzed the gaseous products of the irradiation of an extensive list of liquid hydrocarbons, saturated and unsaturated aliphatic, and aromatic, with 170 kev cathode rays. They found that the saturated hydrocarbons reacted to give relatively large quantities of gaseous product, principally hydrogen, but with some saturated hydrocarbon of lower molecular weight than that irradiated, and high molecular weight condensation products, solid and liquid. Increasing molecular weight of the straight chain paraffins increased the percentage composition of H_2 in the gaseous phase (which, however, decreased in total yield) and decreased the methane and other gaseous hydrocarbon components. With increasing methyl substitution, the yield of methane increased.

Burton[9] pointed out from this data that the ratio of H_2 to CH_4 plotted against the ratio of C-H to $C-CH_3$ bonds was approximately linear for a series of n-hydrocarbons, hexane to tetradecane, exhibiting a statistical dependence of the respective product yields on the availability of its constitutive components. The high yield of H_2, however, indicated an intrinsic preference for hydrogen formation not in conformity with the fact that the C-H bond is stronger than the C-C bond.[10]

The unsaturated aliphatic hydrocarbons yielded considerably less gas than the saturated hydrocarbons, though it was of a similar composition, and the aromatic hydrocarbons yielded practically no gas at all. The lower gas yields of the irradiation of olefins was ascribed by Schoepfle and Fellows,[8] and by Burton[11] to the capture of the free atom and radical components of a potential gaseous product by the unsaturated bonds. A second radiolytic characteristic of

olefins, and unsaturated bonds in general, is a tendency toward considerable polymerization.[12] Ethylene deposits a liquid product and gives moderate quantities of gaseous product, principally hydrogen.[12]

Triply bonded unsaturates are more susceptible to radiolytic condensation. Acetylene deposits a solid similar to cuprene,[12] the polymer of acetylene formed catalytically, and gives considerable benzene as the only appreciable gaseous product.[13] There is evidence for a considerable chain effect in these reactions, and presumably the radiolytic action is that of an initiating excitation. Rosenblum[13] cites the acetylene polymerization as a succession of bimolecular reactions between an excited molecule or polymer and a normal acetylene molecule.

$$C_2H_2^* \xrightarrow{C_2H_2} (C_2H_2)_2^* \xrightarrow{C_2H_2} (C_2H_2)_3^*$$

Benzene is formed by cyclization at the trimer stage of some of the polymers.

Radiochemical polymerization is a fairly general functional property as well as those of non-hydrocarbon unsaturated species commonly associated with a susceptibility for catalytic polymerization, for example, acrylonitriles.[2]

Burton and his co-workers have considered the radiolytic decomposition of aromatic hydrocarbons in some detail.[9,11,14-17] They noted that in addition to a very small yield of gaseous product there was only a small yield of polymeric product as well,[15] indicating that the aromatic structure is intrinsically resistant to the effects of ionizing radiation. Burton concludes that the non-localized bonding orbitals of aromatic structures allow such a uniform distribution

of excitation or ionization effects over the molecule that no single bond is sufficiently energized to effect a decomposition before its collisional deactivation. The stability of benzene to such decomposition gives it a deactivating effect on the excitation and resultant chemical consequences of other organic species dissolved in it.[15] Alkyl substituted aromatics in general combined the radiolytic tendencies of aliphatic and aromatic hydrocarbons,[8] with some interaction effects. The principal hydrocarbon products result from dissociative reaction at alkyl C-C bonds β to the aromatic ring.[14,17]

The other functional category that has received some detailed radiolytic consideration is that of the organic acids.[18-23] Sheppard and Burton[22] showed that the principal reactions of the fatty acids: acetic, caprilic, lauric, and palmitic, were the production of hydrogen gas and decarboxylation, i.e., decomposition to carbon dioxide and the hydrocarbon of one carbon less than the acid bombarded. In addition, smaller amounts of carbon monoxide, water, methane, and higher hydrocarbons were detected among the gaseous products. Other complex organic acids reacted similarly. Cyclohexanecarboxylic acid yielded carbon dioxide, some hydrogen and a liquid containing principally cyclohexane, some cyclohexene, and possibly dicyclohexyl ketone.[20] An acid salt, calcium palmitate, yielded relatively more hydrogen and less carbon dioxide than the free acid.[18] Cetyl palmitate, an ester, yielded principally hydrogen, and only a small amount of carbon dioxide.[18] Sebacic acid, a dicarboxylic acid, yielded mostly carbon dioxide, some hydrogen.[18] Trimethylacetic acid gave a relatively high yield of carbon dioxide and a good yield of methane as well as hydrogen.[18] Benzoic acid yielded very little gas, which was mostly

carbon dioxide, and no indication could be found of hydrogen entering the aromatic ring.[23] However, oleic acid yielded hydrogen and carbon dioxide in good amounts, and some stearic acid (saturated) as well.[23]

Hornig[19] noted the relative yield of hydrogen with respect to that of carbon dioxide plus carbon monoxide was roughly proportional to the number of C-H bonds for the three large fatty acids of the Sheppard and Burton experiment.[22]

The interpretation of radiological phenomena is usually made in terms of a free radical mechanism developed and first applied by Eyring, Hirshfelder, and Taylor[24] in a now classical paper, to the radiolytic para-ortho hydrogen conversion. It postulates the ultimate transformation of the electronic ionization and excitation energy of the primary radiolytic interaction into a molecular vibrational energy which results in dissociation in appropriate cases, and the production of various free radicals. The free radicals react among themselves and with unactivated molecules to produce the final products. The evidence of a functional selectivity in the evolution of hydrogen from hydrocarbons, in the radiolytic decarboxylation of the higher acids, and of a functional resistance to radiological decomposition in aromatic compounds has led Burton to the postulation of several modifications of this free radical concept.[9,11,15,16] He suggests that under appropriate conditions the excitation of a radiolytically energized molecule may be transferred from the locus of its indiscriminate inception and be contained in the molecule in such a manner as would tend to promote a selective reaction tendency. The necessary conditions are, in general, a sufficiently complex or symmetrical molecular structure as to allow a distribution of the excitation energy

among several vibrational modes so that the dissociational energy of none is exceeded, and the liquid state, by virtue of which a cage effect of surrounding molecules inhibits any immediate dissociative tendencies which would result in large free radicals. Under such conditions of prolonged excitation, the probability of a selective decomposition by means of a low barrier rearrangement to the ultimate products of the reaction (case of decarboxylation), or of a collisional deactivation, in the case of no such decompositional rearrangement susceptibility (benzene), would be enhanced. Since the small hydrogen atom is largely free of the restrictions of a cage effect, the free radical production of H_2 could proceed to a competitive extent belying the H-C bond energy.

Among the incidental compounds which have been irradiated are dodecylamine and hexamethylamine, with alpha particles, yielding principally hydrogen and ammonia.[18] Cholesterol and octadecyl alcohol irradiated with alphas gave as gaseous products principally hydrogen, with very small amounts of carbon monoxide, carbon dioxide, water, and light hydrocarbons.[18] McLennan and Patrick[25] reported products of the cathode ray bombardment of methyl and ethyl alcohol vapors. Major gaseous products included hydrogen in greatest abundance, carbon monoxide, methane, and carbon dioxide in good yields, and minor amounts of ethylene, acetylene, and in the case of ethanol, ethane. Aqueous extracts of the products showed formaldehyde and acetaldehyde to be formed, in both cases, the methanol favoring formaldehyde, and the ethanol, acetaldehyde. The ethanol produced traces of a yellow oil.

In similar experiments the same authors[25] found cathode rays polymerized gaseous formaldehyde, and decomposed the paraformaldehyde formed to hydrogen, methane and the carbon oxides. Acetaldehyde and

acetone produced yellow condensates and gases hydrogen, carbon monoxide and methane in major yield, with lesser amounts of carbon dioxide, ethylene, acetylene, and ethane, except that in the case of acetone, ethane was in major yield. From kinetic considerations the authors ascribed the formation of the gaseous products of acetaldehyde to decomposition of the polymer product.

The photolysis of alcohols formed products hydrogen, carbon monoxide, and aldehyde.[26-28] Rollefson and Burton cite the primary reaction as probably:

$$RCH_2OH \xrightarrow{h\nu} RCHO + H_2$$

with the aldehyde decomposing secondarily to carbon monoxide and the hydrocarbon, RH. Patet found no free hydrogen atoms in the photolysis reaction, using the para-ortho hydrogen conversion for their detection.[26,29] The photolytic absorption probably does not correspond to a dissociation into hydroxyl and alkyl radicals[26] (although there is controversy on this point).[28] Isopropyl alcohol, in aqueous solution, yielded hydrogen and acetone as photolytic products.[26,30]

Of the several fundamental homologous series available for the study of the effect of functional groups on the products of radiolysis, aliphatic alcohols were chosen for this research for several reasons. All of the lower members and many of the higher are readily available in high purity from commercial sources. They are for the most part liquid at room temperatures, a form convenient for high energy irradiation and subsequent analysis. Their high degree of chemical stability

eliminates the possibility of complicating thermal reactions and endows the products formed with a solvent medium largely devoid of interferences in the procedures employed for their analysis. The carbinol group has a relatively mild functional activity insufficient to mask the non-functional reactant tendencies in radiolysis, but adequate to the objective conceived, and the hydroxyl group gives a convenient tag by which to follow the reactant fragments around.

The following alcohols were irradiated with high energy alpha particles and analyzed for products formed: (1) methyl alcohol; (2) ethyl alcohol; (3) n-propyl alcohol; (4) isopropyl alcohol; (5) n-butyl alcohol; (6) isobutyl alcohol; (7) sec-butyl alcohol; (8) tert-butyl alcohol; (9) n-octyl alcohol; and (10) n-decyl alcohol. These can be regarded as a representative sampling of the lower aliphatic alcohols. A comparison of the effects of several structural modifications is afforded by such a group. Of prime concern in this research was the gross effect of the carbinol substituent classifications, primary, secondary, and tertiary, as represented by the four alcohols, methyl, ethyl, isopropyl, and tert-butyl. Each is the simplest of its classification. (Methanol, being a completely unsubstituted carbinol, has a unique position in this classification.) Of secondary interest was the variation in product yields along the series of normal alcohols. In addition the butanols afford an isomeric group for study of the effects of branching in general.

For analytical reasons, the most complete data is on the radiolysis of methyl, ethyl, isopropyl and tert-butyl alcohols. A less explicit survey of products was carried out on the other alcohols.

II. EXPERIMENTAL PROCEDURES

A. Liquid Target Assembly

The alcohols were irradiated in liquid form in a bombardment target assembly designed and constructed specifically for such a purpose by the University of California Radiation Laboratory according to specifications made by Dr. A. S. Newton of the Radiation Laboratory. Diagrams of the assembly are shown in Fig. 1, and a photograph in Fig. 2.

The apparatus consisted of two chambers, one situated within the other, an inner chamber to contain the liquid being bombarded and the liquid products formed and an outer chamber to collect the gaseous products. During the irradiation, the inner chamber was open to the outer by means of a duct to allow the gaseous products formed to escape.

The target assembly made junction to the window of the 60-inch Crocker Laboratory cyclotron by means of a standard window assembly type "B", which provided an essentially rectangular window 2.5 x 7 cm into the outer chamber of the target assembly. This window was covered by two aluminum foils spaced 3.0 cm apart and cooled during bombardment in a standard fashion by a stream of air passing between them.

The outer chamber of the assembly was a rectangular box of inside dimensions approximately 12 x 13 x 5 cm, constructed of 0.25 in. copper plate with edges silver soldered together, and bolted against a neoprene gasket to the window assembly. It was provided with a thermocouple well with a copper constantan thermocouple installed, and a Bourdon type pressure-vacuum gauge. A needle valve outlet permitted evacuation and removal of gaseous products.

One wall of the outer chamber, being removable, was held vacuum tight in place against a neoprene gasket by a set of quick-opening clamps. This wall was of Teflon to insulate it from the inner target

which it supported within the outer chamber.

Two types of inner chamber were used in the experiments. The first, which for future reference may be called inner chamber A, consisted essentially of a rectangular copper box, 8 x 5 x 1.5 cm inside dimensions, one face of which was a 0.002 in. copper foil to allow passage of the irradiating beam into the liquid contained inside. In the top, an opening was provided for filling the chamber and to allow escape of gaseous products into the outer chamber. This opening could be stoppered closed from outside the assembly by a plug on a shaft through a Wilson seal to prevent spilling the liquid in transporting the apparatus. The inner chamber was also provided with a thermocouple well and copper-constantan thermocouple for temperature measurement during bombardment.

This first inner chamber was found deficient in several respects. It was located approximately centrally within the outer chamber, leaving a considerable gas volume of the outer chamber exposed to the irradiating beam. The opening at the top intended for escape of gaseous products allowed a considerable loss of liquid into the outer chamber, presumably by foaming up and out during the copious gas evolution of the bombardment. This chamber was therefore replaced in later experiments by one of improved design, inner chamber B. Enlarged to 8.5 x 5 x 3 cm inside dimensions, it was suspended as close as possible from the window foil of the outer chamber, to minimize the gaseous volume exposed to the irradiating beam. The opening at the top for filling and removing the liquids was sealed by a gasketed plug, and a separate duct provided for gas escape which was baffled in such a manner as to minimize the mechanical loss of liquid

from the chamber by foaming. This duct could also be externally closed for transportation. Aside from these features the inner chamber B was essentially identical to A.

Both inner and outer chambers were water cooled and both were completely electroplated with gold, as was the copper foil window of the inner chamber, to eliminate direct chemical or catalytic action with any reactant species formed during irradiation. The inner wall of the second aluminum window foil which comprised a part of the wall of the outer chamber was gold plated by molecular evaporation from a hot filament at a low pressure. Since it became radioactive during bombardment, the assembly was provided with a lead box for shielding the experimenter during transportation and removal of the products.

B. Bombardment Procedure

The alcohols irradiated were all commercially obtained highest purity grade (see Table I). Each was purified by refluxing a day or more over calcium oxide and fractionating on a forty-inch adiabatic distilling column packed with 1/8 in. pyrex helices. A middle cut of approximately half the total distillate was taken at the temperatures and pressures indicated in Table I.

The inner chamber of the target assembly was filled with 40 ml or 110 ml (depending on whether inner target A or B, respectively, was used) of the alcohol to be irradiated, and the apparatus assembled. The chambers were evacuated down to the vapor pressure of the alcohol and the alcohol boiled out slowly under vacuum to a sufficient extent as to ensure that no air was present.

Table I

Alcohol	Source and Grade	Boiling Pt. (Lange[31]) (°C)	Boiling Pt. of Middle Cut (°C)	Pressure (mm)
Methyl	Baker's CP analyzed	64.7	63.5	744.5
Ethyl	Commercial Solvents Co., absolute	78.4	77	745
n-Propyl	Eastman Kodak White Label	97.8	96.5	740
Isopropyl	Baker and Adamson, reagent	82.5	81	738
n-Butyl	Eastman Kodak White Label	117	116	740
Isobutyl	Paragon Div., Matheson, reagent	107-108	106	745
sec-Butyl	Eastman Kodak White Label	99.5	99	747.5
tert-Butyl	Paragon Div., Matheson, reagent	82.9	82	745
n-Octyl	Paragon Div., Matheson, reagent	194-195	194	751
n-Decyl	Eastman Kodak White Label	232.9	228-230	742.5

The bombardments were carried out on the 60-inch Crocker Laboratory cyclotron with 39.6 Mev helium ions.[32] Before striking the alcohol, the irradiating beam passed through, in the given order: a 16.5 mg/cm^2 dural aluminum* foil, 3 cm air at atmospheric pressure, a 15.7 mg/cm^2 dural aluminum* foil, 1.5 mg/cm^2 gold plate, and one of four copper foils plated on both sides with 3.7 mg/cm^2 gold (total). These copper foils are listed below with the corresponding final energy of the irradiating helium ions, after correction from standard rate of energy-loss curves[33] for energy degration in the various absorbers through which they passed:

*Alcoa 24ST, composition: Al plus 4.5% Cu, 0.6% Mn, 1.5% Mg.[34]

Foil	mg/cm^2	Mev
1	49.1	27.1
2	54.8	26.5
3	53.5	26.7
4	52.5	26.8

A current measurement of the bombarding ion beam, taken off of the inner chamber and integrated over the length of bombardment time to a measure of the total charge input, yielded the number of helium ions discharged on the inner target, and thus the total energy dissipated in the alcohol could be calculated.

A standard value of 2 μah bombardment was given each alcohol in the later experiments to facilitate comparison between bombardments. It was found that the energy input this figure represented was sufficient to make possible macroanalysis of the major products in the liquid fraction but low enough to ensure that secondary reactions (i.e., radiolysis of primary product) were small. Bombardment to the extent of 2 μah was sufficient to produce somewhat over an atmosphere of gaseous product in the assembly (volume about 800 cc). Since the apparatus was designed essentially for pressures below atmospheric, the production of pressures much exceeding atmosphere entailed the risk of some loss of gaseous product, and thus comprised a limitation on the extent of bombardment.

The operating conditions of the 60-inch cyclotron made it impractical to insist upon a constant beam current during bombardments. However, to standardize kinetic conditions in later bombardments, a maximum of 3 μa was imposed and the runs made at as close to this value as was possible. Thus the bombardment times were of the order

of 45 minutes.

The target assembly was in general water cooled to about 16°C during bombardment. Tertiary butyl alcohol is a solid at this temperature and so that the irradiations could be carried out on the liquid state, allowing convectional dissipation of the localized heat effects of irradiation, the cooling water was heated to a temperature of about 30°C for the tert-butyl alcohol bombardments. Pre-evacuation of the bombardment chamber after filling with this alcohol required the same treatment, but subsequent to irradiation its melting point was lowered sufficiently by the product formed that no special measures were necessary in its analytical treatment.

After irradiation, one of three procedures for handling the gaseous products were employed. When the analysis of liquid product was of prime interest and extensive handling of the liquid fraction thus to be avoided, the gas was simply sampled. The chambers were opened into a calibrated manometer system, the pressure and temperature recorded and a sample of the gas taken. This sample was then directly analyzed mass spectrometrically (Gas Treatment I), or fractionated into components which passed respectively through traps of liquid nitrogen (-196°C), dry ice in trichlorethylene (-78°C) and the nonvolatile residue of the latter. The pressure of each fraction was measured in calibrated volumes, and mass spectrometer analyses made (Gas Treatment II). Treatment II allowed the determination of many more small yield gaseous products than I.

Since it was feared that such a sampling procedure involving expansion through several long narrow connection tubes might yield an unrepresentative sample, another procedure was adopted for

experiments whose emphasis was on the gaseous products (Gas Treatment III). This procedure involved the complete evacuation of the gaseous and an appreciable portion of the liquid fraction from the target chambers by means of an automatic mercury Toepler pump, through the fractionation traps of liquid nitrogen and dry ice in trichloroethylene. The pressures of the two volatile fractions thus obtained were measured in calibrated volumes and mass spectrometric analyses made. The considerable nonvolatile fraction collected in the dry ice trap was added to the residual liquid taken from the inner chamber of the target assembly.

In each case, the liquid fraction was removed quantitatively from the target chamber, measured, and diluted to a near convenient volume. When inner chamber A was employed a fraction of liquid was usually found in the outer chamber, presumably having foamed out with the gas evolution, from where it was removed and added to that obtained from the inner chamber. In using the inner chamber B this difficulty was largely avoided; with a properly slow pre-evacuation before bombardment, the inner target contained completely the liquid fraction.

The liquid fractions thus obtained were kept for analysis in glass stoppered graduated cylinders, sealed with wax.

III. ANALYTICAL PROCEDURES

A. Analysis of the Gaseous Products

The gaseous fractions collected as described were analyzed by means of a Consolidated Engineering Corporation Analytical Mass Spectrometer, type 21-102 manufactured by the Consolidated Engineering Corporation of Pasadena, California. The instrument was used essentially according to the manufacturers recommendations and the procedures involved have been extensively described elsewhere.[35-39]

The instrument runs were made by Dr. A. S. Newton and Mr. Lorin Tolman of the University of California Radiation Laboratory and the analysis of the mass spectral data by Dr. Newton.

The analysis of gaseous mixtures by mass spectrometry depends on the formation by electron bombardment of a characteristic spectrum of charged molecular fragments, each of a given mass to charge ratio, which are accelerated through an electric field and resolved magnetically. The mass spectrum of each component of a mixture adds linearly in proportion to its respective partial pressure, and thus a comparison with a calibration spectrum of the pure component affords a determination of its contribution to the complex pattern. The analysis is effected when the sum of the constituent spectra matches that of the observed for the mixture. The mass spectrometric method affords a very precise analysis of a complex sample if all of its components are known, and their calibration patterns available. On the other hand, the presence of components in the mixture which cannot be identified or which are unobtainable in pure form for calibration purposes can seriously interfere even with the analysis for products known to be present and for which calibration patterns are available. This is

especially the case for high molecular weight compounds, whose contribution to the lower mass peaks, if unknown, may effectively obscure the contribution of the known components. Very complex mixtures of components near the same molecular weight or mixtures in which one component predominates by far over the others are difficult to analyze with precision.

All of these difficulties were encountered in the analysis of the gaseous products of the radiolysis of alcohols. Though the several principal products were fairly easily identifiable in each case, there were observed a considerable multitude of minor products, whose identification was uncertain or which were difficult to obtain pure for calibration patterns. The gaseous fractionations simplified the mixtures, and made possible an accurate analysis of the major components. Of necessity, however, several minor components remain unidentified or in uncertain yield.

Most noteworthy among those products which could not be accounted for were several small peaks at or in the neighborhood of masses 103 or 104, 90, 88, 74, and 73. These peaks occurred detectably in the spectrums of methanol, ethanol, and isopropyl alcohol gaseous fraction which had passed through -30°C traps, becoming more predominant in less volatile fractions, and significantly present in the more volatile cuts obtained on distillation of the liquid fraction. The appreciable volatility of whatever was responsible for fragments of such high molecular weight suggested that they might derive from a condensation of a lighter species after fractionation. Their masses being close to integral multiples of the molecular weight of formaldehyde and acetaldehyde, known to be produced in good yield in the radiolysis,

it can be suggested that they represent aldehyde polymers of some sort. On distillation of an alcohol solution of acetaldehyde and formaldehyde the more volatile cuts were found to contain similar high mass peaks. This research was not pursued extensively, and the problem of a calibration pattern of these species, which may be of limited stability and variable composition, is as yet unsolved. Other small peaks occurring at high mass values in volatile fractions of product from the other alcohols are similarly unexplained.

B. Analysis of Liquid Products

Mass Spectrometric Procedures

Although the Consolidated mass spectrometer is designed to allow analysis of liquid mixtures, the relatively small yield of product in a large quantity of alcohol made direct analysis of the liquid fraction impractical. Some crude fractionations of the irradiated ethanols indicated small amounts of both very low and very high boiling components, the latter well over 150°C, but the mass spectral patterns were too complicated for explicit analysis.

It was thought that the chemical isolation of a homologous group might simplify the system and concentrate the product sufficiently to allow explicit analysis. A procedure was worked out for the isolation of aldehydes from the alcohol as their 2,4-dinitrophenylhydrazones, with regeneration by replacement with pyruvic acid and distillation out of an oxalate-bioxalate buffered acid solution into water with considerable concentration. This line of research was not further pursued, however, when it seemed that an extensive investigation would be required to develop it.

Chemical Procedures

In the early experiments considerable development and modification of wet chemical organic analytical methods was undertaken as they were found to be necessary for the analysis of the liquid fractions of the irradiated alcohols. Outlined below are the methods employed for the determination of water, total carbonyl, total aldehyde, formaldehyde, acetaldehyde, ketone, total glycols, vicinal glycols and their carbonyl products upon oxidative splitting with periodic acid, acids, esters, peroxides, and ethylenic unsaturation. Because of the large excesses of interfering alcohol inevitably present, no analysis of (other) alcohols nor of ethers, i.e., alkoxyl determinations, were attempted. The methods used were derived from standard analytical organic techniques and usually scaled down considerably, so that as much information as possible could be obtained on each bombarded sample. This resulted in the unavoidable loss of some analytical precision. In all analyses high purity reagent grade chemicals were used.

1. Water Determination.-- Water was detected and determined by the Karl Fischer method.[40] The reaction, taking place in pyridine, is organically complicated, but analogous to:

$$I_2 + SO_2 + 2H_2O \longrightarrow 2HI + H_2SO_4 .$$

Samples were titrated in flasks fitted by glass seals in the bottom with platinum and tungsten electrodes to allow an electrometric endpoint determination by means of the titrimeter described by Mitchell and Smith.[40] The titrant was admitted into the flask, from an automatic burette, protected from atmospheric moisture

by phosphorus pentoxide, through a hypodermic needle attached to the tip of the burette and inserted through a rubber cap covering the mouth of the flask. A duct near the top of the flask, fitted with a ground glass joint by which a desiccant tube was attached, allowed for pressure adjustment in the flask during titration. The samples were magnetically stirred during titration.

The reagent was standardized before and after determinations by titrating a standard solution of water in methanol.

Reagent. Karl Fischer Reagent was prepared by dissolving 54 g C.P. resublimed iodine in 265 ml dry pyridine, adding 666 ml of dry methanol. This solution was cooled in an ice bath and 45 ml of liquid sulfur dioxide, condensed in a dry ice-acetone bath, added rapidly. The reagent was allowed to stand a day or two before being used. It was standardized by titrating a 2 ml sample of a standard solution of water in methanol.

A standard solution of approximately 11 mg/ml water in methanol was prepared by adding a weighed 5 g quantity of distilled water to 500 ml reagent grade methanol. The titre of Fischer reagent equivalent to the added water was obtained by subtracting a blank of the methanol used from the total titre of the standard solution. This standardization of the reagent allowed evaluation of the total water content of the standard solution.

Procedure. Two to five ml samples of irradiated alcohol were diluted with 5 ml dry methanol and titrated rapidly with intermittent stirring (magnetic) to an electrometric

endpoint stable for at least one-half minute. A blank on the unirradiated alcohol was similarly determined. Two ml of the standard was diluted with 5 ml dry methanol and titrated, from which titre was subtracted a blank of the methanol dilution. Direct comparison of the difference titres thus obtained of irradiated alcohol and standard allowed evaluation of the net water in the irradiated alcohol. The difference titres were employed in the determinations to avoid an apparently constant vessel blank of about 0.5 mg of water consistently present although the titrating flasks were kept under desiccation at all times when not in use. In the case of the higher alcohol samples, the addition of methanol was necessary for the determination of the electrometric endpoint and served to prevent precipitation of reaction products during the titration.

Mitchell and Smith[40] described the interference of carbonyl compounds with the Fischer water titration as a rapidly fading endpoint and high evaluation of the water content, due to formation of acetals or ketals and water by reaction of the carbonyl with the methanol of the reagent. They suggested a modified procedure in which the interfering carbonyl was made inert by prior reaction with hydrocyanic acid. On applying the procedure in this research to the irradiated alcohol solutions, relatively dilute in carbonyl, values for water were obtained in agreement, within the precision error of the small samples used, with those of the rapid unmodified titration outlined above. The endpoints of the unmodified titration did fade but slowly enough to allow a fairly accurate determination of the water present.

Formaldehyde is cited by Mitchell and Smith as not interfering in the standard Karl Fischer titration. Neither ethylenic unsaturation nor peroxides interfere.

2. Carbonyl Determinations.-- The carbonyl group was initially detected in irradiated ethanol samples as aldehyde by means of the Tollins ammoniacal silver reagent test[41] and by precipitation of the 2,4-dinitrophenylhydrazone.

(a) Total Carbonyl. Total carbonyl was determined by the hydroxylamine hydrochloride method of Bryant and Smith.[42] It involved the titration with suitable indicator of the acid liberated on formation of the oxime in a reaction buffered and taken to completion by a pyridine medium.

$$RCHO + HONH_3Cl + C_5H_5N \longrightarrow RCH{=}NOH + H_2O + C_5H_5NHCl$$

$$R_2CO + HONH_3Cl + C_5H_5N \longrightarrow R_2C{=}NOH + H_2O + C_5H_5NHCl$$

Reagents. 0.5 M hydroxylamine hydrochloride reagent was prepared by dissolving 35 g of hydroxylamine hydrochloride in 160 ml of distilled water and diluting to 1 liter with 95% ethanol.

The buffer-indicator solution was prepared (at double strength to allow for dilution by the alcohol of the sample being determined) by diluting a solution of 20 ml of pyridine and 1 ml of 1% alcoholic bromphenol blue indicator to 500 ml with 95% ethanol.

0.5 N methanolic NaOH was prepared by diluting 13 ml of approximately 19 M NaOH (saturated water solution filtered

free of carbonate) with 27 ml of water, and then to 500 ml with methanol.

Procedure. To a quantity of irradiated sample containing an estimated 0.3 to 1.0 millimoles of carbonyl (2 to 5 ml in these experiments) and diluted to 5 ml with absolute ethanol was added exactly 3 ml of 0.5 M hydroxylamine hydrochloride reagent and 5 ml of buffer-indicator solution. A blank of the unirradiated alcohol was identically prepared and carried through the procedure. After sealing in a pyrex test tube, the samples were heated for two hours in a water bath at 100°C, and allowed to cool spontaneously to room temperature. In the samples containing carbonyl, the acid liberated turned the indicator yellow, while the blank remained blue green. The tubes were broken, their contents transferred quantitatively to small flasks each with 3 ml of absolute ethanol. The yellow samples were titrated with 0.5 N methanolic NaOH by means of a semimicro burette, to the blue green of the blank, whose volume was adjusted with 90% methanol - 10% water solution somewhat before the end-point to that of the sample being titrated. The number of moles of NaOH consumed was taken, after a small correction for acidity initially present in the irradiated alcohol, as a direct measure of the carbonyl in the sample.

Bryant and Smith cite the average precision of their method as ±1% with results stoichiometric within the limits of experimental error. An ethanol solution of formaldehyde, standardized by precipitation of its dimedone derivative (see aldehyde determination, page 30)

at 3.85 ± 0.05 mg/ml analyzed 3.80 ± 0.03 mg/ml by the procedure described above. An ethanol solution of acetone prepared gavimetrically to 0.133 ± 0.003 millimoles analyzed 0.133 ± 0.002 moles/ml by the above described procedure.

Excessive acid in the sample destroys the buffered conditions under which the reaction goes to completion. In small amounts, however, the interference is presumably simply additive and may be corrected for.

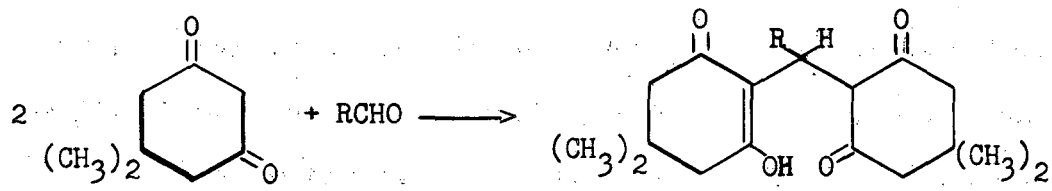
Smith and Mitchell[43] reported a hydroxylamine hydrochloride method for the determination of carbonyl compounds in the presence of organic acids, by titration of the strong acid liberated on oxime formation to an indicator endpoint of pH 2.5, at which the weak carboxylic acids were not neutralized. Since it could be applied in the cold and involved only a short reaction time, an attempt was made to use it as a substitute for the above procedure. However, on titrating to a visual endpoint it unfailingly gave results 10% low. An alternative to the visual endpoint, a potentiometric titration to pH 2.5 described by the authors was not tried.

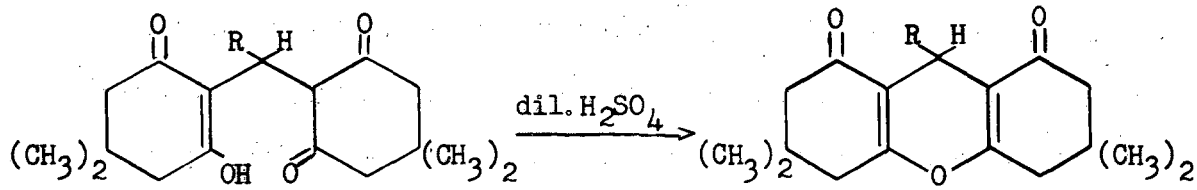
By subjecting this reaction to a heat treatment 100°C for two hours, the acid hydrolysis of any acetals present renders them susceptible to determination as carbonyl.[43] Thus the difference in basic titre between the hot and cold method constitutes a determination of the carbonyl combined as acetal. No such difference could be detected in either the standard carbonyl or irradiated alcohols samples indicating at least that acetal formation was not the cause of the above discrepancy and less certainly that acetals were not formed appreciably in the irradiated alcohols.

Organic peroxides, specifically tert-butyl peroxide, were found to interfere in the carbonyl determination, giving high results, presumably by the oxidative destruction of hydroxylamine.

(b) Precipitation of Aldehydes with 5,5-Dimethylcyclohexanedione-1,3(dimedone). Yoe and Reid[44] have reported the quantitative precipitation of formaldehyde under buffered conditions with dimedone, i.e., 5,5-dimethylcyclohexanedione-1,3 (also called methone and dimedon and known commercially as dimethyldihydroresorcinol).

Vorlander[45] has developed a method whereby the formaldehyde and acetaldehyde derivatives formed in the precipitation could be separated by dehydrating the latter in several ways including treatment with dilute sulfuric acid to a non-acidic anhydride, insoluble in the basic carbonate solution which will dissolve the formaldehyde derivative.





The extreme sensitivity of this method made it valuable in the determination of the small amounts of aldehyde products of irradiated alcohols.

Reagents. A saturated aqueous solution of dimedone was prepared by adding 2 or 3 grams of Eastman Kodak White Label dimethyldihydroresorcinol to 500 ml of distilled water, allowing the preparation to stand a few days with intermittent shaking, and then filtering. (The solubility of dimedone at room temperature is about 0.004 g/ml.)[44]

A buffer solution of pH 4.6 was prepared by mixing two volumes of 1 N sodium acetate with one volume of 1 N HCl. 10% sodium carbonate solution was prepared by dissolving 10 g of Na_2CO_3 in 90 ml of distilled water.

Procedure. To a sample of irradiated alcohol containing an estimated 10 to 20 mg formaldehyde and/or acetaldehyde (1 or 2 ml in these experiments) was added 75 ml of buffer solution of pH 4.6 and a quantity of saturated reagent solution equivalent to a 10-15% stoichiometrical excess (2.6 x mg formaldehyde + 1.7 x mg acetaldehyde present). After allowing at least three days with occasional shaking for complete precipitation, 4 ml (approximately 1/30 the total volume of the solution) of concentrated H_2SO_4 was added and the preparation shaken overnight. The solution was then filtered from the precipitate by vacuum through a 15 ml medium porosity sintered glass filtering crucible. 5 ml of 10% Na_2CO_3 solution were added to the precipitate in the crucible, the slurry stirred for a couple of minutes and the carbonate solution then drawn through the crucible by vacuum and collected. The remaining precipitate was treated similarly with another 5 ml portion of 10% Na_2CO_3

and washed several times with small portions of distilled water. This precipitate comprised the non-acidic acetaldehyde derivative. The collected carbonate filtrates plus washings were acidified slowly with concentrated HCl to the copious evolution of CO_2, at which buffered point the acidic formaldehyde derivative was reprecipitated. This precipitate was filtered with a 15 ml medium porosity sintered glass filtering crucible and washed with several small portions of distilled water. Both precipitates were dried under vacuum at room temperature to constant weight and were taken as a measure respectively of the acetaldehyde and formaldehyde present in the irradiated alcohol. The conversion factor for the formaldehyde to mg formaldehyde was 0.1027 and for the acetaldehyde derivative to mg acetaldehyde was 0.153, after addition of a 0.004 g solubility correction onto the weight of the acetaldehyde derivative.

The yield of formaldehyde derivative in this procedure was reproducibly 100 $\pm$ 2% on ethanol solutions of aldehyde standardized by the hydroxylamine hydrochloride method. Much larger reagent excesses than the 10-15% over the stoichiometrical and lesser volumes of buffer solution yielded high results, up to 106%. When precipitated alone, the acetaldehyde derivative lacked 5 to 6 milligrams, of its stoichiometrical weight before the sulfuric acid dehydration. Since this corresponds approximately to the solubility of the derivative in excess reagent,[44] the reaction was assumed essentially complete and the necessary correction an absolute solubility loss. The additional solubility due to the H_2SO_4 treatment brought the

correction on the acetaldehyde derivative in the above procedure to 8 or 9 milligrams.

When the acetaldehyde was coprecipitated with formaldehyde, the solubility of its derivative was considerably reduced, and a 4 milligram additive correction on the acetaldehyde derivative yielded quantitative values within $\pm 2\%$. For an accurate determination of the acetaldehyde in irradiated isopropyl alcohol, it was coprecipitated with a formaldehyde acetaldehyde standard in which a blank was taken and subtracted. This yielded an absolute measure of the acetaldehyde in the irradiated sample with no solubility uncertainties.

The above procedure was applied with no success to propionaldehyde, n-butyraldehyde, and iso-butyraldehyde. It was thought, as suggested by Walker,[46] that the behavior of these higher aldehydes would approximate that of acetaldehyde and afford a unique determination of formaldehyde in any mixture, but such was not the case. Though apparently precipitating well under the prescribed conditions, the products derived from the dehydration procedure with dilute sulfuric acid were found to be partially but not completely soluble in the basic carbonate solution, contaminating the formaldehyde derivative. The residue of the n-butyraldehyde derivative insoluble in basic carbonate was very soluble in distilled water, making an aqueous washing impossible.

A qualitative difference in the rate of precipitation and physical appearance of the precipitates was useful in anticipating the aldehyde being determined. The formaldehyde derivative precipitated voluminously within a few minutes of ading the reagent, forming a rather light fluffy precipitate. The acetaldehyde derivative on

the other hand, precipitated much more slowly and sparsely, appearing denser and somewhat more granular. The propionaldehyde derivative resembled the formaldehyde derivative, precipitating more rapidly than the acetaldehyde derivative, and in a lighter form. The derivative of n-butyraldehyde likewise precipitated rapidly and profusely, while that of isobutylraldehyde required a considerably longer time.

Vorländer[45] has outlined several other methods for the distinction of the formaldehyde and acetaldehyde dimedone derivatives, based on their differing acidity. It is possible that they might be applicable to the determination of formaldehyde in the presence of higher aldehydes than acetaldehyde.

(c) Oxidation of Aldehydes with Silver Oxide. The method of Mitchell and Smith[47] was employed with some success for the estimation of total aldehyde. Silver oxide was used to oxidize the aldehyde to the corresponding acid, which could be titrated with no apparent interference from whatever ketones may have been present.

$$RCHO + Ag_2O \longrightarrow RCOOH + 2Ag$$

Reagents. Silver oxide, 0.5 N aq. NaOH, standard 0.1 N HCl.

Procedure. A sample of irradiated alcohol containing up to 5 millimoles of aldehyde (10 ml in these experiments) was added to 3 grams of Ag_2O in a 100 ml Kjeldahl flask calibrated at 110 ml, and the mixture diluted to 50 ml with distilled water. A blank of unirradiated alcohol was prepared identically and the two flasks, with rubber stoppers wired in place, heated for 1/2 hour at 80°C in a water bath. A silver mirror readily formed in the flasks containing

aldehyde. The flasks were cooled and exactly 25 ml of 0.5 N NaOH was added to each. After dilution to a total volume of 110 ml and thorough mixing, the samples were filtered through filter paper and aliquots of the filtrate titrated with standardized 0.1 N HCl to a phenolphthalein endpoint. The difference in titre between sample and blank was taken as a measure of the acid formed by oxidation of the aldehyde, which was thus determined.

This procedure yielded results within ±5% of the formaldehyde plus acetaldehyde in ethanol solutions as determined by the hydroxylamine method. The formation of slight silver mirrors on the walls of the flasks containing the pure alcohol blanks indicated some reaction with silver oxide which may have not been duplicated in the aldehyde samples to the same extent, producing an error. On irradiated solutions the values for aldehyde derived from the procedure were somewhat lower than those obtained by independent and seemingly reliable determinations using the hydroxylamine and dimedone methods, and rather variable. For this reason, the values derived were considered only semiquantitative and illustrative merely of general magnitudes of aldehyde present in the irradiated solutions.

The procedure when carried out without heating determined reproducibly a given fraction of the total aldehyde (formaldehyde and acetaldehyde) in an ethanolic standard which had been made up several months before. This was probably an indication of the "free" aldehyde uncombined in polymeric or acetal form in the solution, since the heat treatment allowed determination of the total aldehyde. When the aldehyde in irradiated solutions is newly formed, it is

possible that the reaction carried out in the cold would determine it completely, and avoid the increased possibility for interference from the alcohol present in the hot procedures.

No change was made in the procedure when applied to alcohols immiscible in water, except that percentage aliquots of only the water phase were taken for titration, it being assumed that all of the excess base was extracted into the aqueous phase. One attempt to carry out the oxidation in homogeneous solution by the addition of enough ethanol to bring decyl alcohol and water into one phase was made, with considerably higher results being obtained for aldehydes than the hydroxylamine hydrochloride determination indicated for total carbonyl (117%). Mitchell and Smith[47] used 1,4-dioxane to bring aldehydes insoluble in water into solution, and it is possible that this would comprise a solvent for a single phase application of the procedure to higher alcohols.

(d) Bisulfite Determination of Aldehydes. The potentiometric bisulfite procedure of Siggia and Maxcy[48] was tried on a standard alcoholic solution of aldehyde (formaldehyde and acetaldehyde). The excess of an added quantity of bisulfite after reaction with the aldehyde in the cold was determined by an alkali titration which was monitored and the endpoint ascertained by a pH meter. The method yielded only a fraction of the aldehyde present in the rather old standards used, the same fraction as was indicated by the Ag_2O oxidations in the cold, and which probably represent uncombined or "free" aldehyde. On recently irradiated samples, the method could in some probability be quantitatively applied, but it was not further utilized in this research.

(e) Leys Reagent Test for Aldehydes. Leys reagent, prepared by dissolving one gram of mercuric oxide in 100 ml of 5% aqueous Na_2SO_3 solution, has been reported to be a sensitive reagent for the qualitative detection of acetaldehyde in the presence of other carbonyl compounds.[46,49] An attempt was made to work out conditions for a semi-quantitative determination of acetaldehyde using this reagent. It was found that when 1 ml of an alcoholic aldehyde solution (5 mg/ml acetaldehyde, 1 mg formaldehyde), diluted with 5 ml of distilled water, was added slowly to 10 ml of Leys reagent, then 1 ml of 1 N NaOH added slowly, and several hours allowed for complete precipitation, the reaction was stoichiometrically complete within ±10% according to the formula, $C_2Hg_2O_2H_2$, cited by Leys[49] as representing the complex formed. However, acetone gave a profuse precipitate under the same conditions; somewhat larger concentrations of formaldehyde reduced the Hg apparently completely; and propionaldehyde and butyraldehyde gave small interfering precipitates. Any appreciable or rapid dilution of the reagent with water or alcohol gave a precipitate, as did exposure to air for some time, and an appreciable blank had always to be subtracted. The extent of these interferences increased with increasing concentration of alkali present, as did the rate of the acetaldehyde precipitation. Even the qualitative tests advocated by Walker[46] involving addition of small quantities of the reagent to alkaline aldehyde solutions for detection of acetaldehyde were hampered by precipitation in the blanks. The method was abandoned for lack of reliability.

(f) KCN Determination of Formaldehyde. Walker[46] reported the Elvove modification[50] of Romijn's cyanide determination of formaldehyde[51]

gave accurate results in the presence of 5% acetaldehyde and 50% acetone. The method involved the iodometric determination of excess cyanide after reaction of a known quantity with formaldehyde. Its application to an alcoholic standard of 3.8 mg/ml formaldehyde and 13.0 mg/ml acetaldehyde yielded 6.8 mg/ml formaldehyde, appreciable interference.

An accurate formaldehyde method for use in the presence of higher aldehydes than acetaldehyde would be of considerable value in these studies, since formaldehyde is an anticipated product of radiolysis of all normal alcohols. Of possible applicability are the chromotropic acid method[52] and several others outlined in the extensive review article on aldehyde determinations by Reynolds and Irwin.[53]

(g) Ketones. The values of ketone reported in the data were derived from the difference in total carbonyl and total aldehyde, the latter taken from the dimedone determination, when possible, as the most reliable. No direct identification or measurement on ketones in the irradiated solutions was made.

Mitchell and Smith[47] report a determination of acetone in complex mixtures involving aldehydes by oxidation of the latter with silver oxide. The acetone was then distilled from the mixture and determined by their pH 2.5 hydroxylamine-hydrochloride carbonyl method.[43] The method was tried on standard solutions containing aldehydes with encouraging results but was abandoned when the pH 2.5 carbonyl method gave discrepancy results on standard carbonyl solutions.

3. Glycol Determinations.-- Glycols were qualitatively detected in irradiated ethanol by oxidation with periodic acid and precipitation

of the iodate thus formed with silver ion, a qualitative test specified by Shriner and Fuson[41] for vic-glycols as well as for several other vicinal group compounds.

(a) Distillation Separation and Acetylation of Total Glycols. The total high boiling hydroxyl equivalent in the irradiated alcohols was determined by a modification of the method of Shaffer,[54] who separated glycols from large quantities of water by careful fractional distillations of the water out of a solvent medium boiling intermediate to the water and the glycol, specifically pyridine. This isolation of the high boiling hydroxyl allowed its determination by acetylation with acetic anhydride, the excess of reagent being determined acidimetrically upon hydrolysis.

$$CH_2OHCH_2OH + 2(CH_3CO)_2O \longrightarrow \begin{matrix} CH_2OCCH_3 \\ \| \\ O \\ | \\ CH_2OCCH_3 \\ \| \\ O \end{matrix} + 2CH_3COOH$$

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH$$

This principle was applied in the analogous separation of glycol products from the large quantity of alcohol in which they were produced.

Reagent. Approximately 3.2 N pyridine-acetic anhydride reagent was prepared by diluting 15.4 ml of acetic anhydride to 100 ml with pyridine. (This reagent discolors slowly over a period of time, so should be made up in small batches.)

Procedure. To a sample of irradiated alcohol containing an estimated two millimoles of glycol or less (10-20 ml in these experiments) was added 50 ml of the pure alcohol and this mixture fractionated at a moderately fast rate on an 18-inch column packed with 1/8-inch glass helices until about 25 ml remained in the distilling flask. (This step may be called the "predistillation," and was included to eliminate any possible interference from the more volatile radiolysis products in the subsequent procedure.) 50 ml of dry pyridine was added to the distillation flask and the fractionation continued at a moderately slow rate until 50 ml more distillate were collected, at least the last 10 ml at the boiling point of pyridine 114-115°C. The column was rinsed with 10 ml of dry pyridine and the residue solution thus obtained reacted at boiling under total reflux for 15 minutes with exactly 5 ml of the 3.2 N pyridine-acetic anhydride reagent. 10 ml of distilled water was then added to the hot solution to hydrolyze the excess acetic anhydride, and on cooling, the solution was titrated with 0.5 N NaOH to a phenolphthanein endpoint, taking care that no excess of base was present before the endpoint was reached. A standardization of the reagent was made by similarly refluxing, hydrolyzing, and titrating a blank of 5 ml reagent in 35 ml pyridine. The difference in base titre, blank (B) minus sample (A), was taken as a direct measure of the moles of high boiling hydroxyl, after division by an empirical factor 0.979 which represents the degree to which the reaction

approaches stoichiometric completion under the above condition,[54] i.e.,

$$\frac{(B-A) \times \text{normality of NaOH}}{\text{ml sample} \times 0.979 \times 2} = \text{millimoles glycol/ml}$$

This procedure gave yields 100 $\pm$ 1% on standard solutions of ethylene glycol in ethyl alcohol, prepared by weighing the pure glycol directly. In order to approximate the irradiated alcohol mixtures, glycol solutions containing 0.1 millimoles/ml formaldehyde, 0.3 millimoles/ml acetaldehyde, and 1 mg/ml water were tested. Unless eliminated, the aldehydes could be expected, on addition of the pyridine, to form basic (aldol) condensation products which could not be distilled out and would possibly present hydroxyl groups for interference in the determination. The acetaldehyde would presumably be removed during the predistillation but by analogy with dilute formaldehyde-water solutions, in which distillation concentrates the formaldehyde in the still residue,[46] the formaldehyde would be difficult if not impossible to completely remove from polar solvents such as alcohols. Indeed, these solutions did discolor appreciably to a brown in the steps involving the pyridine, but gave glycol yields within 2 or 3% of the standardized value. The brown discoloration interfered with the visual phenolphthalein endpoint but did not obscure it until somewhat higher formaldehyde concentrations were involved. Methanol solution irradiated in target A, yielding a high concentration of formaldehyde as the only aldehyde formed, gave so great a discoloration that detection of a visual endpoint was not possible.

To rectify this, a non-polar predistillation solvent from which presumably the formaldehyde could be completely distilled was tried. Instead of the pure alcohol, 40 ml of purified 1,4-dioxane was added to the irradiated alcohol, and the fractionation carried out at a moderate rate until an appreciable amount of distillate, 5-10 ml, had been taken over at the boiling point of dioxane, 100-101°C. The pyridine was added and the solution further fractionated slowly until 5 to 10 ml more dioxane had been distilled at its boiling point, in order to ensure that all water (which forms a pyridine hydrate, $C_5H_5N \cdot 3H_2O$ with a constant boiling point at 94.4°C)[54] was eliminated. Though the discoloration in the steps where pyridine was involved was not avoided entirely, it was reduced a great deal, allowing the phenolphthalein endpoint to be readily discerned. Yields of 100 $\pm$ 1% were obtained on standard glycol solutions which was taken as evidence that the acetylation factor was not greatly different at the reflux temperature of the dioxane pyridine solution as that cited in the standard procedure, i.e., 97.9%. Although the dioxane method gave fairly precise results on standard solutions, when applied to irradiated ethanol and methanol samples it indicated glycol values somewhat low and rather variable, as compared to an alternative method (periodic oxidation equivalent) which evidenced considerable reliability.

It was then found, however, that the methanols and ethanols irradiated in the larger target B, with low concentrations of product, did not discolor badly in the procedure using the alcohol predistillation and gave results in accord with the other glycol methods. Since formaldehyde was not included among the radiolysis

products of isopropyl and tertiary butyl alcohols, the simple procedure was anticipated as adequate for them as it proved to be. A discoloration in the pyridine solution did occur, however, with the tert-butyl alcohol, in which case no aldehydes were included as radiolysis products. The nature of the brown discoloration in these procedures thus remains unclear.

The standard procedure could be applied, of course, only to those alcohols with boiling points substantially below that of pyridine, (115°C), i.e., methyl (64°), ethyl (78°), isopropyl (82°), and tert-butyl (82°) alcohols. Though no attempt was made, it could possibly be applied as well to n-propyl (97°) and sec-butyl (99°) alcohols but for n-butyl and isobutyl alcohols, a higher boiling intermediate solvent was necessary. For the two alcohols, n-octyl and n-decyl, the whole procedure was invalid, for the ethylene glycol anticipated among the glycol products, boils at a temperature nearly equal to or below the boiling point of alcohol concerned, and even if the distillations were uncomplicated by high temperature chemical phenomena, or could be carried out under reduced pressure, only the heavier glycol products could be retained.

For the intermediately boiling alcohols, an attempt was made to use di-n-butyl ether (b.p. 142°C) as a solvent medium out of which the alcohols could be distilled. The procedure employed was identical to the standard procedure outlined, except that 40 ml of di-n-butyl ether was substituted for the pure alcohol in the predistillation step, and the solution distilled through the column at a moderate rate until 5 to 10 ml of distillate had been collected at the boiling point of the ether. Thirty milliliters of dry

pyridine was then added and a few milliliters of distillate collected at its boiling point to ensure the elimination of any water present. The standard acetylation procedure was employed, and the titration with aqueous alkali, though it involved two phases, presented no difficulty.

The irradiated butyl alcohol solutions gave results of apparently semi-quantitative validity, which are reported in the data. Ethylene glycol standards, however, gave completely negative results. In accord with reports[55] that it forms an azeotope with n-butyl ether, boiling at 140°C, it was probably eliminated in the predistillation. The results obtained on the butyl alcohols were at best, therefore, indicative of the glycols other than ethylene glycol. However, if by analogy to simpler alcohols ethylene glycol was a minor component, the discrepancy is not serious.

It is interesting to note that such a selective elimination of ethylene glycol comprises a potentially valuable analytical separation, especially in studies such as was undertaken here. The existence of such azeotropes demands, however, that such solvent distillation procedures as utilized here be carefully studied before being accepted as proficient.

(b) Precipitation of Glycols as Ditryl Ethers. The isolation of glycols as their di-triphenylmethyl ethers from pyridine solutions, after eliminating the alcohol by distillation, was attempted by the method of Seikel and Huntress,[56] but the difficulty in getting a product in near quantitative yield free of triphenylcarbinol and the mono-ether seemed to reduce the applicability of the technique to a qualitative status, and no attempt was made to use

it on the irradiated solutions.

(c) Determination of Vicinal Glycols - Periodic Acid Reduction Equivalent. The well known oxidative action of periodic acid on compounds with vicinal functional groups, including glycols, allowed an explicit characterization of the glycol components in the irradiated alcohols with respect to the relative positions of the hydroxyl groups. A determination of the equivalent of periodic acid consumed gave a measure of the total quantity of vic-glycol present and characterization of the products of oxidation by precipitation of the aldehyde dimedone derivatives gave an indication of the nature of the molecule in which they were involved.

$$H_2COHCH_2OH + HIO_4 \longrightarrow 2HCHO + H_2O + HIO_3$$

$$RCH(OH)-CH(OH)-R' + HIO_4 \longrightarrow RCHO + R'CHO + H_2O + HIO_3$$

$$R_2C(OH)-CH_2(OH) + HIO_4 \longrightarrow R_2CO + HCHO + H_2O + HIO_3$$

The determination of the total vic-glycol components present in the irradiated alcohols was accomplished by the method of Siggia.[57] The excess of a measured quantity of periodic acid was determined iodometrically after reaction with the vic-glycol.

Reagents. The periodic acid reagent was prepared by adding 800 ml of glacial acetic acid to a solution of 6 g of paraperiodic acid (H_5IO_6) in 200 ml of distilled water. It was kept in a dark, well stoppered bottle.

Potassium iodide solution was prepared by dissolving 200 g KI in a liter of distilled water. Standard 0.1 N $Na_2S_2O_3$ was prepared by dissolving 24.82 g of $Na_2S_2O_3 \cdot 5H_2O$ in several hundred milliliters of distilled water, adding 1 ml of 0.1 N NaOH, and diluting to 1 liter. The standardization was against the iodine liberated by weighed samples of KIO_3 on addition of excess KI and dilute HCl.[58]

Procedure. To a sample of irradiated alcohol or aliquot of the predistillation residue of the total glycol procedure containing an estimated 0.5 millimoles of vic-glycol was added 50 ml of the periodic acid reagent, and the solution allowed to stand at room temperature for 1/2 hour. Ten milliliters of KI solution were added, and the liberated iodine titrated with standard 0.1 N $Na_2S_2O_3$. A standardization blank was run on the reagent and the difference in titre, blank minus sample, divided by two was taken as a direct measure of the amount of vic-glycol in the sample.

This procedure yielded values of 100 ± 2% on standard alcohol solutions of ethylene glycol in the presence of formaldehyde and acetaldehyde. In early determinations, the method was applied directly to samples of the irradiated alcohol with highly reproducible results. The yields obtained, however, were in some 20% excess to those values of total glycol derived from the distillation-acetylation procedure of the previous section. On subjecting the irradiated samples to a predistillation treatment identical to that employed prior to the distillation-acetylation procedures,* the values

*The two determinations, total and vicinal glycols, were in fact usually made on aliquots of the same alcohol solution derived from the predistillation treatment as described in the standard procedure for total glycols.

obtained for a presumed vic-glycol component were reduced to within the limits set by the total glycol determinations. It was assumed that the high values, obtained with irradiated solutions which had not undergone the pretreatment, resulted from other oxidizable components among the radiolysis products, sufficiently volatile as to be eliminted in the predistillation treatment.

An alternative method for the determination is cited by Jackson.[59]

(d) Characterization of Aldehydic Products of Periodic Acid Oxidation of Vic-glycols by Precipitation with 5,5-Dimethylcyclohexanedione-1,3. The carbonyl fragments resulting from the oxidative splitting of the vic-glycols were determined by the dimedone precipitation method considered in the aldehyde analyses, in the instances where that could be applied, i.e., when the only separation required was that involving formaldehyde and acetaldehyde.

Reagents. 0.044 N aqueous periodic acid was prepared by dissolving 1 gram of paraperiodic acid (H_5IO_6) in 100 ml of distilled water.

The saturated aqueous dimedone solution and the pH 4.6 buffer solution were prepared as described under the determination of aldehydes (page 30).

Procedure. To a quantity of irradiated alcohol containing 10 to 20 mg total formaldehyde and/or acetaldehyde equivalent directly and in vic-glycol equivalents and no more than 0.1 moles of vic-glycol (0.5 to 2.0 ml in these experiments) was added 10 ml of aqueous periodic acid reagent, and one drop of concentrated HCl. After about two minutes with a couple of swirlings, 75 ml of buffer

solution and a quantity of saturated aqueous dimedone reagent, established by rough predeterminations to be in 10-15% stoichiometrical excess to the total aldehyde equivalent present, was added. This solution was stoppered and allowed to stand at room temperature for 4 to 7 days to ensure complete precipitation. It was then filtered through a 15 ml medium porosity sintered glass filtering crucible, dried by vacuum at room temperature and weighed. (The drying and weighing were unnecessary, except that it allowed a later estimation of any solubility correction required on the precipitates.) The precipitate was transferred mechanically, with a "policeman" and 50 ml distilled water, out of the crucible into a flask. Ten milliliters of dimedone reagent and 2 ml of concentrated H_2SO_4 were added and the preparation shaken overnight. The standard carbonate separation of acetaldehyde and formaldehyde derivatives was made by the procedure outlined in the aldehyde analyses, the precipitates dried in vacuum at room temperature, and weighed. A blank of the aldehydes initially present was obtained by omitting the periodic acid treatment of an irradiated alcohol sample carried through the same procedure. Subtraction of the blank samples from the treated samples gave a measure of the formaldehyde and acetaldehyde equivalents of the vic-glycols present. Conversion factors from mg formaldehyde derivative to mg ethylene glycol and from mg acetaldehyde derivative to 2,3-butylene glycol were 0.106 and 0.156, respectively.

Tests on pure alcohols showed the reagent gave negligible blanks for reagent times up to an hour, but the two minutes prescribed above seemed sufficient for essentially complete reaction on the simple glycols concerned and minimized the loss of the more volatile carboxyl compounds by evaporation. The oxidation of vic-glycols with periodic acid takes place most rapidly under acidic conditions.[60] Experiments indicated that the sulfuric acid could not be added directly to the solution containing the excess reactant periodic and product iodic acids of the oxidative reaction, without a destruction of the dimedone precipitates. Filtration was consequently adopted as an intermediate step and the drying and weighing as an expedient check at this point on the precipitate formed, for later estimation of a solubility correction.

The transference of the dry, light and flaky dimedone precipitate was most efficiently accomplished by a simple mechanical scraping out of the filtering crucible with a rubber "policeman." This gave 97-98% recovery as compared to somewhat lower yields for dissolution and reprecipitation procedures involving solvents acetone, alcohol, and 10% aqueous Na_2CO_3 solution. The presence of excess dimedone reagent in the sulfuric acid treatment reduced the solubility of the dimedone precipitates considerably, as noted in a general way by Yoe and Reid.[44] The subtraction of the aldehyde blanks made the determination of the glycol aldehydic equivalents quantitative without empirical correction (assuming that the aldehyde dimedone reaction is stoichiometric with only solubility losses reducing the yield, as was indicated in the aldehyde dimedone discussion to be apparently the case). This was checked by comparing solubility losses in the

sulfuric acid dehydration steps of blank and sample. They were small, 1 to 2 mg, and within reasonable error, the same.

Standard ethylene glycol samples in ethanol, with and without aldehydes present, gave stoichiometrical glycol values within ±5%.

A characterization of the aldehydic products of periodic and oxidations of vic-glycols not restricted to acetaldehyde and formaldehyde would allow wider applicability of the method. Procedures for such have been reported by Hoepe and Treadwell[61] and by Reinke and Luce.[62]

(e) Non-vicinal Glycols. The difference between total glycols as determined by the distillation acetylation experiments, and vic-glycols as determined by the periodic acid reduction equivalent was taken as the yield of non-vicinal glycols present. In no case, was there any non-vicinal glycol detected, within the error limits of the two determinations cited.

4. Determination of Acids and Acid Derivatives.-- Acids were qualitatively found, by titration with aqueous 0.1 N NaOH, not to be a major product of the irradiation of alcohols, but definitely present in very small amounts. Though minor products were in general neglected in the liquid fraction, the ease of the acidity determination prompted that it be generally, if somewhat perfunctorily, carried out.

The determination of acidity in the irradiated alcohols was made by semi-micro titration of 5 ml samples with either standard 0.1 N aqueous or 0.05 N methanolic (80% methanol - 20% water) NaOH to a phenolphthalein endpoint. The irradiated ethanol and methanol samples were diluted with several milliliters of distilled water and

titrated with the aqueous NaOH, while the higher alcohol samples were titrated, without dilution, with the methanolic NaOH. Small blanks taken on unirradiated alcohol samples were subtracted in all cases.

Titrations of acidity with aqueous NaOH are reputedly inaccurate in the presence of active aldehydes[47] but the degree of error cited, less than 1%, may be considered negligible in these experiments unless it represents an absolute error on these author's samples. They suggest using standardized sodium methylate in dry methanol for accurate acidity determinations under these conditions. The possibility of an enhancement in actual acidity of the irradiated solutions by oxidative action on aldehydes, either by possible peroxide radiolysis products or atmospheric oxygen in handling the alcohols after irradiation, must be realized.

These uncertainties reflect on the validity of the acidimetric measurements recorded in this work, but certainly the titrations have established a maximum on such products.

Early qualitative tests on irradiated ethanol solutions indicated a NaOH saponification equivalent small enough that, assuming even no additive interference from the aldehydes present, the acid derivatives could be considered negligibly minor products.

Mitchell and Smith[47] describe an ester saponification method free from the interference of any aldehydes present. By reaction with hydroxylamine they converted the aldehydes to oximes which were stable enough toward alkali that the ester could be saponified without interference.

5. Determination of Peroxides.-- The destruction of several indicators, the apparently slightly high values on the hydroxylamine hydrochloride determination of carbonyl, and the demonstration of their presence in the irradiated methanol gaseous fraction prompted several unfruitful attempts to find a method for determination of peroxides, applicable to the irradiated alcohol solutions. Addition of potassium iodide in acid solution[57] indicated in early experiments that the yield of the more reactive peroxides, hydrogen peroxides and hydroperoxides was probably negligible. The test was not applicable to the more stable dialkyl peroxides.[40] A qualitative test for peroxides employing Middleton's reagent[63] gave positive results for all of the irradiated alcohols, but exhibited as well a slow positive test on aldehydes.[64] A quantitative application of the test involving determination of ferric ion formed on oxidation with peroxides by back titration with titanous ion to disappearance of a ferric thiocyanate complex, indicated reaction of less than one-half of a diethyl peroxide sample, and practically none of a di-tert-butyl peroxide sample.[64] Oxidation of sodium iodide in boiling isopropyl alcohol and glacial acetic acid[65] determined less than 10% of a di-tert-butyl peroxide sample. Fifty percent hydriodic acid in glacial acetic acid solution reduced di-tert-butyl peroxide quantitatively, but comprised such a strong reducing system that interferences made it inapplicable to irradiated alcohols.[66]

Mitchell and Smith[40] reported verification of Wieland and Franke's[67] determination of diethyl peroxide using a ferrous ion catalyzed hydriodic acid reduction but got poor yields on di-tert-butyl peroxides. These authors[40] aquametric method employing reduction with

zinc and simultaneous esterification of the alcohol formed to yield two moles of water was inapplicable to alcohol solutions.

6. Determination of Unsaturation.-- Imprecise qualitative experiments testing for the presence of ethylenic double bonds in the liquid fraction of early ethanol bombardments by the method of Shriner and Fuson,[41] involving bromination, indicated that at maximum the yield of such unsaturation was negligibly small, less than 2% of the aldehydic products present, which could interfere to this extent in the determination by a substitutive or reductive reaction. No tests for unsaturation were made on the higher irradiated alcohols.

IV. YIELDS OF CHEMICAL PRODUCTS

In the Tables II-XI are presented the yields of radiolysis products of the various alcohols as analyzed by procedures discussed in the previous chapter. The bombardment data for each alcohol is cited as follows: first, the integrated beam, a measure of the number of particles discharged on the inner target chamber, is given in microampere hours (μah); then the energy of the helium ions after passing through the various foils (see page 18); the length of time of bombardment; and derived from this, the average beam current over this time. The method of treating the gaseous products for mass spectroscopic analysis is cited according to the designations made on pages 19 and 20. The significant difference in minor products observed in the alternate bombardments is probably due to the difference in treatment of the gaseous fraction. Lastly, the conversion factor from total millimoles to molecules/100 ev for the particular bombardment is noted.

The products are cited qualitatively to the specificity obtainable in the analysis. Where an analytical distinction could be made between isomers or individual members of a functional series, this distinction has been explicitly designated, but when it derives of an inference from the structural system involved, it is parenthesized following the analytical citation. For example, in tertiary butyl alcohol no mass spectroscopic distinction of which isomeric butene was formed was possible but the nature of the alcohol irradiated makes it likely that it was isobutene. It is designated butene (iso).

The first section of the product yield data includes all products found in the gaseous fractions as defined in the various gas treatments

and analyzed for mass spectrometrically. Hydrogen, H_2, carbon monoxide, CO, and methane, CH_4, were the usual components of the fraction volatile at liquid nitrogen temperature. Acetylene, C_2H_2, ethylene, C_2H_4, ethane, C_2H_6, propylene, C_3H_6, propane, C_3H_8, occasionally methylacetylene, $CH_3C{\equiv}CH$, the isomeric butenes, C_4H_8, and butanes, C_4H_{10}, and traces of less volatile products were present in the fraction volatile at dry ice temperatures. The residue fraction, when analyzed mass spectrometrically, contained hydrocarbons above butanes and some of the more volatile liquid products.

The value for total gases is cited as that obtained on expanding the gaseous products directly from the target assembly into a calibrated manometer system. It must be regarded as approximate since it is uncorrected for the solubility of any product in the liquid phase and for the partial vapor pressure of whatever alcohol was present. Since the measurements were not conducted under conditions as to ensure equilibrium in these respects, no attempt at correction has been made. In general, the sum of gaseous products obtained in complete removal of the gaseous fraction by procedure III is somewhat larger than the preliminary total gas measurement, indicating appreciable solubility effects.

The second section is devoted exclusively to the chemical analysis of the liquid fraction. This analysis yielded information concerning essentially the functional groups present, and the data is presented on this basis. Acid indicates the alkali equivalent necessary for neutralization of a sample of the liquid to a phenophthalein endpoint. Water, H_2O, was determined by the Fischer titration (page 24). The carbonyl yields were determined by the neutral hydroxylamine

method (page 27). Aldehyde indicates is a semiquantitative estimation by means of the silver oxide oxidation method (page 34) and under this are given the yields of formaldehyde, HCHO, and acetaldehyde, CH_3CHO, as determined by the dimedone precipitation procedures (page 30). In all cases where these aldehydes are explicitly cited, no higher aldehydes than these were present since the presence of the higher derivatives made the formaldehyde-acetaldehyde determination impossible. Ketone is given as the difference between carbonyl and total aldehyde, the total aldehyde being taken from the sum of the dimedone formaldehyde-acetaldehyde determinations where possible, and is cited different from zero only if the difference is beyond the precision of the measurements involved. Total glycols represent the results of the distillation acetylation procedures (page 39). Those employing dioxane or di-n-butyl ether predistillation are noted as to be regarded with some reservations, in line with the discussion of the glycol determinations. Vic-glycols, as determined by the periodic acid reduction equivalent (page 45), are qualified by whether they were determined on a raw sample, which procedure gave results apparently 10-20% high, or on one predistilled, which gave results independently verifiable. The designations H_2COH- and CH_3CHOH- under vic-glycols indicate the equivalents of formaldehyde and acetaldehyde, respectively, formed on oxidation of the vic-glycols with periodic acid, and determined by dimedone precipitation (page 47). The difference between the total vic-glycols and the aldehyde equivalent of such is taken as a measure of the ketone equivalent, R_2COH-, of the vic-glycol components, provided the difference is significant within the estimated limits of error of the determinations it involves. If not so, it is cited as

zero. A value for nonvic-glycols is similarly taken as the difference between the total glycols and the vic-glycols. Within some uncertainty with regard to the validity of the methods involved, no nonvic-glycol was found in the analyses.

The yields of products are reported in total millimoles produced in the given bombardment, and in a normalized yield per energy value, molecules per 100 ev, obtained by the conversion factor cited.

A few of the more volatile liquid products analyzed for (acetaldehyde and acetone) were detected in the gaseous phase as well, and the sum of these is cited in the third section of the data.

The fourth section indicates the sum of, respectively, the oxidation and reduction equivalents of product determined, in units of single electron charges.

The estimated limits of analytical precision have been noted for the chemical analyses in total millimoles. The detailed computational methods employed in the analysis of mass spectral data makes it inexpedient to attempt a precise ascertation of the precisional uncertainty of the gaseous analyses, in the face of overriding imprecision in other aspects of the experimental procedures. In general, however, the data has been presented so that a variance of plus or minus three or four units in the last integer cited in any case is a fair estimate of the precision of the analysis. Such uncertainties apply strictly to the analytical measurements. The study was regarded as cursory to the extent that no quantitative estimation of the probable deviation of results due to imprecise control of other variables was attempted.

The later bombardments, designated by the inner chamber B, should be taken with greater confidence than those earlier irradiations carried out in chamber A, due both to an elimination of mechanical defect in the later apparatus, and to the accumulation of procedural experience.

Table II - Yield of Chemical Products of the Helium Ion Irradiation of Methyl Alcohol

	Bombardment 1 2.00 μah 27.1 mev 20 min 6 μa(av.) Foil 1 Chamber A Gas Treatment I Conversion: 0.099		Bombardment 2 2.00 μah 27.1 mev 35 min 3.4 μa(av.) Foil 1 Chamber A Gas Treatment III Conversion: 0.099		Bombardment 3 2.00 μah 26.5 mev 45 min 2.7 μa(av.) Foil 2 Chamber B Gas Treatment II Conversion: 0.101		Bombardment 4 2.00 μah 26.7 mev 42 min 2.9 μa(av.) Foil 3 Chamber B Gas Treatment III Conversion: 0.100	
Product	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev
H_2	39.7	3.93	41.1	4.07	34.1	3.44	34.6	3.46
CO	3.09	0.306	2.48	0.243	2.25	0.227	2.39	0.239
CO_2	--	--	--	--	0.01	0.001	0.02	0.002
CH_4	3.89	0.385	3.93	0.389	3.39	0.342	3.68	0.368
C_2H_6	--	--	0.13	0.013	0.13	0.013	0.14	0.014
CH_3OCH_3	1.01	0.100	1.29	0.128	0.30	0.030	0.32	0.032
CH_3OOCH_3	--	--	0.056	0.006	0.03	0.003	0.01	0.001
Unident. 60 cpd.	--	--	0.18[d]	0.018[d]	--	--	0.005[d]	0.0005[d]
Methylal	--	--	--	--	0.08	0.008	0.001	0.0001
Total Gas	48.0	4.75	52.9	5.24	44.1	4.45	44.8	4.48
Acid	0.22 ± 0.02	0.022	--	--	0.11 ± 0.02	0.011	--	--
H_2O	9.5 ± 0.5	0.94	--	--	9.2 ± 0.3	0.93	9.3 ± 0.3	0.93
Carbonyl	16.4 ± 0.5	1.62	--	--	16.6 ± 0.4	1.68	16.3 ± 0.4	1.63
Aldehyde	--	--	--	--	(14)[a]	(1.4)[a]	--	--
HCHO	16.7 ± 0.3	1.65	--	--	16.7 ± 0.5	1.69	--	--
RCHO	0	0	--	--	0	0	--	--
Ketone	0	0	--	--	0	0	--	--
Total Glycols	(13.5 ± 0.5)[b]	(1.34)[b]	--	--	(14. ± 1)[b]	(1.4)[b]	16.0 ± 0.5	1.60
Vic-glycols	(14.8 ± 0.3)[c]	(1.47)[c]	--	--	17.3 ± 0.3	1.75	16.7 ± 0.3	1.67
H_2COH-	30.0 ± 0.3	2.97	--	--	34.4 ± 0.5	3.48	--	--
RCHOH-	0	0	--	--	0	0	--	--
R_2COH-	0	0	--	--	0	0	--	--
Nonvic-glycol	0	0	--	--	0	0	0	0
Red. Equiv.	86.2	8.53	90.4	89.5	75.2	76.0	76.8	76.8
Ox. Equiv.	76.0	7.52	--	--	77.4	78.2	76.2[e]	76.2[e]

Table III - Yield of Chemical Products of the Helium Ion Irradiation of Ethyl Alcohol (Cont. next page)

	Bombardment 1 3.53 μah 27.1 mev 27 min 7.9 μa(av.) Foil 1 Chamber A Gas Treatment I Conversion: 0.056		Bombardment 2 3.00 μah 27.1 mev 30 min 6 μa(av.) Foil 1 Chamber A Gas Treatment III Conversion: 0.066		Bombardment 3 2.61 μah 27.1 mev 30 min 5.2 μa(av.) Foil 1 Chamber A Conversion: 0.076	
Product	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev
H_2	31.4	1.76	31.8	2.10		
CO	1.30	0.073	1.27	0.084		
CO_2	--	--	--	--		
CH_4	3.88	0.217	4.26	0.281	gases not analyzed	
C_2H_2	--	--	0.23	0.015		
C_2H_4	1.42	0.795	1.32	0.087		
C_2H_6	1.46	0.818	1.55	0.102		
Total Gases	41.7	2.34	~45	~3.0		
Acid	<0.3	<0.02	<0.26	<0.017	0.15 ± 0.02	0.011
H_2O	12.7		11.8	--	7.4 ± 0.3	0.56
Carbonyl	18.3 ± 0.2	1.03	--	--	14.0 ± 0.5	1.06
Aldehyde	--	--	--	--	--	--
HCHO	4.0 ± 0.2	0.22	4.0 ± 0.2	0.26	2.7 ± 0.2	0.21
CH_3CHO	11.5 ± 0.5	0.65	11.0 ± 0.5	0.73	10.5 ± 0.5	0.80
Ketone	small	--	--	--	0	0
Total Glycols	11 ± 2	0.6	--	--	7.5 ± 0.3	0.57
Vic-glycols	--	--	--	--	(9.1 ± 0.3)[c]	(0.69)[c]
H_2COH-	--	--	--	--	2.0 ± 0.1	0.15
RCHOH-(CH_3CHOH-)	--	--	--	--	13.0 ± 0.5	1.0
R_2COH-	--	--	--	--	0	0
Nonvic-glycols	--	--	--	--	0	0

Table III (Continued) - Yield of Chemical Products of the Helium Ion Irradiation of Ethyl Alcohol

	Bombardment 4 2.00 μah 26.5 mev 34 min 3.5 μa(av.) Foil 2 Chamber B Gas Treatment III Conversion: 0.101		Bombardment 5[f] 2.00 μah 26.7 mev 60 min 2.0 μa (av.) Foil 3 Chamber B Gas Treatment II Conversion: 0.100	
Product	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev
H_2	29.5	2.98	32.1	3.21
CO	1.17	0.118	1.28	0.128
CO_2	<0.02	<0.002	<0.17	<0.017
CH_4	3.68	0.373	3.98	0.398
C_2H_2	0.44	0.044	0.29	0.029
C_2H_4	1.39	0.140	1.13	0.113
C_2H_6	1.47	0.148	1.23	0.123
$CH_3{\equiv}CH$	0.01	0.001	--	--
C_3H_8	<0.28	<0.028	<0.15	<0.015
CH_3CHO	0.38	0.038	0.21	0.021
$CH_3OC_2H_5$	0.33	0.033	0.008	0.001
$C_2H_5OC_2H_5$	0.02	0.002	0.08	0.008
Butenes	<0.01	<0.001	<0.005	<0.001
Butanes	<0.11	<0.011	<0.11	<0.011
Total Gases	--	--	--	--
Acid	--	--	0.12 ± 0.02	0.012
H_2O	--	--	8.1 ± 0.3	0.81
Carbonyl	18.5 ± 0.2	1.87	21.1 ± 0.2	2.11
Aldehyde	--	--	(19)[a]	(1.9)[a]
HCHO	3.0 ± 0.1	0.30	3.0 ± 0.1	0.30
CH_3CHO	14.8 ± 0.5	1.49	17.1 ± 0.5	1.71
Ketone	0	0	0	0
Total Glycols	10.0 ± 0.5	10.1	(7.8 ± 0.5)[b]	(.78)[b]
Vic-glycols	10.0 ± 0.3	10.1	11.4 ± 0.3	1.14
H_2COH-	2.7 ± 0.2	0.28	3.2 ± 0.2	0.32
RCHOH-(CH_3CHOH-)	16.2 ± 1.0	1.64	18.2 ± 1.0	1.82
R_2COH-	0	0	0	0
Nonvic-glycol	0	0	0	0
Total Carbonyl	18.9	1.91	21.3	2.13
Total CH_3CHO	15.2	1.54	17.3	1.73
Red Equiv.	70.0	70.7	75.2	7.52
Ox. Equiv.	64.0[g]	64.6[g]	72.8	7.28

Table IV - Yield of Chemical Products of the Helium Ion Irradiation of Isopropyl Alcohol

	Bombardment 1 2.00 μah 27.1 mev 35 min 3.4 μa(av.) Foil 1 Chamber A Gas Treatment I Conversion: 0.099		Bombardment 2 2.00 μah 27.1 mev 30 min 3.6 μa(av.) Foil 1 Chamber A Gas Treatment III Conversion: 0.099		Bombardment 3 2.00 μah 26.7 mev 46 min 2.6 μa(av.) Foil 3 Chamber B Gas Treatment II Conversion: 0.100		Bombardment 4 2.00 μah 26.7 mev 45 min 2.7 μa(av.) Foil 3 Chamber B Gas Treatment III Conversion: 0.100	
Product	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev
H_2	19.6	1.94	17.6	1.75	26.1	2.61	27.1	2.71
CO	0.54	0.053	0.54	0.053	0.60	0.060	0.83	0.083
CH_4	8.5	0.85	8.3	0.82	10.1	1.01	11.4	1.14
C_2H_2	0.11	0.011	0.11	0.011	0.16	0.016	0.19	0.019
C_2H_4	0.72	0.071	0.33	0.033	0.06	0.006	0.22	0.022
C_2H_6	1.35	0.134	1.32	0.131	1.29	0.129	1.71	0.171
C_3H_6	1.90	0.188	1.11	0.110	1.49	0.149	2.67	0.267
C_3H_8	0.2	0.02	0.2	0.02	0.56	0.056	0.88	0.088
CH_3CHO	1.44	0.143	2.12	0.21	0.37	0.037	0.83	0.083
Butenes	0.06	0.006	0.06	0.006	0.02	0.002	0.07	0.007
Butanes	--	--	--	--	0.21	0.021	0.42	0.042
$(CH_3)_2CO$	0.3	0.03	--	--	0.04	0.004	0.03	0.003
$CH_3OCH(CH_3)_2$	--	--	--	--	0.03	0.003	0.08	0.008
Total Gas	38.4	3.80	33.1	3.97	42.5	4.25	43.9	4.39
Acid	.08 ± 0.01	.007	--	--	0.05 ± 0.01	0.005	--	--
H_2O	--	--	--	--	8.9 ± 0.3	0.89	--	--
Carbonyl	19.5 ± 0.2	1.93	--	--	28.4 ± 0.2	2.84	30.2 ± 0.2	3.02
Aldehyde	(9)[a]	(.9)[a]	--	--	--	--	--	--
HCHO	0	-	--	--	0	0	--	--
RCHO(CH_3CHO)	6.9 ± 0.3	0.68	--	--	9.4 ± 0.5	0.94	--	--
Ketone	12.6 ± 0.4	1.25	--	--	19.0 ± 0.6	1.90	--	--
Total Glycol	(2.95 ± 0.3)[b]	(0.29)[b]	--	--	4.0 ± 0.5	0.40	--	--
Vic-glycol	(3.8 ± 0.3)[c]	(0.38)[c]	2.8 ± 0.3	0.28	3.9 ± 0.3	0.39	--	--
H_2COH-	0.30 ± 0.05	0.03	--	--	0.35 ± 0.10	0.035	0.35 ± 0.10	0.035
RCHOH-(CH_3CHOH-)	2.1 ± 0.2	0.21	--	--	2.8 ± 0.3	0.28	2.9 ± 0.3	0.29
R_2COH-	3.5 ± 0.4	0.35	--	--	4.8 ± 0.7	0.48	--	--
Nonvic-glycol	0	0	--	--	0	0	--	--
Total Carbonyl	21.2 ± 0.2	2.10	--	--	28.8 ± 0.2	2.88	31.1 ± 0.2	3.11
Total CH_3CHO	8.3 ± 0.3	0.82	--	--	9.8 ± 0.5	0.98	--	--
Total Ketone	12.9 ± 0.4	1.28	--	--	19.0 ± 0.6	1.90	--	--
Red. Equiv.	59.6	5.90	54.8	5.43	76.6	7.66	83.0	8.30
Ox. Equiv.	51.2	5.06	--	--	68.6	6.86	74.0	7.40

Table V - Yield of Chemical Products of the Helium Ion Irradiation of Tert-Butyl Alcohol

	Bombardment 1[h]		Bombardment 2[h]		Bombardment 3[h]	
	2.00 μah 27.1 mev		2.00 μah 26.7 mev		2.00 μah 26.7 mev	
	65 min 1.9 μa(av.)		60 min 2.0 μa(av.)		60 min 2.0 μa(av.)	
	Foil 1 Chamber A		Foil 3 Chamber B		Foil 3 Chamber B	
	Gas Treatment I		Gas Treatment II		Gas Treatment III	
	Conversion: 0.099		Conversion: 0.100		Conversion: 0.100	
Product	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev
H_2	6.7	0.66	11.4	1.14	12.4	1.24
CO	Small		0.48	0.048	0.46	0.046
CH_4	7.6	0.75	13.9	1.39	16.0	1.60
C_2H_2	--		0.08	0.008	0.14	0.014
C_2H_4	0.64	0.063	0.23	0.023	0.91	0.091
C_2H_6	2.87	0.285	4.05	0.405	5.20	0.52
$CH_3{-}C{\equiv}CH$	--	--	0.06	0.006	0.09	0.009
C_3H_6	--	--	0.09	0.009	0.20	0.020
C_3H_8	--	--	0.10	0.010	0.17	0.017
Butene(iso)	1.44	0.142	1.15	0.115	2.72	0.272
Isobutane	0.74	0.073	0.54	0.054	1.15	0.115
Neopentane			0.29	0.029	0.76	0.076
$(CH_3)_2CO$	0.38	0.038	0.26	0.026	0.09	0.009
$CH_3OC(CH_3)_3$	--	--	0.02	0.002	0.02	0.002
Total Gas	23.8	2.35	34.0	3.40	35.3	3.53
Acid	0.07 ± 0.02	0.007	0.03 ± 0.01	0.003	--	--
H_2O	7.5 ± 0.3	0.74	10.4 ± 0.3	1.04	9.9 ± 0.3	0.99
Carbonyl	14.6 ± 0.2	1.45	26.2 ± 0.2	2.62	27.8 ± 0.2	2.78
Aldehyde	--	--	--	--	--	--
HCHO	0	0	0	0	0	0
RCHO	0	0	0	0	0	0
Ketone	14.6 ± 0.2	1.45	26.2 ± 0.2	2.62	27.8 ± 0.2	2.78
Total Glycol	--	--	1.0 ± 0.5	0.10	--	--
Vic-Glycol	0.7 ± 0.3	0.07	1.0 ± 0.3	0.10	--	--
$H_2COH{-}$	0.5 ± 0.1	0.05	1.2 ± 0.2	0.12	--	--
RCOH	0	0	0	0	--	--
$R_2COH{-}$	0.9 ± 0.6	0.09	0.8 ± 0.4	0.08	--	--
Nonvic-glycol	--	--	0	0	--	--
Total Carbonyl	15.0 ± 0.2	1.49	26.5 ± 0.2	2.65	27.9 ± 0.2	2.79
Total Ketone	15.0 ± 0.2	1.49	26.5 ± 0.2	2.65	27.9 ± 0.2	2.79
Red. Equiv.	35.8	3.54	60.6	6.06	71.4	7.14
Ox. Equiv.	31.6	3.13	57.2	5.72	60.0i	6.00[i]

Table VI - Yield of Chemical Products of the Helium Ion Irradiation of n-Propyl Alcohol

	Bombardment 1 2.00 μah 27.1 mev 22 min 5.5 μa(av.) Foil 1 Chamber A Gas Treatment I Conversion: 0.099		Bombardment 2 2.00 μah 26.8 mev 47 min 2.6 μa(av.)J Foil 4 Chamber B Gas Treatment II Conversion: 0.100	
Product	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev
H_2	20.6	2.04	29.1	2.91
CO	3.14	0.311	0.63	0.063
CH_4	1.32	0.131	1.06	0.106
C_2H_2	--	--	0.33	0.033
C_2H_4	1.26	0.125	2.50	0.250
C_2H_6	3.82	0.378	4.32	0.432
C_3H_6	0.45	0.045	0.80	0.080
C_3H_8	1.10	0.109	0.85	0.085
$n\text{-}C_4H_{10}$	--	--	0.22	0.022
Pentenes and Pentanes	--	--	0.12	0.012
Unident.	--	--	0.17	0.017
Total Gas	32.0	3.17	40.77	4.08
Acid	0.20 ± 0.05	0.020	0.12 ± 0.01	0.012
H_2O	--	--	10.2 ± 0.3	1.02
Carbonyl	16. ± 1.	1.6	19.7 ± 0.2	1.97
Aldehyde	(13)[a]	(1.3)[a]	--	--
Ketone	0[k]	0[k]	--	--
Total Glycols	--	--	--	--
Vic-glycols	(7.5 ± 0.3)[c]	0.74)[c]	(6.7 ± 0.3)[c]	(0.67)[c]
Nonvic-glycols	--	--	--	--
Red. Equiv.	54	5.3	71.2	7.12
Ox. Equiv.	60	5.9	56.4	5.64

Table VII - Yield of Chemical Products of the Helium Ion Irradiation of n-Butyl Alcohol

	Bombardment 1 2.00 μah 27.1 mev 42 min 2.9 μa(av.) Foil 1 Chamber A Gas Treatment I Conversion: 0.099		Bombardment 2 2.00 μah 26.8 mev 65 min 1.8 μa(av.) Foil 4 Chamber B Gas Treatment II Conversion: 0.100	
Product	Total Millimoles	Molecules 100 ev	Total Millimoles	Molecules 100 ev
H_2	26.4	2.62	35.9	3.59
CO	<0.36	<0.036	0.66	0.066
CH_4	0.52	0.051	0.53	0.053
C_2H_2	--	--	0.16	0.016
C_2H_4	1.44	0.143	0.71	0.071
C_2H_6	0.30	0.030	0.28	0.028
C_3H_6	1.59	0.157	0.99	0.099
C_3H_8	2.82	0.279	2.35	0.235
Butenes	0.34	0.034	0.20	0.020
n-Butane	0.55	0.054	0.37	0.037
Unident.	--	--	0.28	0.028
Total Gas	35.1	3.47	42.6	4.26
Acid	0.18 ± 0.02	0.018	0.12 ± 0.01	0.012
H_2O	6.8 ± 0.3	0.67	6.3 ± 0.3	0.63
Carbonyl	10.8 ± 0.2	1.07	15.2 ± 0.2	1.52
Aldehyde	(10)[a]	(1.0)[a]	--	--
Ketone	0[k]	0[k]	--	--
Total Glycols	(6.2 ±0.3)[l]	(0.61)[l]	--	--
Vic-glycols	(8.4 ± 0.3)[l]	(0.83)[l]	(9.2 ± 0.3)[c]	(9.2)[c]
Nonvic-glycols	0	0	--	--
Red. Equiv.	61.2	6.06	78.8	7.88
Ox. Equiv.	40.6	4.02	52.2	5.22

Table VIII - Yield of Chemical Products of the Helium Ion Irradiation of Isobutyl Alcohol

	Bombardment 1 2.00 μah 27.1 mev 45 min 2.7 μa(av.) Foil 1 Chamber A Gas Treatment I Conversion: 0.099	
Products	Total Millimoles	Molecules 100 ev
H_2	25.3	2.50
CO	0.64	0.063
CH_4	1.46	0.145
C_2H_2	--	--
C_2H_4	0.94	0.093
C_2H_6	0.29	0.029
C_3H_6	5.73	0.567
C_3H_8	5.14	0.509
Butenes	0.34	0.034
Isobutane	1.21	0.120
Total Gas	41.8	4.14
Acid	0.28 ± 0.02	0.027
H_2O	7.7 ± 0.3	0.76
Carbonyl	13.9 ± 0.2	1.38
Aldehyde	(14)[a]	(14)[a]
Ketone	0[k]	0[k]
Total Glycol	(8.5 ± 1.0)[l]	(0.84)[l]
Vic-glycol	(7.3 ± 1.0)[l]	(0.73)[l]
Nonvic-glycol	0	0
Red. Equiv.	66.8	6.61
Ox. Equiv.	48.4	4.79

Table IX - Yield of Chemical Products of the Helium Ion Irradiation of Sec.-Butyl Alcohol

Bombardment I
2.00 μah 27.1 mev
45 min 2.7 μa(av.)
Foil 1 Chamber A
Gas Treatment I
Conversion: 0.099

Product	Total Millimoles	Molecules 100 ev
H_2	18.7	1.86
CO	<0.04	<0.004
CH_4	2.87	0.284
C_2H_2	<0.15	<0.015
C_2H_4	3.65	0.362
C_2H_6	5.61	0.555
C_3H_6	0.13	0.013
C_3H_8	0.39	0.039
CH_3CHO	2.09	0.207
Butenes	0.67	0.066
n-Butane	1.24	0.123
Total Gas	36.6	3.62
Acid	0.05 ± 0.02	0.005
H_2O	6.3 ± 0.3	0.62
Carbonyl	18.5 ± 0.5	1.83
Aldehyde	(11)[a]	(1.1)[a]
Ketone	(7.5)[m]	(0.74)[m]
Total Glycol	(2.15 ± 0.3)[l]	(0.21)[l]
Vic-glycol	(2.35 ± 0.3)[l]	(0.23)[l]
Nonvic-glycol	0	0
Red. Equiv.	57.6	5.70
Ox. Equiv.	46.6	4.61

Table X - Yield of Chemical Products of the Helium Ion Irradiation of n-Octyl Alcohol

Bombardment 1
2.00 μah 26.5 mev
48 min 2.5 μa(av.)
Foil 2 Chamber B
Gas Treatment II
Conversion: 0.101

Product	Total Millimoles	Molecules 100 ev
H_2	34.5	3.48
CO	0.51	0.052
CH_4	0.22	0.022
Dry Ice Frac.[n]	1.06	0.107
Non-vol.[c]	0.36	0.036
Total Gas	36.4	3.68
Acid	0.11 ± 0.01	0.011
H_2O	4.3 ± 0.3	0.43
Carbonyl	8.6 ± 0.2	0.87
Aldehyde	(7)[a]	(0.7)[a]
Ketone	0[k]	0[k]
Vic-glycol	(5.6 ± 0.3)[c]	(0.57)[c]
Red Equiv.	72	7.3
Ox. Equiv.	30	3.0

Table XI - Yield of Chemical Products of the Helium Ion Irradiation of n-Decyl Alcohol

Bombardment 1
2.00 μah 26.5 mev
50 min 2.4 μa(av.)
Foil 2 Chamber B
Gas Treatment II
Conversion: 0.101

Product	Total Millimoles	Molecules 100 ev
H_2	34.4	3.47
CO	0.44	0.044
CH_4	0.18	0.018
Dry Ice Frac.[n]	1.70	0.172
Non-vol[p]	0.26	0.026
Total Gas	36.0	3.63
Acid	0.08 ± 0.01	0.008
H_2O	3.1 ± 0.3	0.31
Carbonyl	7.5 ± 0.2	0.76
Aldehyde	(10)[a]	(1.0)[a]
Ketone	0[k]	0[k]
Vic-glycol	(5.0 ± 0.3)[c]	(0.51)[c]
Red. Equiv.	73	7.4
Ox. Equiv.	27	2.7

DATA NOTES

a. Semiquantitative estimate from Ag_2O oxidation.

b. Dioxane predistillation not too reliable for total glycols.

c. A maximum; periodic acid reduction on raw sample.

d. Estimate from order of magnitude of parent peak sensitivities of other compounds.

e. Assuming 0.11 millimoles acid.

f. Contained 5.5 millimoles air; 0.6 millimoles O_2 consumed in reactions.

g. Assuming 0.12 millimoles acid.

h. Heated to about 30°C.

i. Assuming 1.0 millimoles total glycol.

j. Unsteady beam current during bombardment; up to 4 μa on occasion.

k. Undetected within error of aldehyde estimation.

l. Di-n-butyl ether distillation procedure questionable.

m. Semiquantitative estimate from carbonyl minus aldehyde.

n. Gaseous fraction volatile at dry ice temperature (-78°C), but non-volatile at liquid nitrogen temperature (-196°C).

o. Gaseous fraction non-volatile at dry ice temperature (-78°C), hydrocarbons from butane through heptanes and other unidentified products probably present.

p. Gaseous fraction non-volatile at dry ice temperatures (-78°C). Hydrocarbons from butane to nonane and other products present.

V. DISCUSSION OF PRODUCT YIELD DATA

A. Functional Reactant Tendencies

The data make possible several immediate generalizations. It can be noted that with the exception of carbon monoxide no gaseous product nor functional group of more than one organic oxidation state removed from alcohol is formed to a very appreciable extent, and that among the oxidation states thus allowed, certain structural limitations exist. There are no ketonic products of primary alcohols, no aldehydes higher than formaldehyde from methanol, no formaldehyde from secondary alcohols and no aldehyde whatsoever from tertiary alcohols. Analogous tendencies, not so rigorous, apply to the carbonyl equivalents of the vicinal glycols. These facts would seem to indicate that, to a first approximation, the products of radiolysis are confined to those substances which are the formal results of a single primary chemical event, the recombination of radicals formed from single bond ruptures, or equivalently the results of simple rearrangements.

A second generalization derives from the manifestation of a selective reactant tendency, as evidenced by the appreciably high yields of only a few of the products designated as possible by the above rule. In the case of the normal alcohols, hydrogen, water, the aldehyde corresponding to the alcohol irradiated, and what may be termed analogously a "corresponding" glycol, RCHOHCHOHR from RCH_2OH, comprise by far the major products of the reaction. In the simple secondary and tertiary alcohols, an increasingly appreciable yield of methane is to be noted. These facts may be summarized in

a statement to the effect that the products of the irradiation of the (lower) aliphatic alcohols result primarily from reactions which involve those groups bonded to the carbon of the functional carbinol ($-\overset{|}{\underset{|}{C}}OH$) group.

In addition to the major product yield tendencies, there may be cited in support of such a generalization the fact that within the errors of the determinations involved, no glycols but those having vicinal hydroxyl groups were detected. This indicates a definite preference for a mode of reaction in, for instance, ethanol:

$$2CH_3CH_2OH = CH_3CHOHCHOHCH_3 + H_2$$

involving the bonding positions of the functional carbon, over a reaction

$$2CH_3CH_2OH = CH_2OHCH_2CH_2CH_2OH + H_2$$

involving bonding positions on a non-functional carbon. Less explicit is, in the same case, the empirical predominance of a product acetaldehyde over ethylene glycol, since there is no restriction of probably analogous mechanism for the formation of the two products, but a general decrease in susceptibility to reaction on a non-functional carbon is implied. It is indeed a fact that even the smaller yield of ethylene glycol can be explained by the reactions:

$$CH_3CH_2OH \longrightarrow CH_3 + CH_2OH$$

$$2CH_2OH \longrightarrow H_2COHCH_2OH$$

involving the bonds associated with the carbinol carbon, and thus eliminate the necessity for postulation in this instance of any

susceptibility to reaction at non-functional bonding positions.

The other alcohols show similar tendencies, the n-1 hydrocarbons being the principal hydrocarbon product of normal alcohols of n carbons (Figure 5), and the other hydrocarbons appropriate to the case of secondary and tertiary alcohols similarly so.

This reactant tendency may be qualitatively explained by the polarizing effect of the electronegative hydroxyl group on the other bonds of the carbinol carbon, weakening them and increasing their susceptibility to rupture or other reaction.

That the hydroxyl group, OH, be considered as included in the reactivity generalization, could be inferred from the predominance of water as a product of the radiolysis, but certain discrepancies in correlation of product yields into stoichiometrical reactions, to be considered later, indicate that a closer consideration of its value in such a principle is required. The simple application of the concept would suggest a correspondingly high yield of a stoichiometrical coproduct involving the residue alkyl group, a hydrocarbon, ether, or higher alcohols which was not detected.

B. Stoichiometry

There are several indications that a fairly complete stoichiometrical evaluation of the radiological phenomena has been made in the analysis of products, at least for the simpler alcohols. Obviously in a closed system, the equivalents of oxidized and reduced products must be equal. (The input of charge and helium of the irradiating beam was chemically negligible.) The reduced products of the simpler alcohols, hydrogen and hydrocarbons are all gaseous,

and the virtually complete analysis of the gaseous fraction that has been made yields not only the magnitude of the oxidative-reductive effects of the radiation, but allows inferences on the nature of whatever oxidized products have escaped elucidation.

The other possible net actions of radiolysis are non-oxidative, and the possible products of such are not difficult to list. Water, other alcohols, ethers, and ethylenic hydrocarbons essentially complete the simple possibilities. Neither the alcohols nor ethers are provided for in the analytical techniques employed, but the water, in all probability a predominant stoichiometrical coproduct of higher alcohols and ethers,* as well as of the ethylenic hydrocarbons, has been determined. Water can, of course, be formed in the oxidation-reduction reactions also, as well as in incidental ways, for example, formation of the acetals of aldehydes and glycol rearrangements, but its yield represents probably close to a maximum measure on the equivalents of alcohol transposed in non-oxidative-reductive reactions.

With this limitation then there is a fairly reliable indication of the effective total extent of radiological reaction for simple alcohols. It is the stoichiometrical equivalent of the total reduced product, as found in the gaseous fraction, plus the equivalent of water unaccounted for in the oxidation-reduction reactions.

The formulation of stoichiometrical reactions which account for the products observed with some indication of the relative extent to which each reaction is manifested thus comprises a fairly complete

*This assumes the predominant reactivity of the C-H bond over the C-C bonds on the functional group. Tertiary alcohols, having no such C-H bonds, cannot subscribe to this generalization.

description of the gross chemical effects of radiation on the alcohols, under the conditions of the irradiations. Such a description should not be construed to imply a mechanism, nor any kinetic tendencies. The details of its formulation are somewhat variable, as well. The selection of products to balance into a reaction is not all unique, but the alternatives that exist are by definition equivalent.

For methanol, bombardment 4, such a descriptive system is comprised by the following reactions, with the number of molecules/100 ev of product formed by each indicative to the extent to which it contributes to the total radiolysis:

CH_3OH	=	$HCHO + H_2$	1.35
$2CH_3OH$	=	$H_2COHCH_2OH + H_2$	1.67
$2CH_3OH$	=	$HCHO + CH_4 + H_2O$	0.37
CH_3OH	=	$CO + 2H_2$	0.24
$2CH_3OH$	=	$CH_3OCH_3 + H_2O$	0.03
$3CH_3OH$	=	$HCHO + C_2H_6 + 2H_2O$	0.01
$2CH_3OH$	=	$HCOOH + H_2 + CH_4$	0.01*
$2CH_3OH$	=	$CH_3OOCH_3 + H_2$	0.001

In effect, this is nothing more significant than a balancing of oxidation-reduction equivalents into equality and atoms into their ratio of the original alcohol, but it illustrates the interdependence of products, and gives a lucid indication of the deficiencies in the analysis. The amount of each product indicated as formed in these reactions conform within reasonable error limits to that actually found in the bombardment, with the exception of water. Only 4.2

*From bombardment 3.

millimoles of water are accounted for as compared to 9.9 millimoles detected, a discrepancy of about 5.7 millimoles. This amount of water must be taken as being formed in conjunction with some product not indicated by the analyses.

For ethanol bombardment 4 (bombardment 5 was probably contaminated with air), a similar consideration yields the following system of equations, in which a few minor products have been neglected:

CH_3CH_2OH	=	$CH_3CHO + H_2$	1.49
$2CH_3CH_2OH$	=	$CH_3CHOHCHOHCH_3 + H_2$	0.82
CH_3CH_2OH	=	$HCHO + CH_4$	0.28
$2CH_3CH_2OH$	=	$H_2COHCH_2OH + C_2H_6$	0.14
CH_3CH_2OH	=	$C_2H_4 + H_2O$	0.14
CH_3CH_2OH	=	$CO + CH_4 + H_2$	0.12
CH_3CH_2OH	=	$C_2H_2 + H_2 + H_2O$	0.04
$2CH_3CH_2OH$	=	$CH_3OC_2H_5 + CH_3OH$	0.03
$2CH_3CH_2OH$	=	$HCHO + C_3H_8 + H_2O$	<0.03
$3CH_3CH_2OH$	=	$CH_3CHO + C_4H_{10} + 2H_2O$	<0.01
$2CH_3CH_2OH$	=	$CH_3COOH + C_2H_6 + H_2$	0.01*

This tabulation accounts within reasonable error for the products observed, with the exception of 0.5 molecules/100 ev of hydrogen and about 0.6 molecules/100 ev of water.**

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*From bombardment 5.

**The water, undetermined in bombardment 4, is assumed approximately equal to that of bombardment 5.

For isopropyl alcohol bombardment 3:

$(CH_3)_2CHOH$	=	$(CH_3)_2CO + H_2$	1.88
$(CH_3)_2CHOH$	=	$CH_3CHO + CH_4$	0.92
$2(CH_3)_2CHOH$	=	$(CH_3)_2COHCOH(CH_3)_2 + H_2$	0.24
$2(CH_3)_2CHOH$	=	$CH_3CHOHCHOHCH_3 + C_2H_6$	0.14
$(CH_3)_2CHOH$	=	$C_3H_6 + H_2O$	0.15
$(CH_3)_2CHOH$	=	$CO + 2CH_4$	0.06
$2(CH_3)_2CHOH$	=	$(CH_3)_2COHCH_2OH + C_3H_8$	0.04
$2(CH_3)_2CHOH$	=	$(CH_3)_2CO + C_3H_8 + H_2O$	0.02
$2(CH_3)_2CHOH$	=	$CH_3CHO + C_4H_{10} + H_2O$	0.02
$(CH_3)_2CHOH$	=	$C_2H_2 + CH_4 + H_2O$	0.02
$(CH_3)_2CHOH$	=	$C_2H_4 + CH_3OH$	0.01

This tabulation accounts within reasonable error for the products observed, with the exception of 0.5 molecules/100 ev hydrogen and 0.75 molecules/100 ev water.

For tert-butyl alcohol bombardment 2:

$(CH_3)_3COH$	=	$(CH_3)_2CO + CH_4$	1.33
$2(CH_3)_3COH$	=	$2(CH_3)_2CO + C_2H_6 + H_2$	0.35
$(CH_3)_3COH$	=	$i\text{-}C_4H_8 + H_2O$	0.12
$2(CH_3)_3COH$	=	$(CH_3)_2COHCH_2OH + i\text{-}C_4H_{10}$	0.1
$(CH_3)_3COH$	=	$CO + CH_4 + C_2H_6$	0.05
$2(CH_3)_3COH$	=	$(CH_3)_2CO + neo\text{-}C_5H_{12} + H_2O$	0.03
$(CH_3)_3COH$	=	$C_2H_4 + CH_3CH_2OH$	0.02
$2(CH_3)_2COH$	=	$2(CH_3)_2CO + C_3H_6 + CH_4$	0.01
$(CH_3)_3COH$	=	$C_2H_2 + H_2 + CH_3CHOH$	0.01
$3(CH_3)_3COH$	=	$2(CH_3)_2CO + C_3H_8 + C_2H_6 + CH_3OH$	0.01

This formulation accounts for the products observed with the exception of 0.5 molecules/100 ev carbonyl, 0.8 molecules/100 ev hydrogen, and 0.8 molecules/100 ev water, thus cannot be considered very adequate. Its inability to account completely for the carbonyl product arises out of the difficulty of producing it without the accompanying formation of hydrocarbons. In this regard it might be that appreciable amounts of heavier hydrocarbon went undetected due to solubility in the liquid fraction. It can be noted that the heavier hydrocarbons are in somewhat greater relative abundance in bombardment 3, in which case a complete removal of gases was effected in the gas treatment. Since only those passing through a trap at dry ice temperatures were analyzed for, it may be that this does not represent a complete assay of the hydrocarbon products.

A less explicit formulation of the reactions for the remaining alcohols can be made, due to the limited yield data available. However, extrapolations of the reactant tendencies noted in the simpler alcohols and generalized in the first part of the discussion may be made. For n-propyl alcohol bombardment 2 this results in:

C_3H_7OH	=	$C_2H_5CHO + H_2$	1.40	1.77
C_3H_7OH	=	$HCHO + C_2H_6$	0.37	
$2C_3H_7OH$	=	$C_2H_5CHOHCHOHC_2H_5 + H_2$		0.67
$2C_3H_7OH$	=	$H_2COHCH_2OH + C_4H_{10}$		
C_3H_7OH	=	$CH_3OH + C_2H_4$		0.25
C_3H_7OH	=	$CH_4 + CH_3CHO$		0.11
$2C_3H_7OH$	=	$C_3H_8 + C_2H_5CHO + H_2O$		0.09
C_3H_7OH	=	$CO + C_2H_6 + H_2$		0.06
C_3H_7OH	=	$CH_3OH + C_2H_2 + H_2$		0.03
$2C_3H_7OH$	=	$C_2H_5COOH + C_3H_8 + H_2$		0.01

This leaves a minimum of 0.76 molecules/100 ev of hydrogen and 0.9 molecules/100 ev water unaccounted for.

For n-butyl alcohol bombardment 2:

C_4H_9OH	=	$C_3H_7CHO + H_2$	1.13	1.30
C_4H_9OH	=	$C_3H_8 + HCHO$	0.17	
$2C_4H_9OH$	=	$C_3H_7CHOHCHOHC_3H_7 + H_2$		0.92
$2C_4H_9OH$	=	$H_2COHCH_2OH + C_6H_{14}$		
C_4H_9OH	=	$HCHO + C_3H_6 + H_2$		0.10
C_4H_9OH	=	$C_2H_4 + CH_3CH_2OH$		0.07
C_4H_9OH	=	$CO + H_2 + C_3H_8$		0.07
C_4H_9OH	=	$C_2H_5CHO + CH_4$		0.05
$2C_4H_9OH$	=	$C_3H_7CHO + C_4H_{10} + H_2O$		0.04
C_4H_9OH	=	$CH_3CHO + C_2H_6$		0.03
C_4H_9OH	=	$C_2H_2 + H_2 + CH_3CH_2OH$		0.02
C_4H_9OH	=	$C_4H_8 + H_2O$		0.02
$2C_4H_9OH$	=	$C_3H_7COOH + C_4H_{10} + H_2$		0.01

This leaves a minimum of 1.3 molecules/100 ev of hydrogen and about 0.6 molecules/100 ev of water unaccounted for.

For isobutyl alcohol bombardment 1:

C_4H_9OH	=	$C_3H_7CHO + H_2$	0.57	1.08
C_4H_9OH	=	$HCHO + C_3H_8$	0.51	
$2C_4H_9OH$	=	$C_3H_7CHOHCHOHC_3H_7 + H_2$		0.73
$2C_4H_9OH$	=	$H_2COHCH_2OH + C_6H_{14}$		
C_4H_9OH	=	$C_3H_6 + CH_3OH$		0.57
C_4H_9OH	=	$C_2H_5CHO + CH_4$		0.15
C_4H_9OH	=	$C_3H_7CHO + C_4H_{10} + H_2O$		0.12
C_4H_9OH	=	$C_2H_4 + CH_3CH_2OH$		0.09
C_4H_9OH	=	$CH_3CHO + C_2H_6$		0.03
C_4H_9OH	=	$C_4H_8 + H_2O$		0.03
$2C_4H_9OH$	=	$C_3H_7COOH + C_4H_{10} + H_2$		0.03

This leaves a minimum of 1.2 molecules/100 ev of hydrogen and about 0.6 molecules/100 ev of water unaccounted for.

For sec-butyl alcohol bombardment 1, in which the aldehyde determination is probably not reliable:

C_4H_9OH	=	$C_2H_5(CH_3)CO + H_2$		~1.3	~2.1
C_4H_9OH	=	$CH_3CHO + C_2H_6$	~0.5	~0.8	
C_4H_9OH	=	$C_2H_5CHO + CH_4$	~0.3		
C_4H_9OH	=	$C_2H_4 + CH_3CH_2OH$			0.36
$2C_4H_9OH$	=	$C_2H_5(CH_3)COHCOH(CH_3)C_2H_5 + H_2$			0.23
$2C_4H_9OH$	=	$CH_3CHOHCHOHCH_3 + C_4H_{10}$			
$2C_4H_9OH$	=	$C_2H_5CHOHCHOHC_2H_5 + C_4H_{10}$			
C_4H_9OH	=	$C_4H_8 + H_2O$			0.07
$2C_4H_9OH$	=	$C_2H_5(CH_3)CO + CH_4 + C_3H_8$			0.04
C_4H_9OH	=	$C_2H_2 + H_2 + CH_3CH_2OH$			<0.02
C_4H_9OH	=	$C_3H_6 + CH_3OH$			0.01

This formulation accounts rather approximately for the observed products with the exception of about 0.6 molecules/100 ev hydrogen and 0.6 molecules/100 ev of water.

For n-octyl alcohol bombardment 1:

$C_8H_{17}OH$	=	$C_7H_{15}CHO + H_2$	0.87
$C_8H_{17}OH$	=	$HCHO + C_7H_{16}$	
$2C_8H_{17}OH$	=	$C_7H_{15}CHOHCHOHC_7H_{15} + H_2$	0.57
$2C_8H_{17}OH$	=	$H_2COHCH_2OH + C_{14}H_{30}$	
$C_8H_{17}OH$	=	$CO + H_2 + C_7H_{16}$	0.05
$C_8H_{17}OH$	=	$C_6H_{13}CHO + CH_4$	0.02
$2C_8H_{17}OH$	=	$C_7H_{15}COOH + 2C_4H_{10}$	0.01

This leaves a minimum of 2.0 molecules/100 ev of hydrogen and about 0.4 molecules/100 ev of water unaccounted for.

For n-decyl alcohol bombardment 1:

$C_{10}H_{21}OH$	=	$C_9H_{19}CHO + H_2$	0.76
$C_{10}H_{21}OH$	=	$HCHO + C_9H_2O$	
$2C_{10}H_{21}OH$	=	$C_9H_{19}CHOHCHOHC_9H_{19} + H_2$	0.51
$2C_{10}H_{21}OH$	=	$H_2COHCH_2OH + C_{18}H_{38}$	
$C_{10}H_{21}OH$	=	$CO + H_2 + C_9H_{20}$	0.04
$C_{10}H_{21}OH$	=	$C_8H_{17}CHO + CH_4$	0.02
$2C_{10}H_{21}OH$	=	$C_9H_{19}COOH + 2C_5H_{12}$	0.01

This leaves a minimum of 2.1 molecules/100 ev of hydrogen and about 0.3 molecules/100 ev of water unaccounted for.

In the above formulations, hydrogen and water present the principal discrepancies to a complete stoichiometrical balancing. The excess hydrogen indicates that one or more oxidized products have

not been determined in the various analyses. It can be noted that the hydrogen unaccounted for is essentially zero for methanol and increases rapidly in going up the series of n-alcohols. Graphical illustration of this is obtained by comparison of the yields of hydrogen (Figure 3) or total reduction equivalent (Figure 10) which is principally hydrogen, with that of the various oxidized products, carbonyl (Figure 8), glycols (Figure 9) and total oxidation equivalent (Figure 10). Such a dependence suggests that the missing oxidation product be of a nature that the probability of its formation increase with increasing alkyl chain length, and since the formation of ethylenic double bond is compatible with that of hydrogen, it can be postulated that the reaction

$$RCH_2CH_2R'OH \longrightarrow RCH=CHR'OH + H_2$$

becomes increasingly pertinent to the radiolysis of alcohols above ethanol, to an extent necessary to account for most of the excess hydrogen. No general analysis for ethylenic unsaturation was employed in the experimental work, when qualitative tests indicated that it was probably negligibly small in preliminary experiments on ethanol.*

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*It is of incidental interest to speculate at this point that the maximum in the region of ethanol in the yield curve of the carbonyl products of n-alcohols (Figure 8) may be partly due to the conversion of an initially formed alpha unsaturated alcohol to the aldehyde, a situation not possible in the case of methanol, and the alpha unsaturation becoming statistically less probable as the alkyl chain length increases. It must be realized, however, that this is not in basic conformity to the selectivity principles advanced with fair justification earlier in the discussion.

This does not account for the small lack of stoichiometrical equivalence with regard to hydrogen in the ethanol and isopropyl alcohol products, and the somewhat more appreciable discrepancy in those of tert-butyl alcohol. Since (dialkyl) peroxides were possibly qualitatively indicated in small amounts in the irradiated alcohols, it seems that they might account for the hydrogen increments observed in these cases by the reaction:

$$2ROH \longrightarrow ROOR + H_2 .$$

The considerable stability of di-tert-butyl peroxide may explain the larger hydrogen discrepancy in the case of tert-butyl alcohol.

The presence of water in the reaction products in quantities stoichiometrically in excess to that expected from the other known products presents a somewhat more serious discrepancy. This excess of water is noted to be approximately constant through the series of normal alcohols, decreasing slightly if anything, but increasing with a higher degree of carbinol substitution, primary to secondary to tertiary.

The determination of water employed did not in general involve measurements to eliminate interference from the carbonyl present. However, the rate at which the endpoint faded indicated that the interfering reaction was negligibly slow with respectto the time of titration, and comparison of the method employing the cyanide modification for the presence of aldehydes with the unmodified procedure indicated no discrepancy beyond the precision limits of the titration. Thus the determination must be considered reliable. Moreover, formaldehyde does not interfere at all in the determination,[40] yet the

water discrepancy exists in the irradiated methanol.

The coproduct of this water must of course be something not included in the analysis. An obvious suggestion is that the water is formed in conjunction with alcoholic products in, for example, reactions such as:

$$2CH_3OH = C_2H_5OH + H_2O$$

$$2C_2H_5OH = C_2H_5CH(CH_3)OH + H_2O .$$

These alcohols could not have been detected by the analytical methods employed. However, application of the concept to isopropyl alcohol would produce a hexyl alcohol:

$$2(CH_3)_2CHOH = (CH_3)_2C(OH)CH(CH_3)_2 + H_2O$$

and to tertiary butyl alcohol, no water at all, assuming reaction at the carbinol group:

$$2(CH_3)_3COH = (CH_3)_2C(OH)CH(CH_3)_2 + CH_3OH$$

or a hexyl alcohol and water if such a selective restriction were not required. The total glycol procedure employed on the irradiated alcohols involved determination of all hydroxyl equivalents of compounds whose boiling points exceeded 115°C. The various hexyl alcohols do boil above this point and if present should have been detected as total glycol. Yet the equivalence of the total glycols with vic-glycols indicated that only dihydroxyl components were present. It is true that considerable difficulty was encountered in the development of the technique for this determination, several higher values being obtained before those reported. However,

these values were not reproducible, and being correlatable to the rate and amount of distillate taken out of pyridine solution, were attributed to inefficient and incomplete elimination of the original alcoholic components. The values reported, obtained on slow and prolonged fractionations, corresponded reproducibly to the periodic acid reduction equivalents (vic-glycols) as reported.

A second possibility of coproduct for the water detected are the ethers, also not analyzed for in the liquid fraction:

$$2ROH = ROR + H_2O .$$

However, the dimethyl ether expected in methanol bombardments is gaseous at room temperatures (b.p. -23.7°C), and though it was detected mass spectrometrically, it was not in sufficient yield to account for the excess water.

The possibility of the third stoichiometrical coproduct of water, the ethylenic hydrocarbon derivative corresponding to the alcohol irradiated,

$$CH_3CH_2OH = C_2H_4 + H_2O$$

suffers from the same objection. In the cases where it could be detected in the gaseous phase, it was not present to a sufficient extent to account for the water.

Several other possibilities of reactive tendencies for forming water in the system may be cited. A mechanism involving free radical hydroxyl substitution of hydrogen or alkyl groups for the formation of aldehydes would yield a product water:

$$OH + CH_3OH \longrightarrow HCHO + H_2O + H$$

but it requires a correspondingly high analogous hydrocarbon yield for stoichiometrical balance, which was not found.

The formation of acetals from aldehydic products and the alcohol medium and analogously the formation of diethers of the glycol products yield water:

$$RCHO + 2R'OH \longrightarrow RCH(OR')_2 + H_2O$$

$$RCH(OH)CH(OH)R + 2R'OH \longrightarrow RCH(OR')CH(OR')R + H_2O \ .$$

Acetals were detected in the gas phase in very small amounts but there was obtained some analytical indication that they were not significantly present in the liquid fraction (page 29). The glycol etherification reaction might involve a tendency of a glycol molecule, in an excited state immediately prior to its formation from appropriate free radicals, for reaction similar to that manifested by ethylene oxide, except at two oxygen positions. It would be unlikely in this event that some yield of the high boiling monohydroxyl-ether were not formed and detected as high boiling hydroxyl compound in the total glycol procedure. Ethylene oxide derivatives themselves do not seem likely answers to the problem since none were detected in the gaseous fractions in propitious cases and since it would form monohydroxy-ethers with the alcohol medium, which could have been detected. The formation of more stable cyclic ethers would yield water also, and no evidence for or against their production was obtained.

Higher polymers of glycols resulting from condensations of the etheric type, or of carbonyls from aldol type condensation with

etherification of the hydroxyl groups remain a possibility both as undetected oxidation products and coproducts of a water formation. In fact, the general question of polymer formation was neglected in the experimental work.

In the secondary and tertiary alcohols where the glycols formed are pinacols, a rearrangement to pinacolone type carbonyl derivatives would produce water, and the increased yield of water in the cases of the non-primary alcohols could possibly be correlated with a tendency of this nature. However, the general application of such an explanation, to any (perhaps excited) glycol molecule would require the production of acetaldehyde among the methanol radiolysis products and butyraldehyde among those of ethanol:

$$H_3COHCH_3OH \longrightarrow CH_3CHO + H_2O$$

$$CH_3CH(OH)CH(OH)CH_3 \longrightarrow C_3H_7CHO + H_2O \quad .$$

Such products have been demonstrated respectively not to be present.

An apparent relationship between the water and glycol yields is suggested by the data. The highest yields of water are found in the cases in which the yield of glycol is lowest, in a manner suggesting that their formation involves a competition, either directly in the radiological reaction, or secondarily in some reaction such as a pinacol-pinacolone transformation.

The status of the water among the reaction products must thus be regarded as uncertain. Water, being very stable, could be expected to have a high tendency to be formed in activated alcohol systems, and its presence is not surprising. Yet, though any or all of the

above concepts may apply to the yield of water in sum or in part, the correlation is not in this regard very satisfactory.

In spite of this last difficulty, it can be seen that a reasonably complete stoichiometrical description, derived of the data and the correlation generalizations the data suggests, of the effect of alpha radiation on alcohols is possible.

C. Variation of Functional Reactivity with Molecular Size

The fairly high degree of functional selectivity manifested in the reactions induced by radiolysis in the simple alcohols is to be especially noted in view of the fact that it has been suggested[9,11,16] that the yield of products of radiolysis of simple molecules might be expected to be in accordance with a fairly random involvement of the various bonds of the molecule. In the case of simple alcohols, however, the products formed in accordance with the functional reactivity principle specified previously, to the effect that the principal products are those involving reactions at the bonding sites of the carbinol carbon, are in overwhelming yield, and not simply by virtue of a lack of other bonding positions, as is evidenced by the secondary and tertiary alcohols.

It has been further suggested[9,11,16] that any functional selective action of radiation may become more pronounced as larger molecular systems are irradiated, i.e., as the increased number of degrees of freedom, and the liquid state allow containment of the energy of excitation until it can effect a low barrier reaction. The series of normal alcohols studied here afford an opportunity to consider effects of this nature, the effect of size or complexity of the

molecule on the degree of selectivity manifested in the radiolysis reactions.

It can be assumed that the selective tendencies which must be considered, i.e., the low barrier reactions, are those brought about by the influence of the functional group, i.e., the reactions resulting in the principal products of the simple alcohol irradiations, carbonyl, glycols, and water, and their coproduct hydrogen and hydrocarbon components, all formed in accordance with the selectivity principle cited. Graphs of the yields of these various products plotted against the number of carbon atoms in the series of normal alcohols are shown in Figures 3 to 10. The tendencies are apparent. Glycol, carbonyl, and water, as well as total (detected) oxidation equivalent, all fall off in yield with increasing length of the alkyl chain. Hydrogen, hydrocarbons, and total reduction equivalent remain approximately constant. The necessary equivalence of oxidized and reduced product demands, of course, that some undetected oxidation products be increasingly present up through the series of n-alcohols, and as suggested previously these may be unsaturated alcohols. But such a product, reflecting in its yield a tendency toward statistical dependence on the availability of its constituents, hydrogen atoms and carbon-carbon bonds, cannot be termed the result of a selective reaction. It is necessary to conclude therefore that the manifestations of a selective radiological reaction in liquid aliphatic alcohols decrease with their increasing size.

It can be conceived that such a falling off in yields of oxygenated products is a necessary consequence of the fact that the irradiations were carried out in liquid state. If in some small

peripheral volume encasing the path of the nuclear particle the number of excitations (including ionizations) of energy exceeding some minimum necessary to bring about the reaction, was comparable to the number of molecules present in the volume, the yield of any product formed necessarily in a maximum one-to-one equivalence to the number of reactant molecules excited would be an inverse function of the size of the reactant molecules. That is, with a lesser number of total molecules in the volume considered, a lesser yield on such a product must result, provided the homogeniously activated volumes were comparable in the cases under consideration. Such oxygenated products as carbonyls and glycols can form a maximum of only one molecule per molecule of alcohol (glycols, one molecule per two molecules of alcohol), and since the densities of the various alcohols are approximately constant (sp. grav. ~0.8), the decrease in the number of reactant molecules in the effectively irradiated volume, due to the increase in the size of each molecule, would require a corresponding decrease in the oxygenated product, provided the excitation was close to or greater than one with respect to the molecules present.

Since the relative density of excitation is unknown for liquid systems, no direct certification of such a condition is possible. However, rough estimates indicate that it is not a likely circumstance. Burton[15] estimates the average distance between excitations (including ionizations) in liquids as between eight and fifteen molecules, or a molecular density of excitation about 0.001. This is probably an average over the considerable volume defined by the alpha trajectory and its peripheral delta rays. But it can be rather simply indicated that the excitation density approaches a value unity or greater only

within a cylinder of radius the order of one molecular dimension around the alpha trajectory. Taking a generous average 5000 ionizations per mm as the specific ionization of an alpha particle in air[68] and correcting by a density factor of 800, there is obtained a value 4000 ionizations per micron of liquid methyl alcohol. As in all such computations, the essential equivalence of liquid and gaseous systems in this respect is assumed. Lea states that one-half the total ionizations of an alpha particle are produced by delta rays of energy exceeding 100 ev, which have a range in organic tissue of about 0.003 microns.[69] This is to say that since the delta rays come off largely perpendicular to the alpha trajectory,[70] the average number of ionizations per micron trajectory in a cylinder of radius a minimum 0.003 microns around an alpha trajectory is somewhat over 2000. This cylinder is of a volume about 3×10^{-5} cubic microns per micron trajectory which will contain about 3×10^{5} methanol molecules, each methanol molecule having an effective volume of somewhat less than 10^{-10} cubic microns. The average molecular density of ionization over this volume is seen to be of the order of 0.01. The 0.003 micron radius corresponds to about 10 molecular radii and since the integral density of an ionization distribution assumed random along the tracks of the delta rays varies inversely as the radius, there is obtained a molecular density of ionization of the order 0.1 in a cylinder of radius one molecular radius around the alpha trajectory. This corresponds approximately to the density of primary ionization by the alpha particle calculated independently. Various determinations of the ratio of chemically effective excitations to ionizations of from two to ten[71] set an approximate density of chemically effective

excitation at a maximum of about one per molecule at the alpha trajectory, falling off as the square of the distance away from it. Since the primary ionizations represent only about one-fifth of the total ionization,[72] it is doubtful that the excitation is sufficiently molecularly homogeneous to produce the desired effect.

The implication of a yield of hydrogen approximately independent of the size of the irradiated molecule in such a situation of homogeneous molecular excitation may be mentioned. If the yield of oxygenated product is equivalent to some totality of reactant molecules in a densely activated volume, and thereby dependent on their size, then the excess of hydrogen over that equivalent to the oxygenated product determined must derive from the same reactant molecule as did the oxygenated product and its equivalent reduced product. This is to say that in addition to the selective functional reaction, in any given molecule there must also occur the statistical unselective reaction which produces the excess hydrogen, i.e., probably the formation of ethylenic double bonds in the alkyl chain. The decrease in the number of excited molecules requires an increase in the average excitation of each one excited, so that a basic energy requirement would be fulfilled. However, unless some positive evidence of the dense molecular excitation that it requires were obtained, the concept of such a localized action of a bombarding particle as to allow essentially simultaneous but independent chemical events at different locales in the molecule could not be regarded favorably.

It is to be noted that these considerations do not reflect on the status of the empirical selectivity conclusions reached previously. Under any circumstances, the selective tendency due to the influence

of the functional group decreases with increasing complexity of the molecule.

D. Effect of Alkyl Substitution on Functional Reaction Products

The nature of the variation in the several reaction tendencies due to substitution of alkyl groups onto the functional carbinol group is illustrated in the product yields of methyl, ethyl, isopropyl, and tert-butyl alcohols. In general, the products support the reactivity principles cited at the beginning of this discussion. Exceptions to this are the small yield formaldehyde equivalents in the glycol components of isopropyl and tert-butyl alcohols. These can be accounted for minor reactions involving possibly free OH radicals at the non-functional carbon:

$$2(CH_3)_2CHOH = CH_3CHOHCH_2OH + C_3H_8$$

$$2(CH_3)_3COH = (CH_3)_2COHCH_2OH + C_4H_{10}$$

The greater susceptibility to reaction of carbon-hydrogen over carbon-carbon bonds is evidenced in the greater yields of acetaldehyde than formaldehyde in ethanol, of ketone than acetaldehyde in isopropyl alcohol, in the analogous components of the glycol fractions of ethyl and iso-propyl alcohol, in the decreased total carbonyl yield in tert-butyl alcohol as compared with isopropyl alcohol and in the increasing yields of water in the series ethyl, iso-propyl, and tert-butyl alcohols. The decrease in acidity noted through the series corresponds in general to the decrease in aldehyde, and is evidence of the secondary nature of its formation, as considered in a later section.

The yield of methane increases approximately in proportion to the number of methyl groups substituted onto the carbinol carbon (Figure 12). Perhaps a better measure of the relative tendency for reaction involving methyl groups is the sum of the methane plus twice the ethane yield as plotted in Figure 13 (Curve A). This function of the methyl group reaction also increases approximately in proportion to the number of substituent methyl groups. An appreciable yield of ethane not derived from combination of methyl groups is possible in ethanol, making its value slightly high as is indicated. The slight increase in the yield function per methyl substituent (Curve B) reflects a tendency for additional alkyl substitution to enhance the reactivity of the bonds of the other groups, a result which is seen to be similarly effected on the hydrogen-carbinol bonds, in the analogous curve for hydrogen (Figure 11, Curve B). The gross yield of hydrogen (Figure 11, Curve A) decreases fairly linearly for methyl, ethyl, and iso-propyl alcohols, and drops off sharply for tert-butyl alcohol.

The effect of increasing alkyl substitution on the various bonding positions of the carbinol carbon is best represented by the various carbonyl and glycol component yields. In Figure 14 are plotted four curves. Curve A is the yield of the carbonyl component derived from oxidation of a carbinol-hydrogen bonding position on the given alcohol molecule, divided by the number of such bonding positions available for reaction; i.e., the formaldehyde from methanol divided by three, the acetaldehyde from ethanol divided by two, and the acetone (ketone) from iso-propyl alcohol divided by one. Curve B is the completely analogous glycol yields function. Curve C is the yield of carbonyl component derived from oxidation of a carbinol-methyl

bonding position, divided by the number of such bonding positions available, and Curve D is the analogous glycol yield function. In Figure 15, Curve A, is plotted the sum of the carbonyl and glycol reactant tendencies represented by the curves A and B of Figure 14. In Curve B of Figure 15 is plotted the sum of the carbonyl and glycol reactant tendencies as represented by Curves C and D of Figure 14.

From these graphs may be taken several notable effects of increasing alkyl substitution on the carbinol group. Such substitution enhances the total oxidative susceptibility of both hydrogen and alkyl bonding positions; it increases the ratio of carbonyl over glycol reactive susceptibility; and it actually decreases the glycol susceptibility. Moreover, all of these effects are damped in the case of the carbon-carbinol bond reactions compared with that of the hydrogen-carbinol bond reaction.

The increased total oxidative susceptibility of the carbinol bonding positions is probably due to some reaction-enhancing polarization by the alkyl substituent of the bonds of the carbinol carbon. The constant ratio of the curves A and B of Figure 15 when referred to an abscissa of the constitutive fragments, CH_2OH, CH_3CHOH, and $(CH_3)_2COH$, which the various products have in common (i.e., when the curve B is moved over under the curve A) indicates that the reactive tendencies of the hydrogen and the methyl groups are enhanced to the same degree by such a substituent effect. It is to be noted that the curve B in Figure 15 does not differ too radically in magnitude and slope from the less explicit Curve B of Figure 11, as should be the case, since both represent the effect of increasing alkyl substitution on the reaction susceptibility of the methyl-carbinol bond. The same

approximate equivalence applies to the analogous curves, A of Figure 15 and B of Figure 11, involving the hydrogen-carbinol bond although it is not so graphically apparent because of differing ordinate scales.

The increased ratio of a carbonyl over a glycol type product reflects a general enhancement of the relative stability of carbonyl over glycol type compounds on increasing alkyl substitution as is evidenced by a pinacol-pinacolone rearrangement. The tendency as represented here can be ascribed to two effects. The linear nature of the glycol decrease suggests that the increasing alkyl substitution imposes an intrinsic inhibition to glycol formation, which would result in a reciprocal increase in a competitive carbonyl formation. The fact that the total oxidative susceptibility increases means that an intrinsic enhancement of the carbonyl formation tendency in addition to that afforded by the glycol inhibition occurs with increasing substitution, and suggests that the polarization tendencies postulated responsible for the increase in total oxidative susceptibility may in actuality apply only to a mode of carbonyl formation. In this respect it is of interest to note that the significant increase in total oxidative susceptibility is on passing from the constituent fragments CH_3CHOH to $(CH_3)_2COH$ while the glycol function is regular through the series.

The damping effect probably represents some desensitization of the various reactant tendencies dependent on the fact that they involve an alkyl-carbinol bond reaction rather than a hydrogen-carbinol bond reaction. Further consideration will be made in the context of the mechanism discussion of the next section.

E. Reaction Mechanisms

The analysis for final products of a reaction conducted under standardized conditions can be expected to yield only the most rudimentary indications of the mechanism by which the reaction proceeds, but a few of these may be mentioned. In the first place, the reactions yielding the products determined here are not to any great extent chain reactions. This is indicated by the modest conversion of alcohol per energy expended that is observed. In gaseous systems the number of ion pairs formed by alpha particles per 100 ev energy expended is about three. The number of excited molecules accompanying this ionization is at least equal to this, since the 30 ev average expenditure of energy per ion pair formed is twice that necessary to ionize the molecule, and very possibly exceeds it to a considerable extent. How many of these excitations are of sufficient energy to bring about the given reactions is hard to estimate, but empirical data suggests that a value the order of magnitude the number of ionizations is not unreasonable.[71] If then one chemical transformation per excitation (including ionization) over a certain value is taken as a normal reaction, then a yield of product equivalent to the order of 5 to 10 molecules/100 ev will be obtained in a normal reaction. Much higher yields will be due to some chain effect initiated by the radiolytic activation. The total yields of observed products of the irradiated alcohols don't exceed seven molecules reactant equivalent/100 ev in the most favorable cases. Some effective product loss, due to the reformation of the original alcohol undoubtedly occurs, but it is evident the alcohol radiolysis corresponds closely to what may be defined as the simple radiological

reaction. The reaction of a free radical with an unexcited molecule producing an effective product plus another radical, is a form of chain reaction. Thus if a free radical mechanism applies to alcohol radiolysis, the recombination of free radicals is a principal means of product formation, rather than extended reaction chains of radicals with neighboring unexcited molecules.

The formation of carbonyl is not a dimolecular reaction, i.e., it does not come about by replacement of a carbinol hydrogen or alkyl group by a hydroxyl group, either in a free radical mechanism or more direct reaction of two molecules. This is evident from the fact that neither the yield of the appropriate hydrocarbon nor of the water co-products of a dimolecular stoichiometrical reaction compares with that of the carbonyl. Two possibilities for monomolecular reaction exist, the formation of an unstable free radical, which decomposes:

$$CH_3CH_2OH \longrightarrow CH_3CHOH + H$$

$$CH_3CHOH \longrightarrow CH_3CHO + H$$

or an ultimate molecular rearrangement:

$$CH_3CH_2OH \longrightarrow CH_3CHO + H_2 .$$

The latter is supported by photochemical evidence to the effect that no hydrogen atoms could be detected in the photolytic oxidation of ethyl alcohol.[26,29] However, in the case of tertiary butyl alcohol, the product data supports the former mechanism. The yields of hydrogen, methane, and ethane obtained are best accounted for by the mechanistic reactions:

$$(CH_3)_3COH \longrightarrow (CH_3)_2COH + CH_3$$

$$(CH_3)_2COH \longrightarrow (CH_3)_2CO + H$$

involving decomposition of an unstable free radical, rather than an immediate formation of CH_4:

$$(CH_3)_3COH \longrightarrow (CH_3)_2CO + CH_4$$

or reaction at nonfunctional hydrogen positions. This is in conformity with mass spectral data which indicate the high tendency of tert-butyl alcohol to form radical species $(CH_3)_2COH$ and CH_3.[64]

In some competition with the carbonyl formation is the glycol formation, which is dimolecular, of course, and probably proceeds by a free radical mechanism. The hydroxyl radical formation, as well as direct reaction involving transfer of a hydroxyl group, is pretty well excluded by the consideration of such as is outlined for carbonyl formation.

In the case of hydrogen and glycol formation from irradiated alcohols, as in the case of hydrogen formation from irradiated hydrocarbons, there exists the necessity of explaining the preponderance of reaction involving H-C bonds over that involving C-C bonds. It does not seem likely that the effect of the hydroxyl group reverses the order of the strengths of these bonds from what they are in hydrocarbons, H-C stronger than C-C. An explanation of the product yields analogous to that for the hydrocarbons requires postulation of a free radical mechanism, which allows the small hydrogen atoms to escape the liquid cage effect restricting the dissociative tendencies of larger fragments.

The glycol can be formed from the residue radicals that remain after such a dissociation either by combinations among themselves or by reaction with quiescent neighboring alcohol molecules. In this regard it is of interest to note that the ratio of glycol to carbonyl remains approximately constant at 0.5-0.6 through the series ethanol to n-decyl alcohol. This is to say that the relative functional tendency to form glycols is independent of the size of the molecules. This is in conformity to a concept of dependence of tendency toward radical formation on only the size of the smaller radical fragment of the dissociation. Such a concept applies here essentially to hydrogen atom dissociations, which are responsible for most of the glycols, and thus may be applicable to only dissociations involving hydrogen. But if increased size is construed to imply any restriction on the subsequent diffusional mobility of the residual oxygenated radicals, then such a constant relative glycol yield is an argument against its formation by interaction of free radical components. However, such an assumption is probably not valid, especially since in the larger alcohols the molecular concentration of the constitutive radicals is higher.

In the reaction of free radicals with neighboring non-activated molecules, the problem of a selective reactivity at H-C bonds arises again. It may be that the cage effect again suffices for explanation, a free radical reaction being inhibited if the group it is replacing cannot dissociate freely from the parent molecule. Thus there seems no possibility for definite choice of mechanism for glycol formation between reaction of radicals among themselves or with neighboring nonactivated molecules; possibly both contribute.

It should be mentioned that the proper form of Figures 14 and 15 depends on such a choice of mechanism. As presented, the figures indicate a situation in which only one of the fragmentary components of the glycol is subject to a competitive carbonyl reaction, corresponding to the formation of glycol by attack of a radical on a quiescent molecule. If, alternatively, only reactions between radicals are involved, then each glycol molecule is equivalent to two carbonyl molecules, and the glycol susceptibility functions of Figure 14 should be increased by a factor of two, with the appropriate analogous correction in the total susceptibility functions of Figure 15. The qualitative features of the previous discussion of the figures are preserved in this alternative case, however, and the mechanistic interpretation can be made in general terms.

The decreasing tendency for glycol formation on alkyl substitution at the carbinol carbon may be ascribed to either a steric hindrance to dimolecular combination or an increased stability of the radical constituents of a potential glycol, lengthening their effective lives and affording more opportunity for a competitive decomposition to carbonyl.

In turn, the tendency for decomposition of the radical to carbonyl may be intrinsically enhanced independently of the processes involving glycol carbonyl competition by an effect of increasing alkyl substitution which promotes more extensive conversion to carbonyl before a back reaction with a hydrogen atom or methyl radical deactivates the radical with no effective product formation. Equivalently the substitution could increase the susceptibility for radical reaction with hydrogen atoms or methyl radicals in such a

manner as to form carbonyl rather than the original alcohol.

Alternatively, the possibility exists that the carbonyl reactive tendency may be enhanced independently of the free radical processes, by the availability on increasing substitution of low barrier decompositions to the final products of the reaction. Whatever the mechanism, the carbonyl enhancement tendency is not large with less than two substituent alkyl (methyl) groups.

The evidence of damped reactant tendencies in the cases where a methyl group must be eliminated from the carbinol carbon to give the specified reaction product may in general be ascribed to an increased tendency for thermal collisional deactivation of the excited molecule before the reactant processes involving the methyl group can take place. Such a situation could occur as a result of the cage restriction on dissociation of the larger methyl group effectively slowing the dissociation of the excited molecule into radicals and allowing more time for deactivation in this case than in the case of a rapid unrestricted dissociation of hydrogen atoms.

A difficulty arises in attempting to account for such a selective deactivational damping of a carbonyl formation proceeding by an ultimate rearrangement decomposition. This may comprise evidence for the free radical alternatives.

The fact that the volume of chamber B was over twice that of chamber A introduced a kinetic variable into the bombardments affecting the concentration buildup of liquid products responsible for secondary product formation. The effect of such a variable is markedly illustrated in Figure 6 where the yield of acid is plotted for the various bombardments. It is noted that as a group the yields of such

products on bombardments carried out in chamber A are much higher than those in chamber B. This may be taken as evidence that the acid is at least in part a secondary product of the irradiation, formed probably by oxidative action on the aldehyde products, which yield curve it resembles.

The carbon monoxide (Figure 4) does not in general seem to subscribe to such a dependence, and may be formed directly.

F. Manifestations of Product Yield Dependence on Rate of Irradiation

No effort was made in the bombardments to study systematically the irradiant kinetic effects on product yields. In fact, when there was indicated in early bombardments that such effects were possibly being manifested, an effort was made to standardize the irradiation rate at as constant and reproducible a value as was expedient. However, an examination of the incidental differences in kinetic conditions under which the bombardments were made yields some conclusions.

The rate of irradiation as expressed by the average beam current on the data sheets is occasionally not indicative of the actual conditions under which the bombardments were run. Especially to be noted in this regard is the n-propyl alcohol bombardment 2, where mechanical difficulties in the cyclotron produced a highly fluctuating beam, with currents up to 4 μa at times, and which was thrown to one edge of the window entry, concentrated to a small effective cross section of irradiation. In general, however, the indicated average beam approximated the actual rate of irradiation.

It is a fact that except for the methanol and tert-butyl alcohol bombardments, and with the exception of the product water, the yields

vary inversely with the average beam current, in several cases of the A bombardments in virtually direct proportion. It was originally thought that the non-reproducibility of yields was due to a mechanical foaming out of the liquid from the inner chamber, reducing its level to a point at which a portion of the irradiating beam missed the liquid, and was effectively lost. However, the above correlation suggests that there may be some more fundamental reason for the variation, involving the effect of the rate of irradiation, aside from its mechanical effects.

The above mentioned n-propyl bombardment 2 and the n-butyl bombardment 2 are of special kinetic interest. Reference to Figures 3, 7, 8, and 9 shows that in the propanol bombardment, the yield of water is high, glycol low, hydrogen probably low, and carbonyl indeterminant, with regard to smooth curves through the other alcohols. Among the n-butyl alcohol products, the yield of hydrogen may be high, and the glycols possibly high. The propanol was bombarded with variable beam currents which were in general fairly high, up to 4 μa. The butanol beam current was steady but unavoidably low. This correlation between water, hydrogen and glycols is interesting in line with the previously discussed lack of stoichiometrical balance on these products. It may be that there is some kinetically dependent competition between the water and glycol-hydrogen yields. A rate study of this tendency might be of value in ascertaining the reaction from which the water derives.

The ratio of formaldehyde to total carbonyl in the ethanol bombardments seems to show a slight kinetic dependence upon the rate of irradiation, decreasing with decreasing intensity of bombardment.

The ratio of the corresponding equivalents in the glycols is approximately constant. Such an effect, if valid, would be difficult to explain on the hypothesis of a unimolecular reaction of aldehydes, one presumably independent of the concentration of other activated species in its environment.

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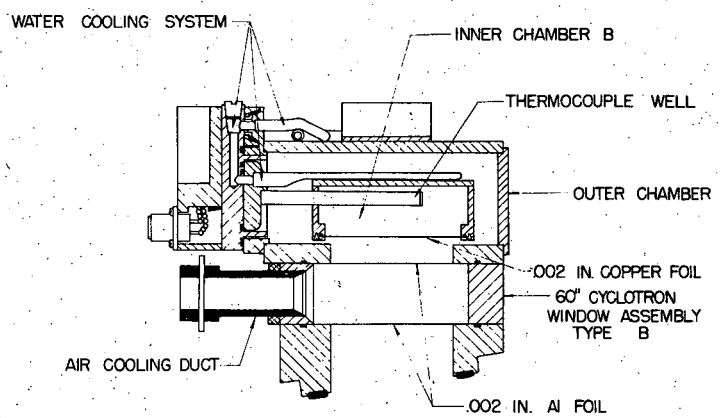

TOP VIEW - ASSEMBLY CLOSED

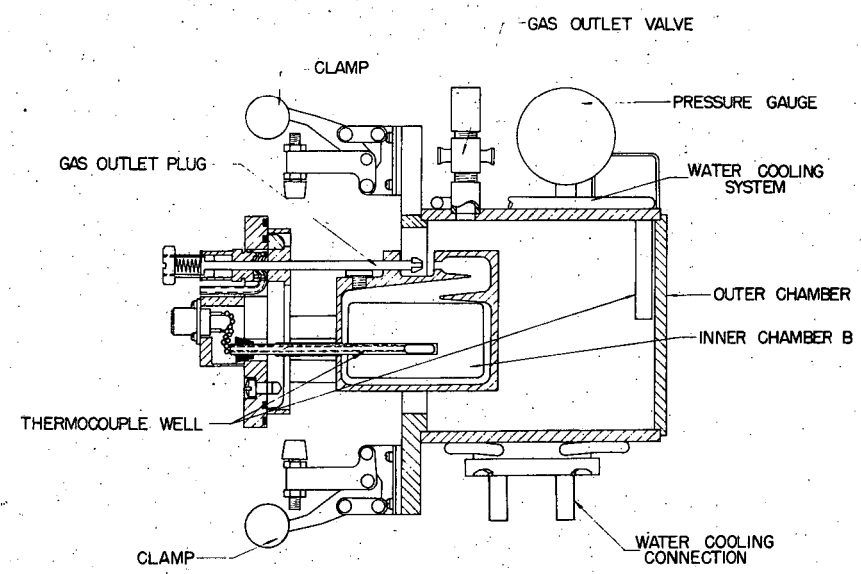

FIG. 1

LIQUID TARGET ASSEMBLY - ASSEMBLY OPEN

2020

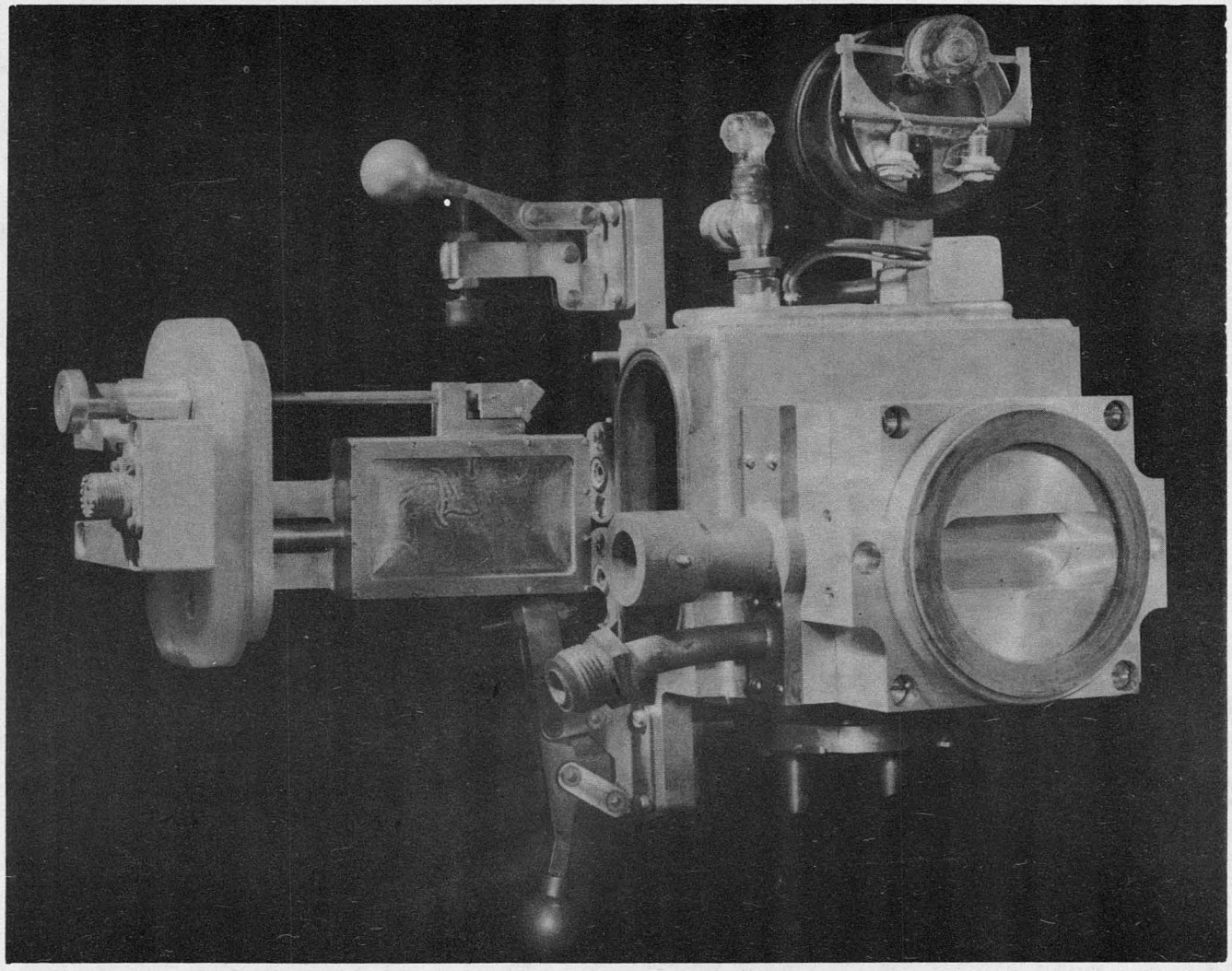

Fig. 2

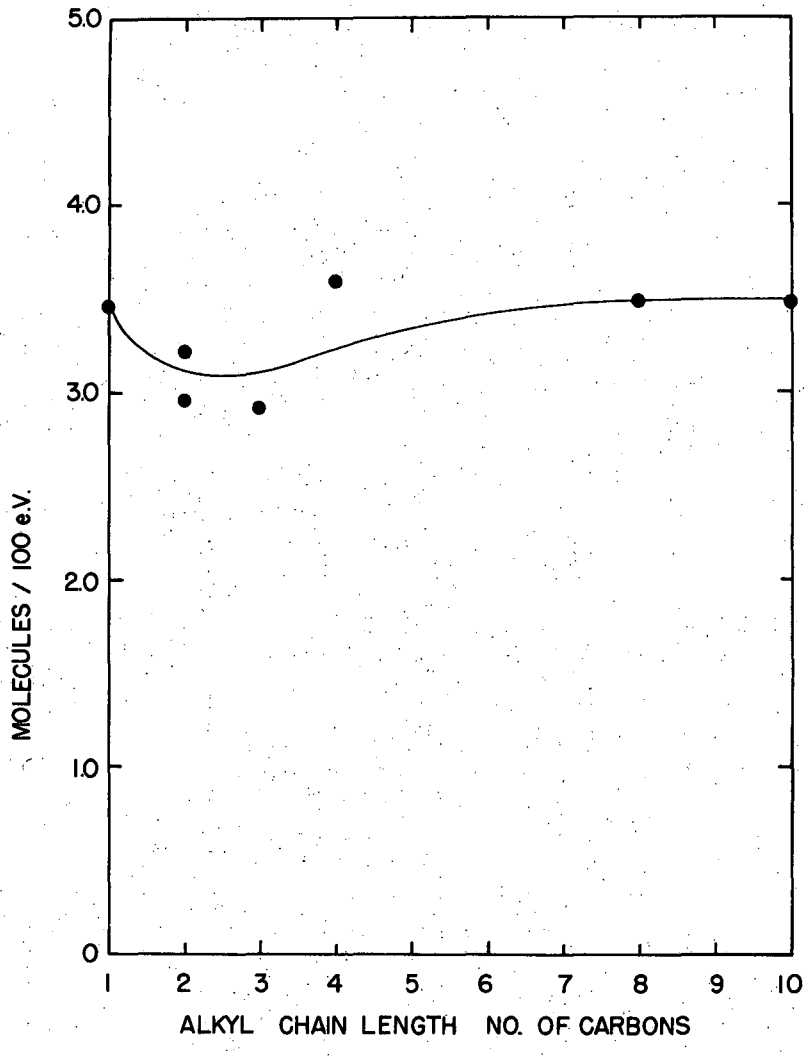

FIG. 3 YIELDS OF HYDROGEN IN IRRADIATED NORMAL PRIMARY ALCOHOLS

MU 2008

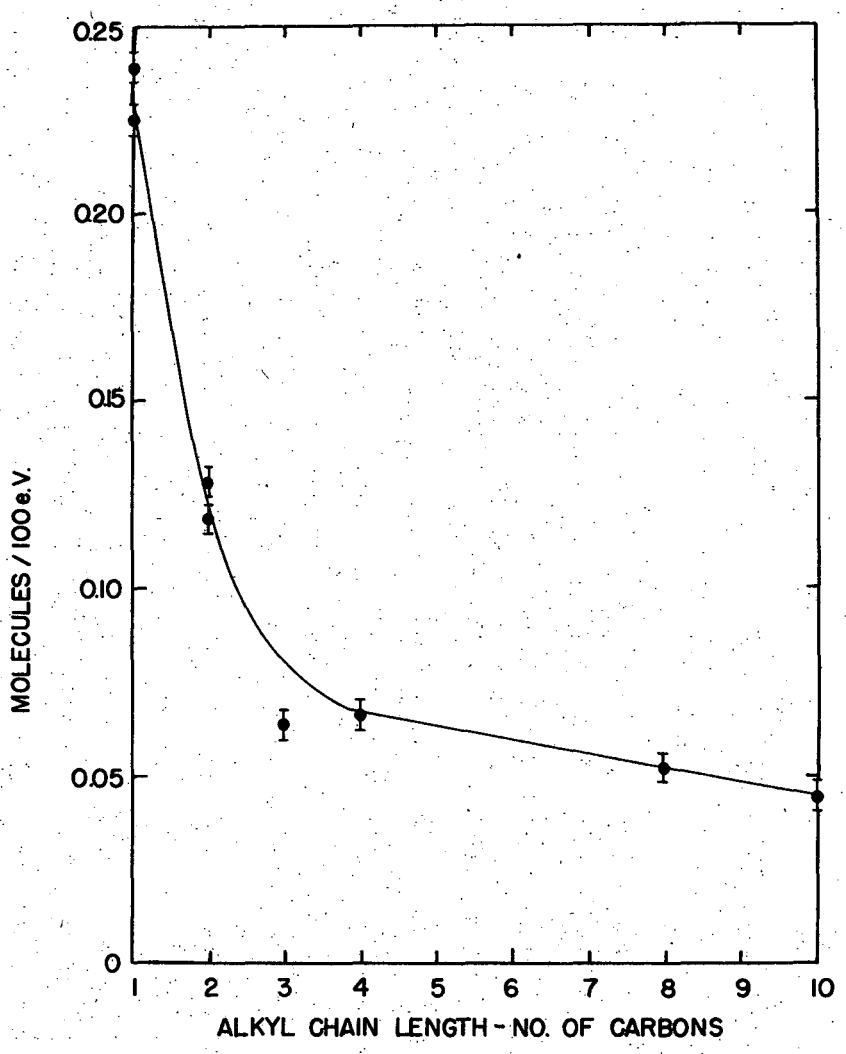

FIG. 4 YIELDS OF CARBON MONOXIDE IN IRRADIATED NORMAL PRIMARY ALCOHOLS

MU 2009

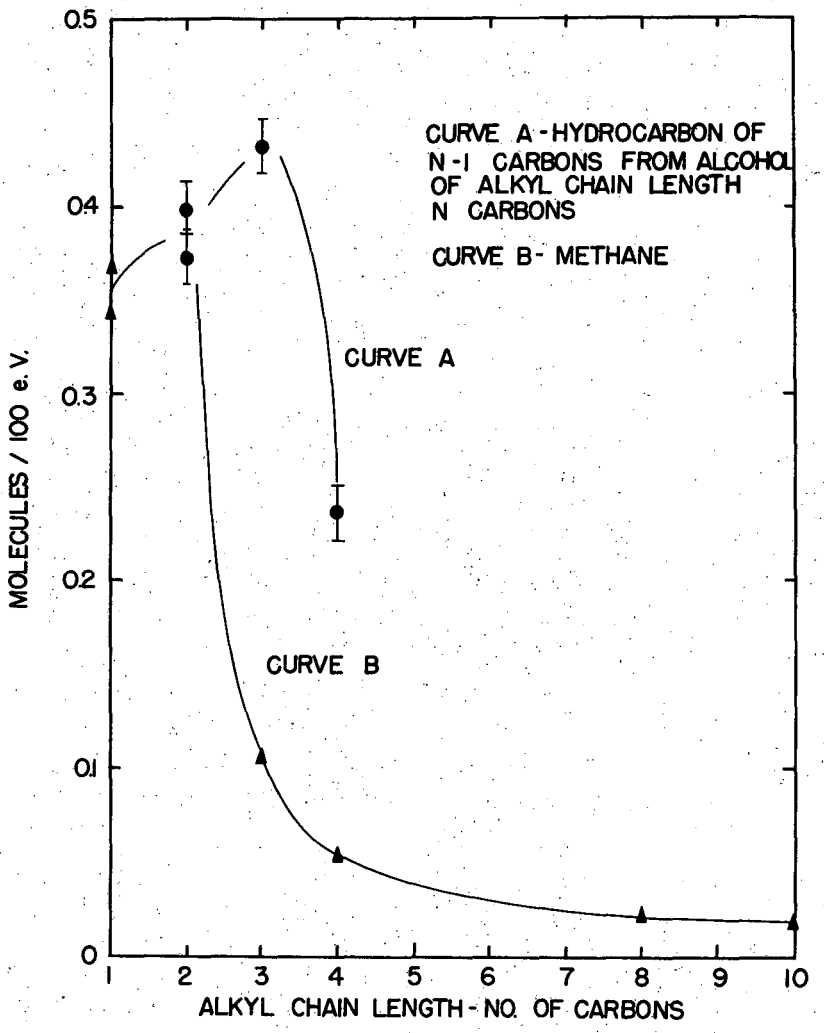

FIG. 5 YIELDS OF HYDROCARBONS IN IRRADIATED NORMAL PRIMARY ALCOHOLS

MU 2010

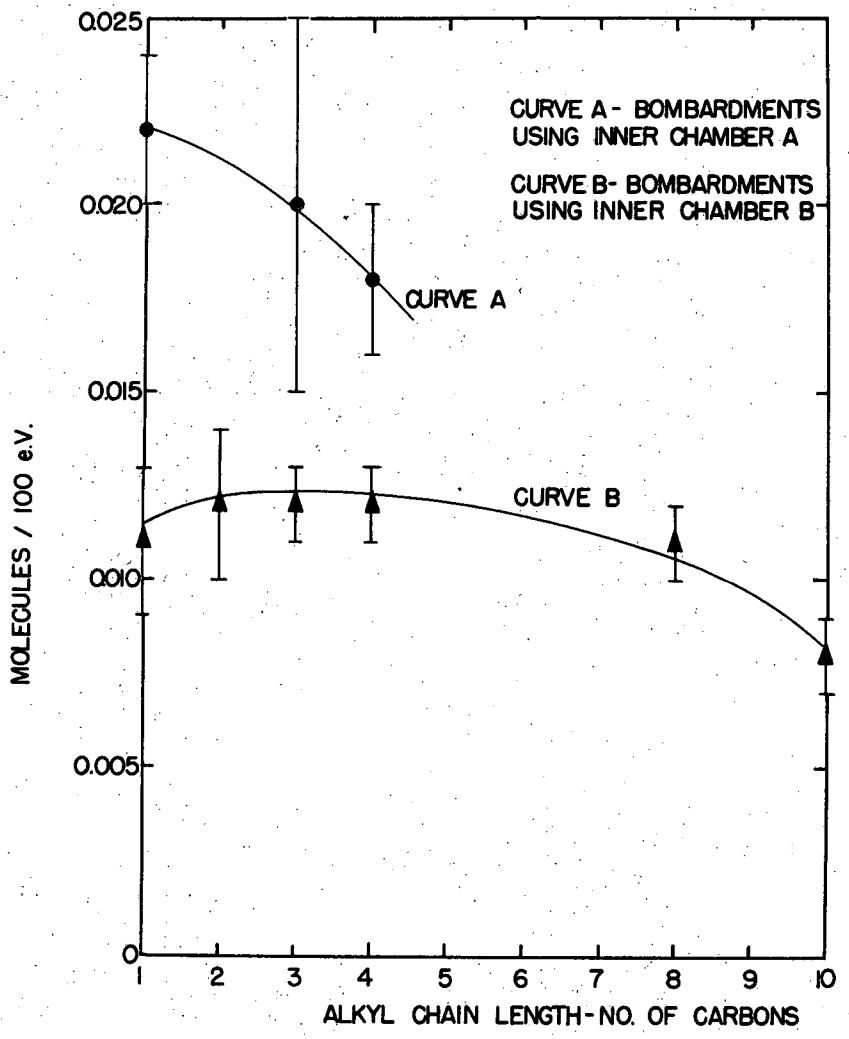

FIG. 6 YIELDS OF ACID IN IRRADIATED NORMAL PRIMARY ALCOHOLS

MU 2011

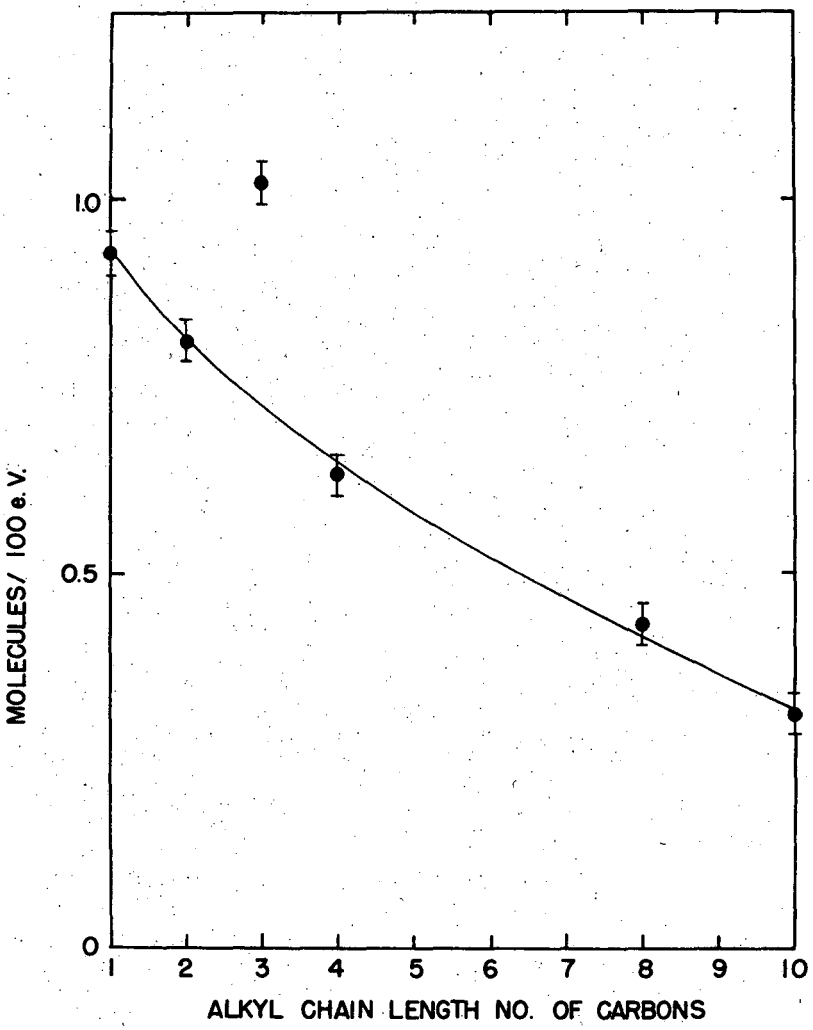

FIG. 7 YIELDS OF WATER IN IRRADIATED NORMAL PRIMARY ALCOHOLS

MU 2012

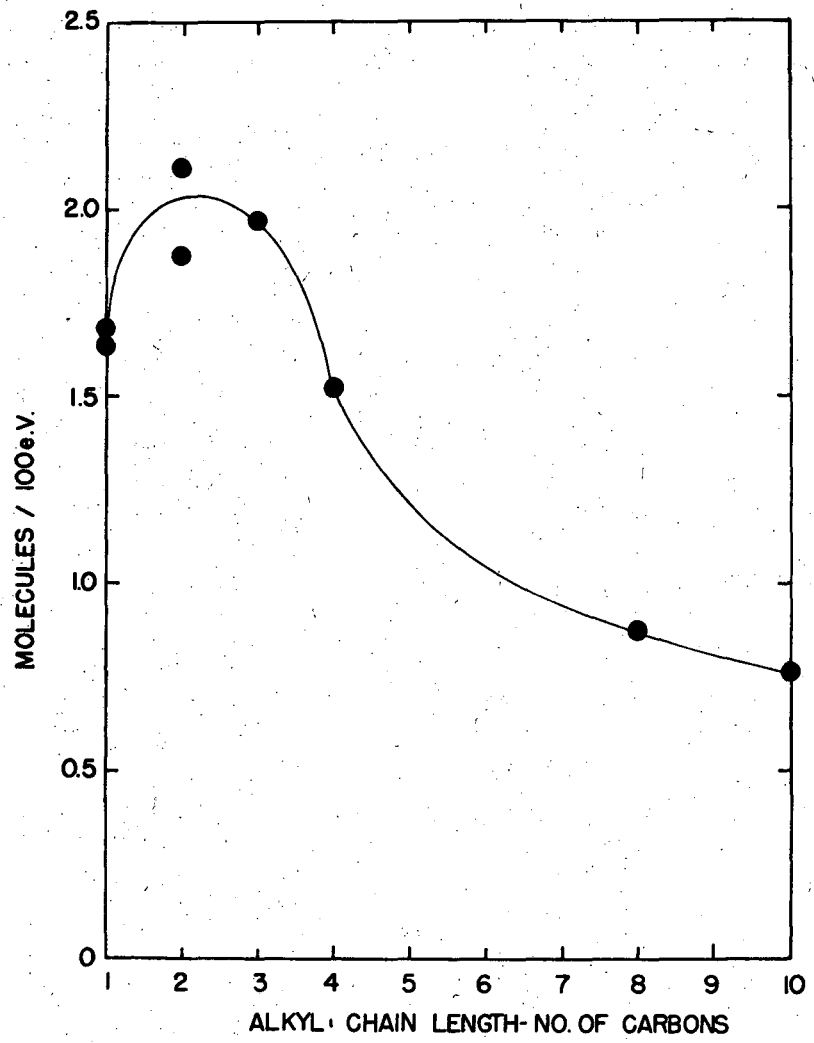

FIG. 8 YIELDS OF CARBONYL IN IRRADIATED NORMAL PRIMARY ALCOHOLS

MU 2013

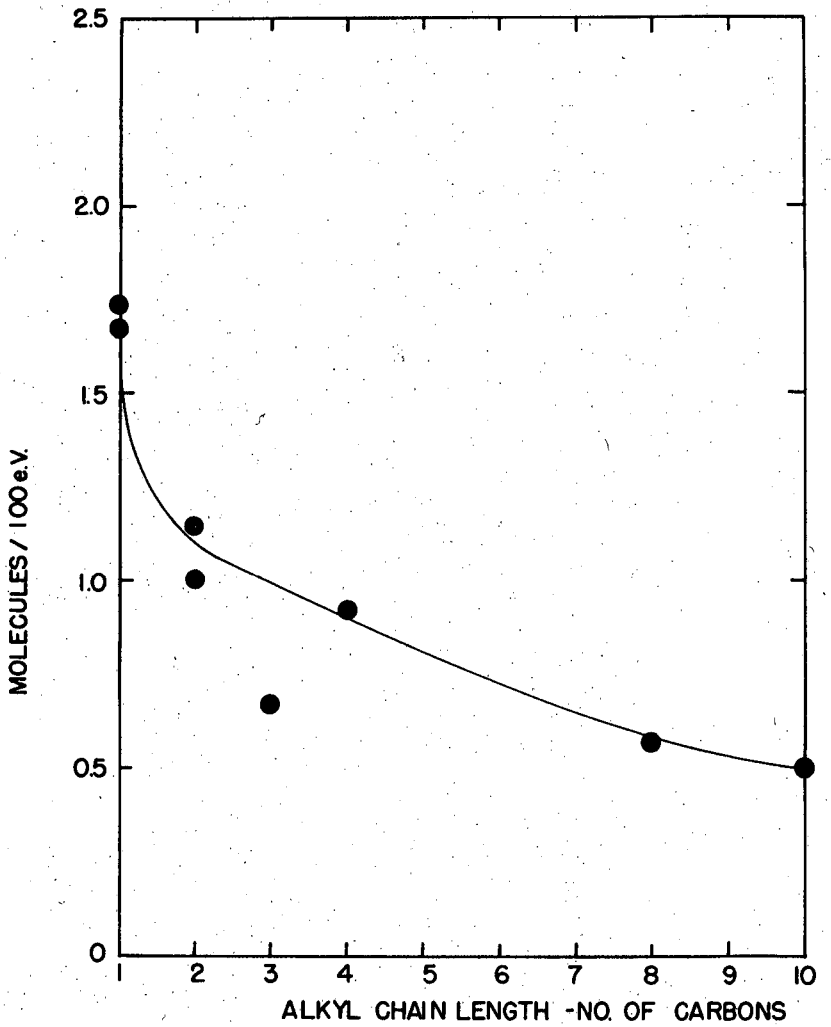

FIG. 9 YIELDS OF VIC-GLYCOLS IN IRRADIATED NORMAL PRIMARY ALCOHOLS

MU 2014

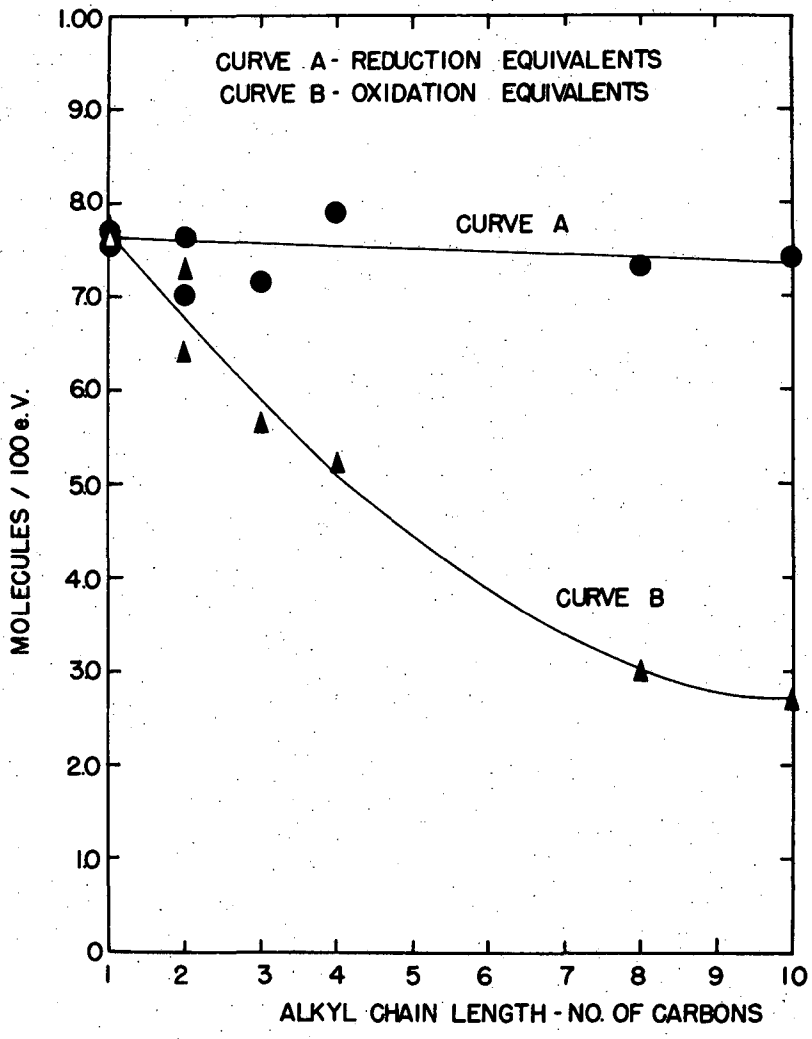

FIG. 10 REDUCTION AND OXIDATION EQUIVALENTS OF PRODUCTS DETERMINED IN IRRADIATED NORMAL PRIMARY ALCOHOLS

MU 2015

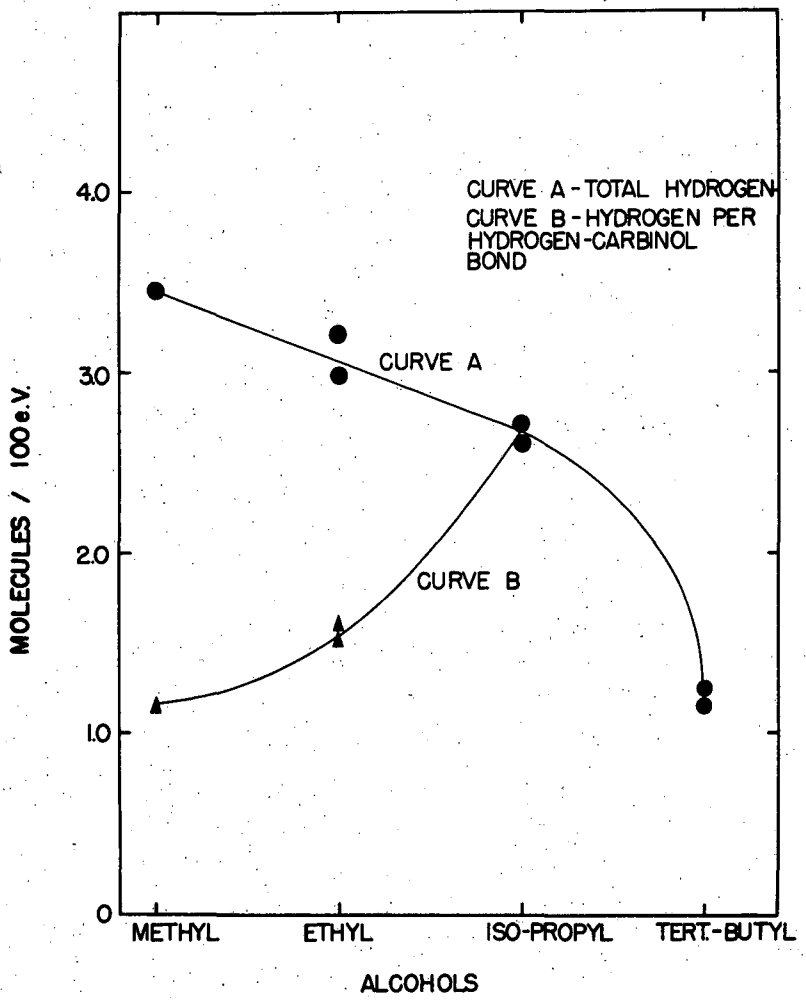

FIG. II YIELDS OF HYDROGEN IN IRRADIATED METHYL, ETHYL, ISO-PROPYL, AND TERT.-BUTYL ALCOHOLS

MU 2021

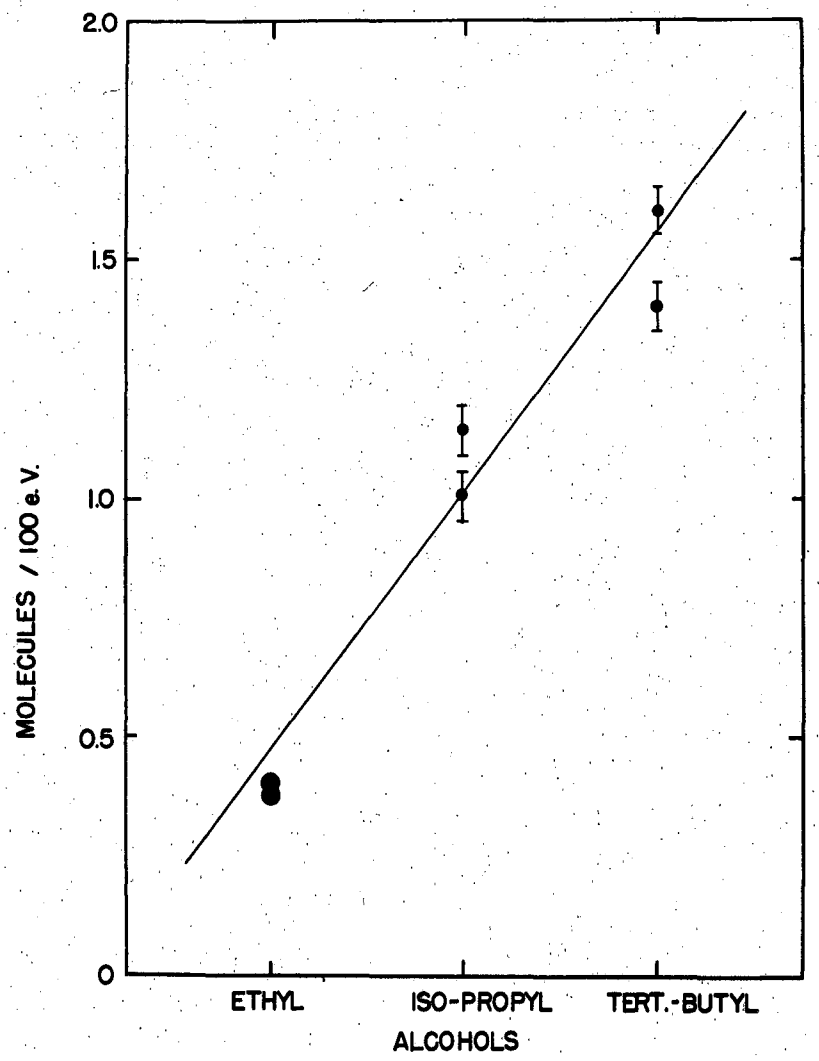

FIG. 12 YIELDS OF METHANE IN IRRADIATED ETHYL, ISO-PROPYL, AND TERT.-BUTYL ALCOHOLS

MU 2016

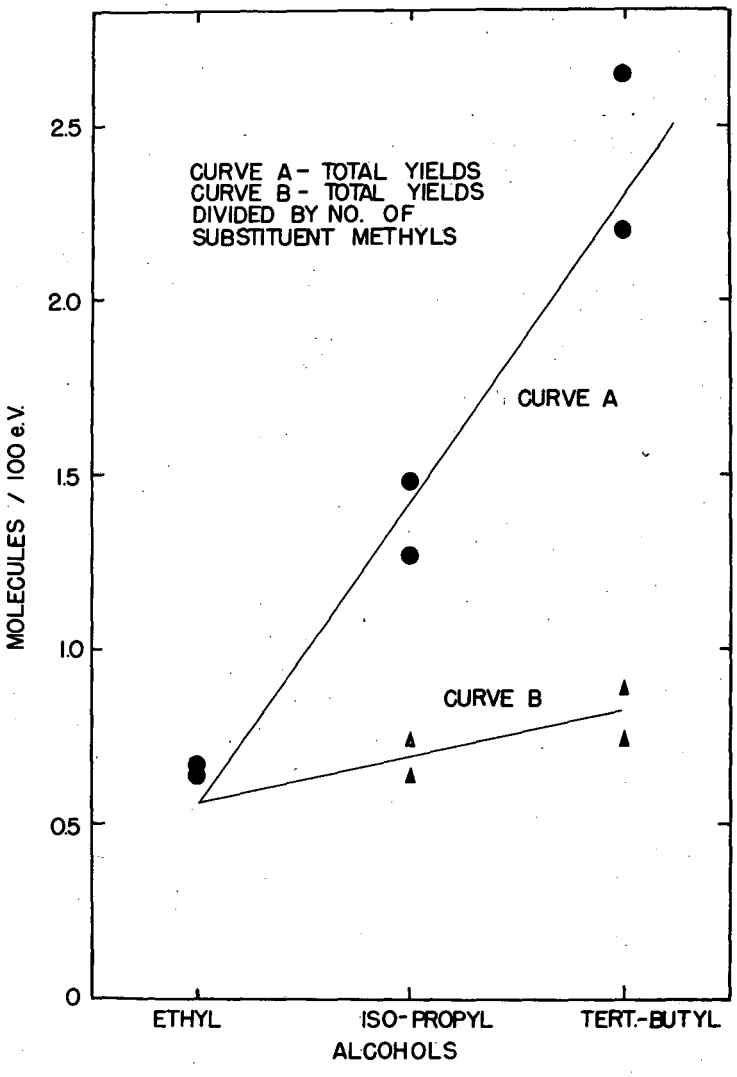

FIG. 13 SUM OF THE YIELDS OF METHANE PLUS TWICE THE YIELDS OF ETHANE FOR IRRADIATED ETHYL, ISO-PROPYL AND TERT.-BUTYL ALCOHOLS

MU 2017

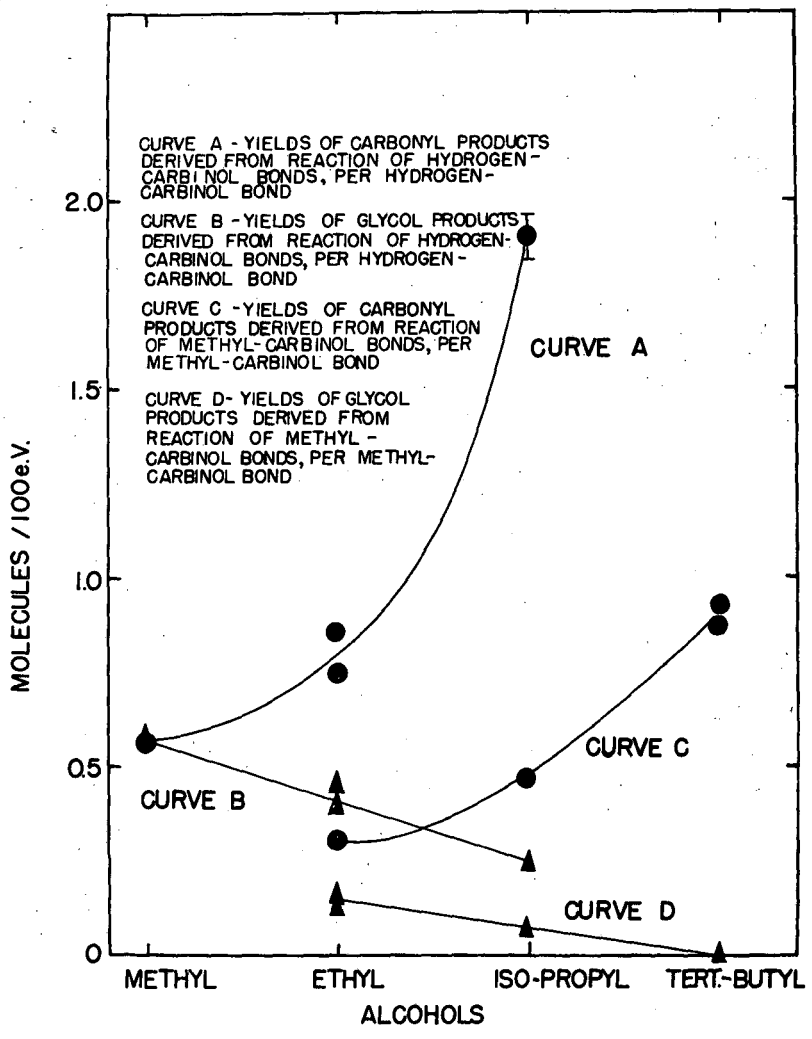

FIG. 14 YIELDS OF CARBONYL AND GLYCOL PRODUCTS IN IRRADIATED METHYL, ETHYL, ISO-PROPYL AND TERT.-BUTYL ALCOHOLS

MU 2018

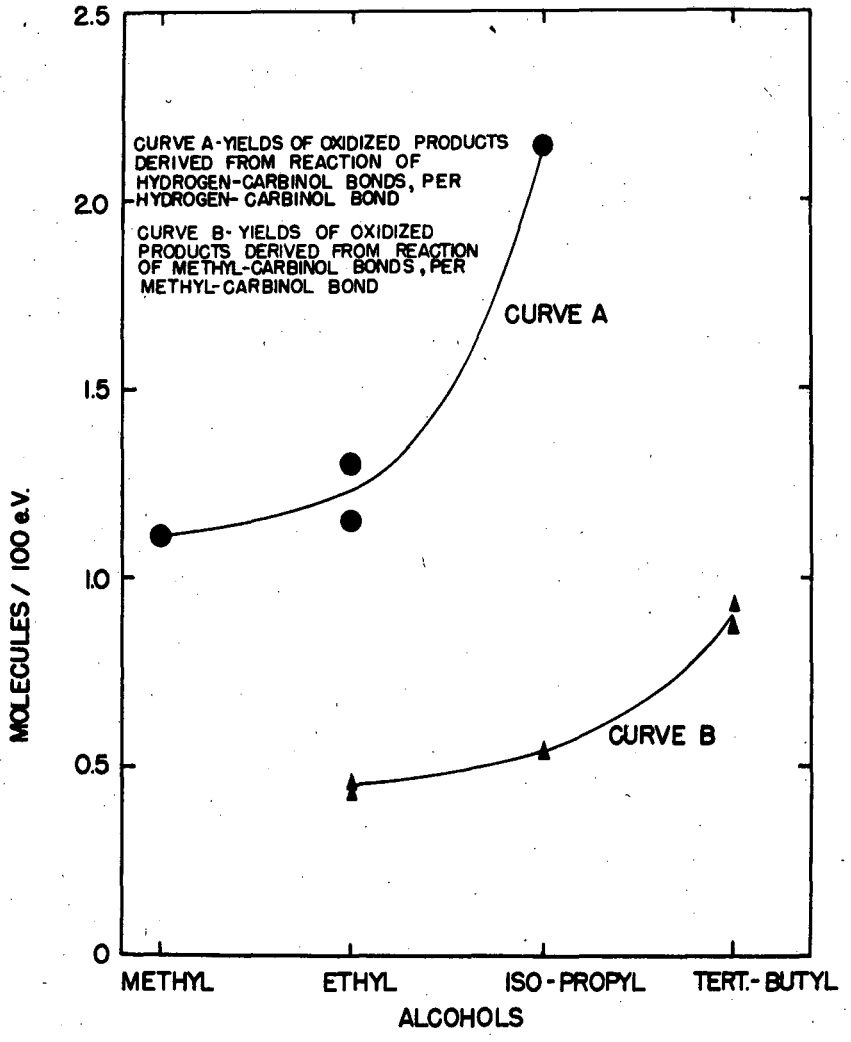

FIG. 15 YIELDS OF CARBONYL AND GLYCOL PRODUCTS IN IRRADIATED METHYL, ETHYL, ISO-PROPYL AND TERT.-BUTYL ALCOHOLS

MU 2019