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RADIATION CHEMISTRY OF ISOPROPYL COMPOUNDS

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RADIATION CHEMISTRY OF ISOPROPYL COMPOUNDS

Michael A. Sweeney

(Ph. D. Thesis)

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ABSTRACT

Purified, degassed samples of eight organic liquids--isopropyl chloride, isopropyl alcohol, isopropyl benzene, isobutyronitrile, isobutyric acid, isovaleric acid, methyl isobutyl ketone, and isopropyl acetate--were irradiated with 48-Mev helium ions and with gamma rays from a cobalt-60 source. The volatile radiolysis products were separated and analyzed. Formation of these products is explained by free-radical reactions and by molecular rearrangements of the type $i\text{-}C_3H_7X = HX + C_3H_6$. The differences in respective product yields between the two types of radiation were in accord with the proposed decomposition patterns. Products considered to be formed by radical-radical reactions were found in larger yield in the more densely ionizing helium-ion irradiations; cobalt-60 irradiations formed larger amounts of products considered to result from radical-molecule reactions. Molecular rearrangement to form HX plus propylene occurs in these radiolyses. For several of the compounds studied it is a major source of radiolytic product. The extent of rearrangement in any given compound depends on the electronic nature of the molecule and on the mechanism by which the rearrangement occurs.

INTRODUCTION

Radiation chemistry is the study of the chemical effects of ionizing radiation. It is related to photochemistry, which is the study of the chemical effects of much less energetic radiation. In photochemistry, molecules are excited to one of a limited number of electronic excited states. This excitation normally occurs randomly throughout an irradiated substance, although intensity gradients can exist in strongly absorbing substances. In radiation chemistry, molecules are ionized or are excited to any of their possible excited states by the radiation. The ionization and excitation are not random, but occur along the tracks of the ionizing particles which transfer energy to the irradiated substance.

The radiation chemistry of many organic and inorganic substances has been investigated. Gases, liquids, and solids have been irradiated, both in the pure state and as mixtures. The field of interest of this work is the radiation chemistry of some pure organic liquids.

Some workers have attempted, in studies of the radiation chemistry of organic liquids, to investigate the initial interaction of radiation with the substance studied. Electron magnetic resonance spectra and optical spectra of the radicals initially produced by radiation have been investigated. Another technique is to add chemicals such as iodine, nitric oxide, ethylene, and diphenylpicrylhydrazyl to organic liquids, in order to scavenge free radicals produced by irradiation of the system. The initial ions produced by electron irradiation of gases are studied by organic mass spectrometry.

Most studies, however, adopt the method used in this work. The stable products formed during irradiation of an organic liquid are measured, and their mode of formation may then be inferred. Often several organic compounds of a generic series--a series of alcohols, for example, or of aliphatic acids--are studied in order to determine the effect of chain branching and chain length on the manner in which the molecules decompose. In this investigation a series of compounds with a similar carbon framework (the isopropyl group) but with different functional groups was studied. The specific compounds chosen were isopropyl chloride, isopropyl alcohol, isopropyl benzene, isobutyronitrile, isobutyric acid, isovaleric acid, methyl isobutyl ketone, and isopropyl acetate.

The goal of the work was (a) to determine how the pattern of radiolytic decomposition varied among these substituted compounds, (b) to investigate the effect of changing radiation type on these decomposition patterns, (c) to find out whether certain molecular rearrangements occurred in the decomposition of the different molecules, and (d) to learn how the nature of the substituent group affected the relative importance of these rearrangements.

The isopropyl group was chosen as the common carbon framework for several reasons. Radical reactions in the radiolysis of larger compounds would have become intolerably complex; because no ethyl radicals are produced during the irradiation of isopropyl compounds, the yield of ethane could be used as a measure of radical-combination reactions; many chemical rearrangements proceed through β hydrogens, and there are six of these in isopropyl compounds; the isopropyl compounds have physical properties well suited to the experimental techniques available in this Laboratory.

The substituents were chosen to span a wide range of electronic properties and to exhibit tractability toward the experimental techniques employed. Methyl isobutyl ketone and isovaleric acid, which may only indirectly be considered substituted isopropyl compounds, were irradiated because evidence from photolysis and mass spectrometry indicates that molecular rearrangement should be an important process in the decomposition of these molecules.

The technique used in this work was as follows. Purified, degassed samples of the organic liquids were irradiated in vacuo with 48-Mev helium ions and with Co^{60} γ rays. The volatile products were separated and were analyzed by means of mass spectrometry and vapor-phase chromatography. Yields of these products are reported in terms of G values--the number of molecules of product formed per 100 electron volts of energy absorbed by the sample.

Once these product yields are determined, a decomposition pattern may be proposed for each compound. These decomposition patterns fulfill the first goal of this work. In order to achieve the second goal, the extent of molecular rearrangement must be determined. This is accomplished by use of the differences in yield between He^{++} irradiations and Co^{60} irradiations. The contribution to the formation of certain products from molecular rearrangement may be separated from the contribution from radical-radical reactions by means of these differences in yield.

In the pages that follow, the techniques of purification, irradiation, and analysis are described in detail. Next the experimental results are presented, and the effect of experimental conditions on these results is discussed. The processes by which ionizing radiation causes chemical decomposition are outlined, and in succeeding sections

a decomposition pattern for each compound is derived from product yields. Finally, the effect of molecular structure on the extent of molecular decomposition observed in these compounds is discussed.

EXPERIMENTAL PROCEDURE

Starting Materials and Purification

General

Most of the organic chemicals used in this work were purified by fractional distillation. Where applicable, a vacuum-jacketed column 6 feet long and packed with Podbielniak No. 3013 stainless steel helices was used for the distillation. Its efficiency when operated at total reflux was 84 theoretical plates. Some compounds decomposed when distilled on the stainless steel packing of this column. These compounds were distilled in a similar, shorter column of 36 theoretical plates, packed with 3-mm glass helices.

In either case, the progress of the distillation was monitored with a Leeds and Northrup recording resistance thermometer. This thermometer, calibrated against a thermometer calibrated by the National Bureau of Standards, made it possible to measure the temperature of the vapors at the top of the column to within 0.002°.

The basic procedure was the same for all distillations. The crude material to be distilled was added to the pot and blanketed with a flow of dry nitrogen. The liquid was heated to its boiling point and the column was operated at total reflux until the temperature at the top of the column reached an equilibrium value. A few milliliters of the equilibrium mixture at the column head, consisting mainly of low-boiling impurities, was collected. This caused an abrupt rise in the recorded temperature. Further operation at total reflux caused the temperature to decrease slowly to a new equilibrium value. Another small sample of impurities was collected, and the process was repeated until the removal of product caused only a small change in the vapor temperature.

Then the column was operated at a reflux ratio between 1000/1 and 100/1 until the vapor temperature was not affected by the reflux conditions under which the column operated. At this time the product collection was started.

The composition of the liquid being delivered was monitored continually by vapor-phase chromatography. The chromatographic columns used were constructed of 5-mm Pyrex tubing and were either 2 or 4 meters long. The choice of stationary phase was dictated by the nature of the sample and of the impurities it contained. For general purposes, dinonyl phthalate or General Electric silicone fluid 9640 adsorbed on 40-60 mesh Sil-O-Cel firebrick was found to be adequate. For high-boiling liquids, Fluorolube HG 1200 from the Hooker Electrochemical Co. was also used as the stationary liquid. A stationary phase of dinonyl phthalate absorbed on 40-60 mesh Fluoropak 80 of the Fluorocarbon Co. was found to give excellent results in the detection of water: more sensitive and less laborious than the conventional Karl Fischer titrations.[1] Helium was used as the carrier gas. Column temperatures ranged from room temperature to 153° C, depending on the requirements of the analysis.

So as long as constancy of boiling temperature and the absence of extraneous peaks in chromatograms of samples indicated delivery of a pure product, the compound was distilled at a reflux ratio of approximately 10/1. If the vapor temperature began to rise, or if chromatograms indicated the presence of a higher-boiling impurity in the product, the distillation was stopped. It was otherwise continued until approximately 10% of the original charge was left undistilled. This procedure yielded high recoveries of extremely pure product. The boiling ranges of the purified compounds are indicated by the standard deviations listed in Table I (page 11).

The purity of the product was measured cryoscopically by the method of Glasgow, Streiff, and Rossini.[2] The freezing curve of temperature versus time was measured with a platinum resistance thermometer, and the purity was calculated from the slope of the freezing curve. The freezing points and purities determined in this way are listed in Table I. Also listed are the refractive index, and the purity as measured by vapor-phase chromatography, for each compound.

The specific purification procedure used for each compound is described below.

Isopropyl Chloride

Isopropyl chloride was purified by a modification of the method of Cowley and Partington.[3] Two liters of Eastman Kodak White Label isopropyl chloride was washed with 250 ml of 5% Na_2CO_3 solution and then with 750 ml of water. The chloride was then shaken with 150 g of anhydrous $CaCl_2$ for 40 min. It was allowed to stand over 150 g P_2O_5 overnight and was then fractionally distilled on the glass column.

Isopropyl Alcohol

Two liters of Baker and Adamson 98% isopropyl alcohol was shaken for 40 min with 75 g of Drierite (anhydrous $CaSo_4$), and filtered into a flask containing 5.4 moles of CaO which had been ignited for 12 days at 910° C. The mixture was refluxed for 16 days in a system protected from atmospheric moisture. The dry isopropyl alcohol was filtered quickly and distilled on the stainless steel column. Only traces of water remained in the pot charge, and these were removed in the distillation.

Isopropyl Benzene

Two liters of Phillips Pure Grade isopropyl benzene was refluxed over sodium for 2 days and then fractionally distilled from the sodium

on the stainless steel column. Pure product was obtained, but it developed impurities upon standing in contact with the atmosphere. The purification was repeated, using the same procedure, and the product was degassed within 12 hours of collection. It was sealed in ampoules under vacuum and stored in the dark. Subsequent tests showed no detectable impurities after months of storage.

Isobutyronitrile

Two liters of Eastman Kodak Yellow Label isobutyronitrile was distilled on the stainless steel column without pretreatment. Water was removed as the azeotrope containing 23% water and boiling at 82.5° C.[4]

Isobutyric Acid

My first attempt to purify isobutyric acid was by the procedure of Schall and Thieme-Wiedtmarckter.[5] This method uses the mixed anhydride of an organic acid and boric acid as a dehydrating agent. The mixed anhydride is refluxed with the acid, and any water present reacts with the anhydride to give boric acid plus the organic acid.

The mixed anhydride used in this attempt was tri-isobutyryl boron, prepared according to the method described by Pictet and Geleznoff:[6] 2 moles of boric acid and 10 moles of isobutyric anhydride were heated to 130° C for an hour and then cooled in an ice bath. The resulting precipitate was filtered, washed with isobutyric anhydride, and recrystallized from an isobutyric acid-ether mixture. One mole of pure crystalline tri-isobutyryl boron was obtained.

In this first attempt at purification, two liters of Eastman Kodak White Label isobutyric acid was refluxed for a day with 220 g of the tri-isobutyryl boron, and then distilled on the stainless steel column. Chromatograms showed that impurities were present in the

product throughout the distillation. The boiling point of the vapor fluctuated, reaching 154.25° C at the highest rate of delivery. The literature value is 154.70° C.[7] This behavior indicated decomposition of the acid on the stainless steel packing of the column.

Another distillation on the glass column, using the mixed anhydride as a dehydrating agent, again yielded impure product. Less decomposition occurred in this distillation, and the boiling point at the highest rate of delivery was 154.54° C. A third distillation without the mixed anhydride showed the same behavior.

Pure acid was finally obtained by a reduced-pressure distillation of Matheson, Coleman, and Bell isobutyric acid on the glass column. Pressure during the distillation was maintained at 10 ± 1 mm of Hg by two Cartesian divers connected in series to a mechanical forepump. The mixed anhydride was not used because it caused bumping, but water was almost completely removed as the azeotrope.[4] The collected product was shown on analysis by VPC (vapor-phase chromatography) to contain only 0.06 mole % water. It has been established that product yields measured in aqueous solutions of acetic acid and extrapolated to 100% acid are the same as product yields measured in dry acetic acid.[8] Therefore the small amount of water in the isobutyric acid should be unimportant.

Isovaleric Acid

Analysis of Eastman Kodak White Label isovaleric acid (β-methyl butyric acid) by VPC indicated 1% water and 1% isobutyric acid to be the only impurities present. Cryoscopic tests on the acid, however, indicated the presence of more than 10% of an unidentified impurity.

Analysis on different VPC columns and at different temperatures failed to resolve this impurity, showing that it had essentially the same boiling point and adsorptive characteristics as the isovaleric acid. It was decided that the impurity must be α-methyl butyric acid, whose boiling point (176.5° C)[9] is the same as that of the isovaleric acid.[10]

The radiolyses performed by Johnsen indicate that the behavior of these two acids under irradiation can be assumed to be similar.[11] The chemical separation of the two isomeric acids is difficult and unpleasant. It was avoided by estimating how much of the measured product yields actually came from the isovaleric acid, and how much came from the impurity. (Table VII will show how this procedure was applied.)

Water was removed as the azeotrope during degassing. Analysis by VPC showed no detectable water in the degassed liquid.

Methyl Isobutyl Ketone

Braun-Knecht-Heimann methyl isobutyl ketone was shown to be pure by VPC and by cryoscopic analysis. It was dried by contact for 42 hours with Na_2SO_4 which had been heated in vacuum to 350° C for 16 hr. The last traces of water were removed as the azeotrope during the degassing.

Isopropyl Acetate

Two liters of Eastman Kodak Yellow Label isopropyl acetate was purified according to the method of Haggerty and Weiler.[12] The ester was shaken with 400 ml of 10% Na_2CO_3 solution, then with 400 ml of 10% $CaCl_2$ solution, and again with 400 ml of 5% $CaCl_2$ solution. It was allowed to stand overnight with 300 g of anhydrous $CaSO_4$. It was then filtered and distilled on the stainless steel column. Water was removed as the azeotrope containing 10.6% water and boiling at 76.6° C.

Table I. Properties of purified compounds

Property	Isopropyl chloride	Isopropyl alcohol	Isopropyl benzene	Isobutyro-nitrile	Isobutyric acid	Isovaleric acid	Methyl isobutyl ketone	Isopropyl acetate
Freezing point (°C, ±.005° C)	-117.143	-88.226	-96.026	-70.561	-46.433	-34.4	-80.387	-73.329
Freezing point (literature)(°C)	-117.18[a]	-88.53[b]	-96.028[c]	-71.5[d]	-46.1[e]	-30.0[f]	-83.5[g]	-73.4[g]
Boiling point (°C)	34.991 ±.004	82.341 ±.003	152.389 ±.006	103.734 ±.002	---	---	---	88.641 ±.005
Boiling point (literature)(°C)	34.8[g]	82.40[e]	152.393[c]	103.85[d]	154.70[e]	176.50[f]	115.65[h]	88.2[i]
n^{25}_D (observed, ± .0001)	1.3748	1.3753	1.4889	1.3712	1.3910	1.4014	1.3939	1.3749
n^{25}_D (observed, literature)	1.3749[a]	1.3747[j]	1.48892[c]	---	---	---	1.3933[k]	---
n^{25}_D (calculated from lit. value at other temp.)	---	---	---	1.3712[d]	1.3908[ℓ]	1.4013[m]	---	1.3750[n]
Purity (from fp) (mole % ± .01%)	100.00	100.00	99.99	99.99	99.95	<90	99.97	100.00
Purity (from VPC) (mole % ± .01%)	100.00	99.99	100.00	100.00	99.94	98.38	99.99	100.00

a from Ref. 13
b from Ref. 14
c from Ref. 15
d from Ref. 16
e from Ref. 17
f from Ref. 10
g from Ref. 17
h from Ref. 18
i from Ref. 12
j from Ref. 19
k from Ref. 1
ℓ from Ref. 20
m from Ref. 129
n from Ref. 130

Degassing

Dissolved air was removed from the liquids by refluxing under vacuum as described by Newton.[21] The apparatus is shown in a generalized form in Fig. 1. The liquid to be degassed was added to the flask F, which contained a Teflon-covered magnetic stirring bar. The Dewar jacket above the flask was filled with a cold bath at a temperature somewhat above the freezing point of the liquid. A slush bath of dry ice in trichlorethylene was commonly used.

The flask was then precooled to prevent bumping, and the system was gradually evacuated through stopcocks A and B until the liquid began to boil. The vapor then condensed on the cold walls of the tube. While the liquid thus refluxed, dissolved gases were released and pumped away. Pumping and refluxing continued until the pressure in the manifold system beyond stopcock A showed no change when the stopcocks were closed for 15 minutes and then reopened.

The cooling bath was next removed from the Dewar jacket above the flask and 5 or 10 ml of liquid was distilled into the trap T. For isovaleric acid and the ketone, which had not been distilled prior to degassing, more than 25 ml of liquid was allowed to collect in the trap. Then stopcock B was closed, and the vessels attached to the manifold could be filled one at a time with the desired amount of liquid by cooling them with a suitable slush bath. After each was filled, the flask F was cooled and the vessel was sealed off. For the alcohol, ester, and ketone there was no danger of contamination with stopcock grease (which is not soluble in them). Therefore a stopcock between

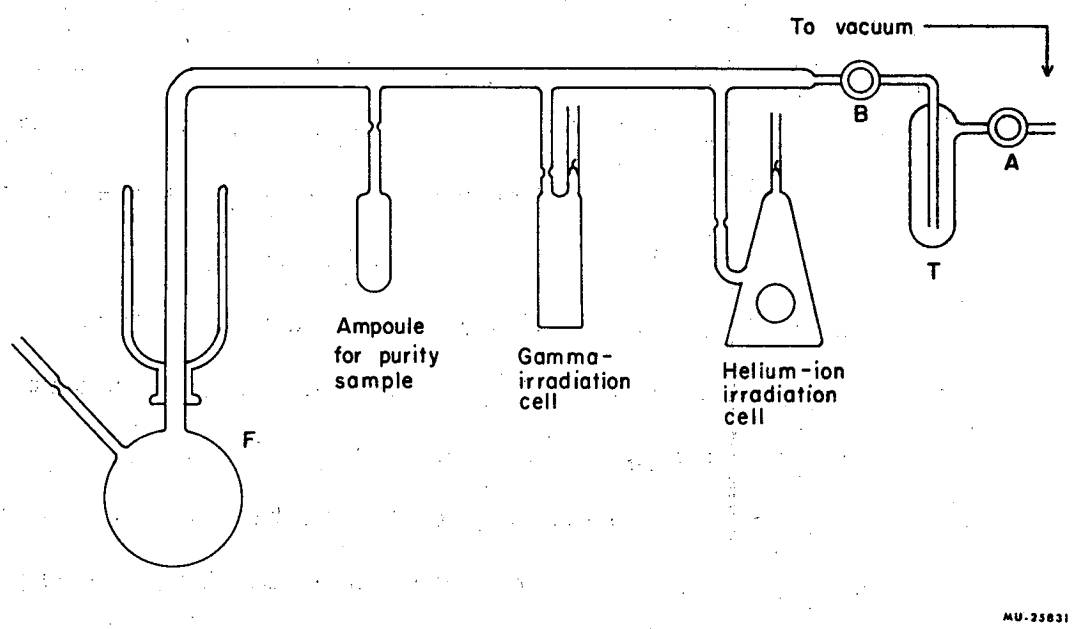


Fig. 1. Apparatus for degassing a target liquid and loading it into irradiation cells.

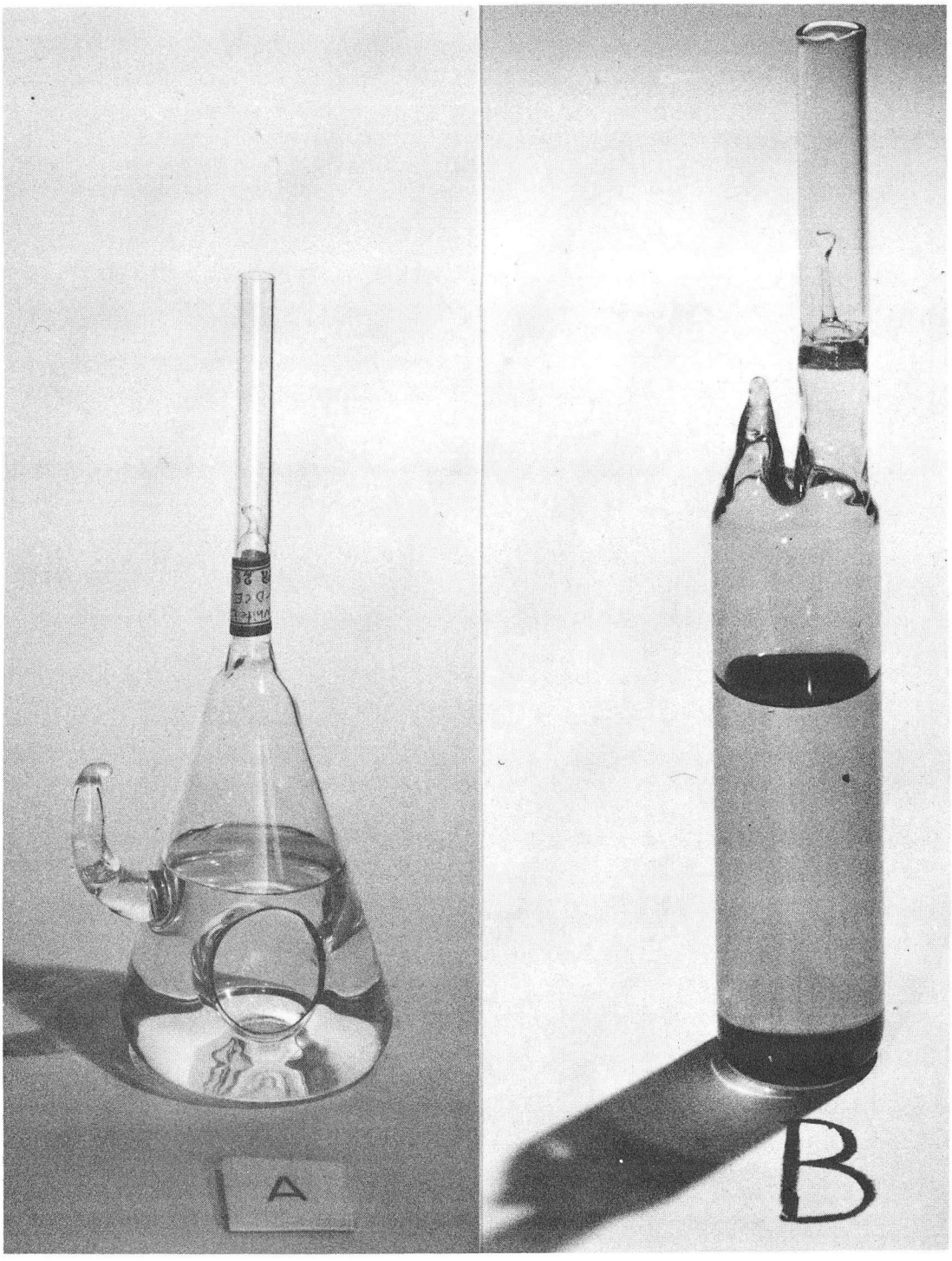
the flask F and the vessels was used to eliminate the necessity of cooling F while sealing off each vessel.

Target Vessels

Two types of target vessel were used, depending on the type of radiation employed. For helium-ion irradiations, the target vessels were modifications of those described by Garrison, Haymond, and Weeks.[22] One such vessel is pictured in Fig. 2A and shown schematically in Fig. 1. It consists of a 200-ml Erlenmeyer flask with a concave window blown into its side for entry of the beam of helium ions.

Each vessel was provided with two outlets. One of these was closed with a hook seal which allowed access to the contents of the flask after irradiation. The other was a sidearm which was used to fill the vessel to a level above the top of the beam window, and which was sealed off after filling. An expansion volume for gaseous products was left above the level of the liquid. After filling, the vessels contained 110 to 140 ml of liquid, and the free gas volume was 30 to 50 ml.

The vessels used for gamma irradiations were cylindrical Pyrex ampoules 1 in. in diameter and 3 in. tall. Each was fitted with a hook seal, and with a constricted opening through which it was filled with approximately 18 ml of liquid. An expansion volume of approximately 12 ml remained above the liquid. One such vessel is pictured in Fig. 2B, and is shown schematically in Fig. 1.



ZN-3051

Fig. 2. Irradiation cells.
(a) For cyclotron irradiation.
(b) For cobalt-60 irradiation.

Irradiation Sources

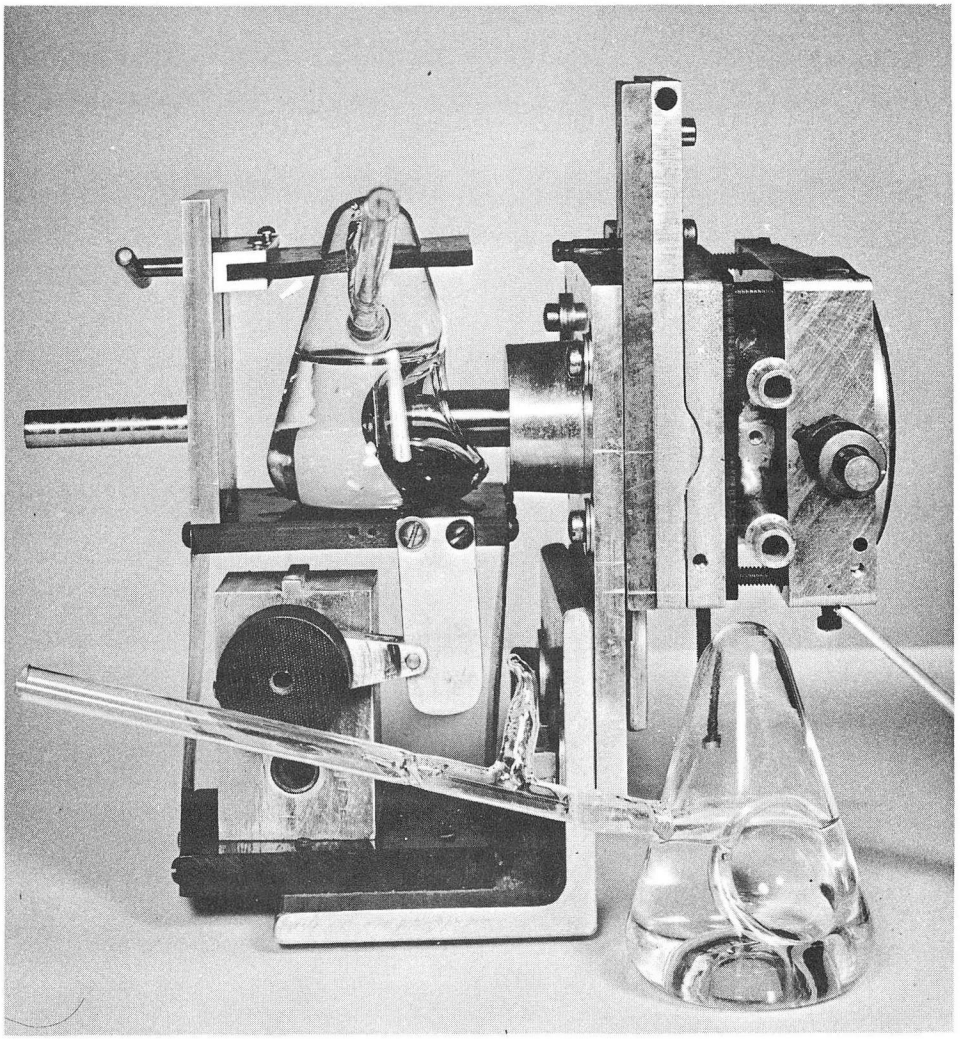
Helium Ions

The external beam of the 60-inch Crocker Laboratory cyclotron was used for helium-ion irradiations. The beam energy was slightly less than 48 Mev. The helium ions were degraded in energy by passage through (a) an aluminum foil window which isolated the cyclotron vacuum from the atmosphere, (b) the air space between this foil and the target vessel, and (c) the glass window of the target vessel. The energy loss caused by passage of the helium ions through these absorbers was calculated, and the energy of the beam impingent on the liquid was calculated for each target vessel.[23] This energy was between 40 and 43 Mev for the vessels used. Helium ions of this energy have a range of 2 to 3 mm in these liquids, and so were completely absorbed in the target.[23]

The total energy input was determined by measuring the accumulation of charge in the target vessel. While the beam was off, the target vessel was isolated electrically from its surroundings. When the beam was on, the column of ionized air which it produced created a conducting path from the target vessel to the cyclotron snout. The snout was connected to integrating meters which measured the total charge input.

Most of the samples irradiated in this work received absorbed doses of between 2×10^{20} and 10×10^{20} ev/ml absorbed in the liquid. Higher doses were required to form enough product for accurate measurement from certain compounds, in particular isopropyl benzene and isobutyronitrile. The beam current was kept below 0.35 μa for most irradiations.

The target was shaken vigorously during bombardment to reduce localized heating and to prevent local accumulation of radiolysis products. The shaker assembly used for this purpose is shown in Fig. 3.



ZN-1971

Fig. 3. Shaker assembly used in cyclotron irradiations.

The temperature of the target liquid was maintained near room temperature by an air blast during irradiation.

Gamma Irradiations

The 2000-curie (nominal) cobalt-60 source described by Tolbert et al. was used for the gamma irradiations.[24] The source consists of a group of parallel "pencils" of Co^{60}, each 1.5 in. long and 1/8 in. in diameter. These are arranged in the shape of a cylinder 2 in. in diameter. The irradiation ampoule was placed in the center of this cylinder. The relative orientation of the target vessel and the Co^{60} during irradiation was that of a barrel partly full of liquid, surrounded by a circular picket fence. A cross-sectional drawing of the source and vessel is shown in Fig. 4.

The energy input was measured with the Fricke dosimeter described by Weiss, Allen, and Schwartz.[25] The value of $G_{Fe^{+++}}$ which these workers reported was 15.45. The dose rate in the 0.8 N H_2SO_4 solution used in the Fricke dosimeter was found to be 2.08×10^{18} ev/ml/min for a liquid volume of 18 ml. The variation of dose rate with liquid volume was also measured, because the volume of the liquid samples irradiated in this work varied from 17 to 20 ml.

Most samples were irradiated for 5 to 15 hours, corresponding to an absorbed dose of between 4×10^{20} and 12×10^{20} ev/ml. Radiation-resistant compounds required longer irradiations. Compounds for which certain product yields showed a strong dependence on energy input were irradiated for shorter periods of time.

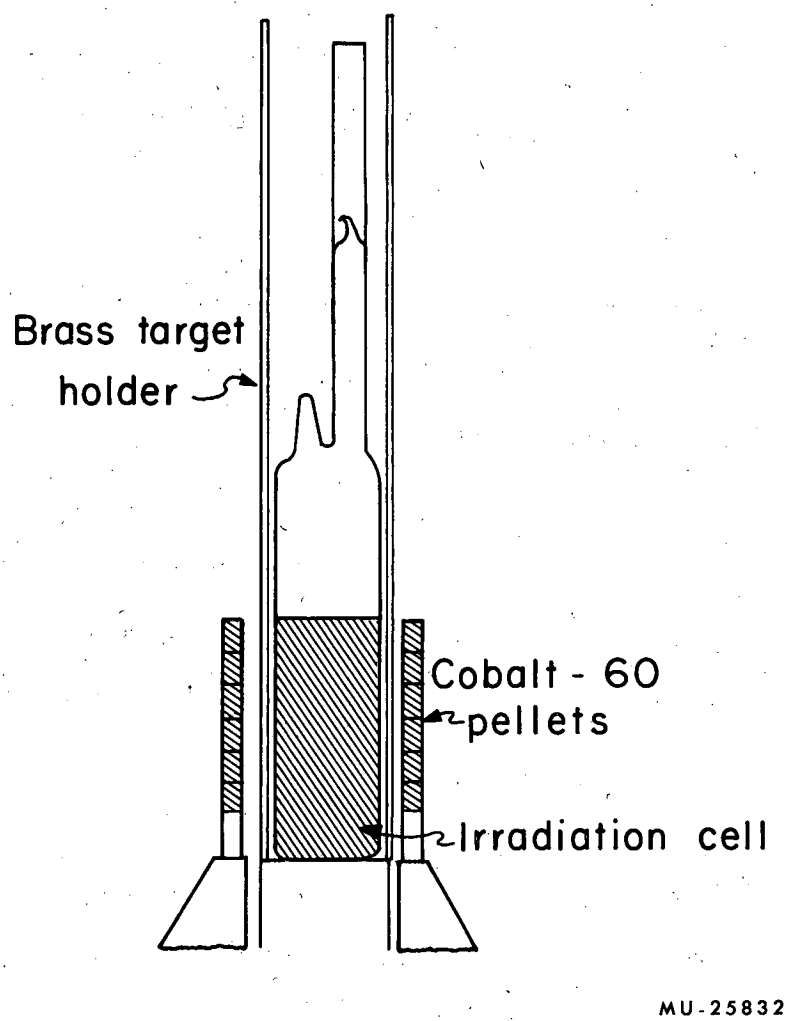


Fig. 4. Cross-sectional drawing of cobalt-60 source and target cell.

Analysis of Products

Separation of Gaseous Products

After irradiation, gaseous products were separated from the irradiated liquid by a method similar to that used for the degassing. The apparatus is shown schematically in Fig. 5. It was composed of, from left to right, (a) a flask for refluxing the liquid under vacuum, (b) a system of traps to separate the gaseous products into fractions according to their volatility, (c) a Toepler pump to transfer these gases to (d) a gas buret, thermostatted at 25.0°, where the pressure and volume of each fraction were measured, and (e) a sample bulb, into which the gases were forced after measurement.

The target vessel was sealed onto the system as shown and the whole system was evacuated. The reflux Dewar was filled with an appropriate slush bath near the freezing point of the irradiated compound, and the stopcocks D and E were closed. The hook seal on the target vessel was broken with a gold-plated iron hammer, and the liquid in the vessel drained into the flask F. With liquid nitrogen traps at A and B, stopcock D was opened, and a portion of the gaseous products entered A and B. D was closed and E was opened, and the gases volatile at -196° were pumped into the gas buret with the Toepler pump. Condensable gases remained in the traps.

After several repetitions of this procedure the pressure in the flask was reduced to a level that allowed the liquid to reflux under vacuum. Dissolved gases were released, and were collected in the traps whenever D was opened. These steps were continued until no more gas could be pumped through the liquid nitrogen traps. The pressure of

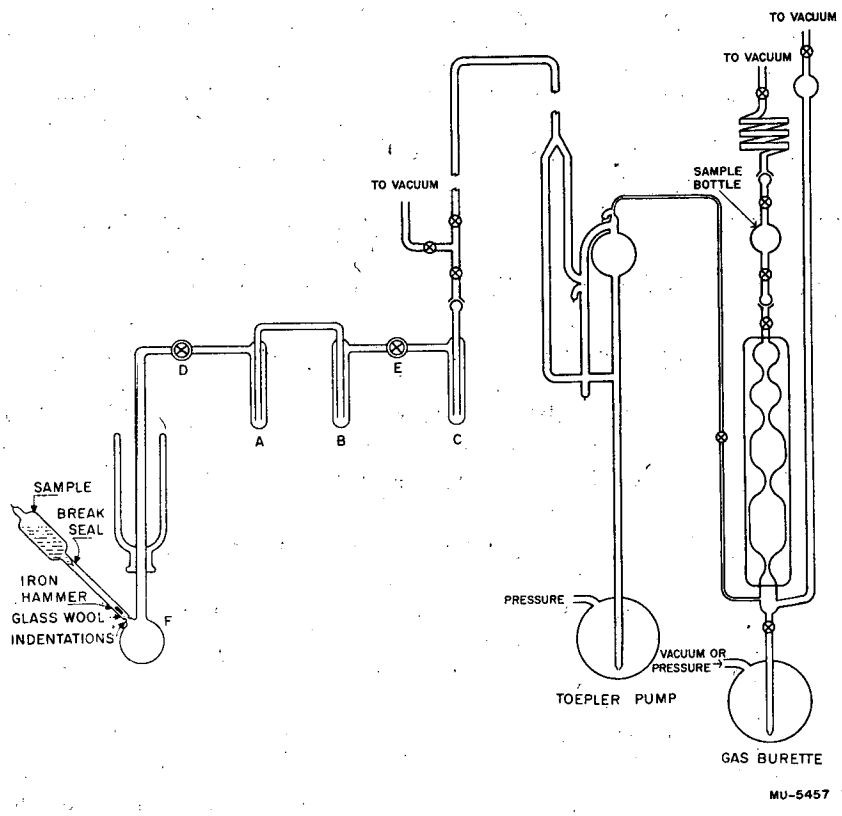


Fig. 5. Apparatus for separation of the volatile products from an irradiated liquid.

the gas in the gas buret was measured at several volumes. After measurement this fraction was pushed into the detachable bulb by raising the mercury in the gas buret. The bulb was saved for analysis of the gases.

The liquid was allowed to reflux for several hours with stopcock E closed. Stopcock D was opened intermittently to remove gaseous products from the flask as they were released from the liquid. The liquid nitrogen trap was removed from B, and all the product gases condensed in A.

The condensable gases were then further fractionated by putting an ethyl bromide slush bath (about -120°) at trap B with D closed and E open, removing the liquid nitrogen trap from A, and placing it at C. The gases with appreciable vapor pressure at -120° were pumped through B into C, while the higher-boiling gases condensed in B. Stopcock E was then closed and the products in C were warmed and pumped into the gas buret. Meanwhile the condensed products were returned to A so that the process might be repeated. As soon as all the gases in this fraction were collected, the gas in the buret was measured and then pushed into a new bulb.

A third fraction, usually of gases volatile at dry ice temperature, was then collected in a similar manner. The liquid that would not pass through the CO_2 trap was transferred to a graduated receiver attached to the system by a standard taper joint. The receiver was removed, capped, and saved for analysis. The liquid left in the flask was poured into a bottle and saved.

HCl Analysis

A modification of this process was necessary in the separation of the products of isopropyl chloride. The HCl formed in the irradiation

is collected in the -120° fraction, but cannot be analyzed with the other gases because it is strongly adsorbed in the mass spectrometer inlet system.

A method described by Futrell for the determination of HCl was employed.[26] The -120° fraction was collected in a bulb equipped with a sidearm which was filled with KOH pellets prior to evacuation. After the gases were added to this bulb, it was removed from the system and the pellets were shaken from the sidearm into the main portion of the bulb. The bulb was then set aside during the rest of the separation (from 1 to 3 hours).

Then the bulb was attached to the manifold and its contents, with the HCl removed by reaction with the KOH, were pumped into the gas buret. Water was removed by passing the gases through a trap at -78° C. between the bulb and the gas buret. The new volume and pressure of the gases were measured, and the gases transferred to a new bulb. The difference between the amount of gas before and after the KOH treatment was a measure of the HCl formed in the irradiation. Gravimetric analysis for Cl^- in the KOH left in the bulb was used as a check on the gas measurement. The values for HCl formation as determined by the two methods agreed within 1.5% for all determinations.

Instrumental Analysis

All analyses were performed on a Consolidated Engineering Corporation model 21-103A mass spectrometer. Whenever these analyses were ambiguous or were insensitive to certain constituents, an aliquot of the gas was analyzed by vapor-phase chromatography. The apparatus used is described above under "Purification".

In the VPC analyses, the mixture of gases was separated into its constituents on the chromatographic column. Each constituent was collected in a separate trap when it emerged from the end of the column. These collected products were then identified by analysis of the contents of each trap on the mass spectrometer. The identification of a constituent was verified by its elution time. For subsequent analyses of gases from other irradiations of the same compound, the constituents were characterized only by their elution time.

Analysis of the mass spectral records and of the chromatograms gives the percentage of each constituent of the mixture. The total number of millimoles of gas in each fraction is calculated from the measured pressure and volume at the given temperature.

EXPERIMENTAL RESULTS

Yields of volatile products are listed in Tables II through IX. (Data from work performed by other investigators are listed in the appropriate table for comparison with this work.) Certain products were only partially collected in the separation process. Although the detection of these products is noted in the Tables, G values for their formation are not reported. Dependence of the yields of the more important products on total energy input is presented graphically in Figs. 6 through 13. Table X summarizes the data for all the compounds studied.

Calculation of Yields

Product yields are reported in terms of G values: the number of molecules of each product formed per 100 electron volts absorbed by the target liquid. The raw data from the analyses are in the form of millimoles of each product formed. To obtain G values the energy input into each sample must be determined.

For the He^{++} irradiations, this is a direct process. The number of microcoulombs of charge accumulated in the target was measured. This is equivalent to a certain number of electronic charges, and therefore to one-half that number of helium ions. The energy of each helium ion impingent on the liquid is also known (see Irradiation Sources), and the total energy input is easily calculable:

$$G = \text{millimoles} \times (6.023 \times 10^{20})/(\text{energy input in units of 100 ev}).$$

Table II

isoPropyl Chloride

Hundred Electron Volt Yields of Volatile Products (G Values)

Product	Electron Volts absorbed per cc of Sample ($\times 10^{-20}$)										
	Helium Ion Irradiations					Cobalt-60 Irradiations					Ref. 44 (b)
	0.0[a]	1.83	4.12	5.92	5.88	0.0[a]	0.81	4.12	7.97	12.68	
H_2	1.31	1.29	1.31	1.32	1.32	1.31	1.30	1.24	1.15	1.14	
CH_4	.24	.21	.24	.25	.25	.25	.24	.25	.25	.22	
C_2H_6	.01	.006	.011	--	.012	.003?	--	--	.004	.001	
C_2H_4	.055	.050	.070	.057	.056	.03	.039	.083	.021	.032	
C_2H_2	.059	.055	.068	.062	.053	.03?	.032	--	.013	.010	
C_3H_8	1.14	.90	1.14	1.16	1.12	3.38	3.14	3.33	3.16	2.97	
C_3H_6	2.68	2.43	2.57	2.52	2.11	~2.16	1.86	.92	.53	.35	
C_3H_4[c]	.065	.068	.056	.032[d]	.059	.03?	.041	.014	.015	.007	
iC_4H_{10}	.040	.037	.038	--[d]	.054	.02	.03	.01	.02	.01	
iC_4H_8	.002	--	.002	--[d]	.003	.002	.002[d]	--	.001	--	
CH_3Cl	.030	.030	.025	.029	.031	.03?	.037	.016	.029	.031	
$CH_2{:}CHCl$	.04	.041	.028	.011[d]	.038	.04	.050	.004	.008	.007	
$CH{:}CCl$	.003	.001	.002	.004	.003	.001	--	--	.001	--	
HCl	5.13	5.21	5.11	5.06	5.09	5.55	5.52	5.06	4.70	4.24	4.7±.6

Products detected but not measured quantitatively: CH_3CH_2Cl, $CH_3CCl{:}CH_2$.

(a) Extrapolation of observed yields to zero dose. See Figure 6.

(b) Average of eight runs from 9.3×10^{20} to 30.8×10^{20} ev/cc; Co^{60} irradiation.

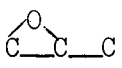
(c) Analytical method will not distinguish between $CH_3{:}CH$ and $CH_2{:}C{:}CH_2$

(d) Minimum yields.

Table III

isoPropyl Alcohol

Hundred Electron Volt Yields of Volatile Products (G Values)

Product	Electron Volts absorbed per cc of sample ($\times 10^{-20}$)										
	Helium Ion Irradiations			Ref. 50	Cobalt-60 Irradiations					Ref. 60	Ref. 59
	0.0 (a)	1.59	7.10	(b)	0.0	1.55	4.80	9.24	15.35	(c)	(d)
H_2	3.48	3.39	3.05	2.71	3.08	2.98	2.97	2.69	2.68	2.77	4.91
CH_4	1.35	1.24	1.46	1.14	1.68	1.68	1.65	1.75	1.62	1.65	1.45
C_2H_6	.16	.15	.17	.17	.079	.076	.078	.083	.080		
C_2H_4	.023	.026	.019	.022	.003	--	.003	.002	--		
C_2H_2	.015	.014	.017	.019	.002	.005?	.002	.001	--		
C_3H_8	.10	.10	.10	.088	.11	.11	.10	.10	.10		
C_3H_6	.37	.36	.35	.27	.25	.19	.13	.079	.050		
C_3H_4 (e)	.022	.021	.020	--	.009	.005	.007	.005	.004		
iC_4H_{10}	.050	.049	.052	~.04	.028		.028	.028	.028		
iC_4H_8	.007	.006	.007	~.007	.002		.002	.002	.001		
CO	.04?	.040	.055	.083	.03?	.026	.019	.021	.030	small	
	.03	.02	.03	--	.03?		.04	.02	.01		

Products detected but not measured quantitatively: CH_3-O-iC_3H_7, iC_3H_7-O-iC_3H_7, C_6H_{14}, CH_3CHO, C_2H_5CHO, CH_3COCH_3.

(a) Extrapolation of observed yields to zero dose. See Figure 7.

(b) 28 Mev helium ions. Average of several runs at 55×10^{20} ev/cc.

(c) Cobalt-60 irradiation. 40×10^{20} ev/cc.

(d) Cobalt-60 irradiation. 0.04×10^{20} ev/cc.

(e) Method of analysis will not distinguish between $H_2C{=}C{=}CH_2$ and $HC{\equiv}C{-}CH_3$.

Table IV

isoPropyl Benzene

Hundred Electron Volt Yields of Volatile Products (G Values)

Product	Electron Volts Absorbed per cc of Sample ($\times 10^{-20}$)											
	Helium Ion Irradiations					Cobalt-60 Irradiations				Other Irradiations		
	0.0[a]	7.8	8.4	44.0	Ref. 70 (b)	0.0[a]	23.0	30.9	47.6	Ref. 72 (c)	Ref. 71 (d)	Ref. 69 (e)
H_2	.27	.28	.25	.26	.31	.21	.19	.18	.16	.10	.21	.17
CH_4	.075	.073	.076	.080	.078	.108	.092	.086	.080	.06	.050	.073
C_2H_6	.0038	.0038	.0035	.0039	.0054	.0016	.0012	.0012	.0020	.01	all C_2H_n= .012	all C_2H_n= .009
C_2H_4	.0028	.0024	.0027	.0036		.0010	.0010	.0016	.0005			
C_2H_2	.0085	.0089	.0078	.0081		.0032	.0033	.0031	.0032	<.01		
C_3H_8	.0069	.0072	.0065	.0067		.012	.012	.013	.012	<.01		
C_3H_6	.028	.0285	.0268	.0280		.017	.017	.017	.017	<.01		
C_3H_4[f]	.003	.0027	.0022	.0030		.001	.0011	.0010	.0013			
iC_4H_{10}	.001	.0010	.0009	.0012		.0005	.0006	.0002	.0004			
iC_4H_8	.0002	.0001	.0002	.0002		.0001	.0001	.00007	.0002			
C_4H_6[f]		.0002	.0001	.0002			.0001	.00003	.00008			
C_4H_4[f]		.0007	.0010	.0006			.0001	.00002	.0001			
C_4H_2		.0002	.0004	.00008			.00006	.00001	.00002			

Products detected but not measured quantitatively: C_6H_6, C_5H_{10}(mainly 2-ene), C_5H_8, C_5H_6.

(a) Extrapolation of observed yields to zero dose. See Figure 8.
(b) 28 Mev helium ions.
(c) 1 Mev electrons (nominal energy). Absorbed energy between 198 x 10^{20} and 305 x 10^{20} ev/cc.
(d) Pile radiation.
(e) 1.50 Mev electrons.
(f) The analytical method used would not distinguish among the different isomers with these formulae.

Table V

isoButyronitrile

Hundred Electron Volt Yield of Volatile Products (G Values)

Product	Electron Volts Absorbed per cc of Sample ($\times 10^{-20}$)							
	Helium Ion Irradiations				Cobalt-60 Irradiations			
	0.0[a]	4.08	8.77	14.64	0.0[a]	7.42	14.70	30.45
H_2	1.06	1.05	1.04	.96	.84	.82	.80	.76
CH_4	.39	.38	.38	.42	.44	.43	.46	.42
C_2H_6	.026	.026	.026	.027	.014	.013	.014	.016
C_2H_4	.032	.032	.031	.032	.023	.023	.020	.023
C_2H_2	.032	.032	.032	.032	.017	.017	.017	.013
C_3H_8	.26	.26	.26	.26	.51	.50	.49	.46
C_3H_6	.79	.78	.77	.76	.63	.60	.56	.49
C_3H_4[b]	.037	.037	.036	.037	.025	.023	.021	.018
iC_4H_{10}	.045	.045	.042	.046	.020	.019	.019	.023
iC_4H_8	.010	.009	.007	.008	.005	.005	.004	.004

Products detected but not measured quantitatively: C_6H_{14}, C_2H_5CN, HCN, CH_3CN, C_3H_7CHNH.

(a) Extrapolation of observed yields to zero dose. See Figure 9.

(b) The analytical method used will not distinguish between $CH_2{=}C{=}CH_2$ and $CH{\equiv}C{-}CH_3$.

Table VI

Isobutyric Acid

Hundred Electron Volt Yields of Volatile Products (G Values)

Product	Electron Volts Absorbed per cc of Sample ($\times 10^{-20}$)										
	Helium Ion Irradiations					Cobalt-60 Irradiations					Ref. 11 (c)
	0.0[a]	2.04	4.16	7.84	4.26[b]	0.0[a]	6.24	9.04	12.29	15.06	
H_2	.84	.84	.84	.84	.86	.73	.70	.68	.66	.67	
CH_4	.091	.090	.090	.094	.095	.102	.097	.093	.089	.092	
C_2H_6	~.01	.012	--	.008	--	$\leq$.005	.007?	--	--	--	
C_2H_4	~.05	.08	.03	.04	.01	~.05	.048	.031	.016	--	
C_2H_2	~.01	--	.008	.005	.01	--	--	--	--	--	
C_3H_8	1.40	1.32	1.40	1.44	1.43	3.47	3.48	3.40	3.43	3.48	
C_3H_6	1.71	1.70	1.73	1.71	1.71	1.04	.94	.86	.82	.80	
C_3H_4[d]	.028	.032	.021	.027	.019	.011	.011	.013	.007	.011	
iC_4H_{10}	.055	.060	.053	.050	.059	.035	.031	.050	.032	.034	
iC_4H_8	.008	.008	.008	.008	.005	.005	.005	.005	.005	.005	
CO_2	4.46	4.42	4.45	4.52	4.51	4.78	4.92	4.71	4.72	4.83	14.4
CO	.33	.32	.33	.32	.33	.42	.35	.36	.31	.32	

Products detected but not measured quantitatively: C_6H_{14}, C_6H_{12}, iC_3H_7CHO, iC_3H_7OH.

(a) Extrapolation of observed yields to zero dose. See Figure 10.
(b) This sample contained ~ 0.5 mole % H_2O.
(c) Average of three Co^{60} irradiations. No energy input listed.
(d) Method of analysis will not distinguish between $H_2C{=}C{=}CH_2$ and $HC{\equiv}C{-}CH_3$.

Table VII

iso Valeric Acid

Hundred Electron Volt Yields of Volatile Compounds (G Values)

Products	Electron Volts absorbed per cc of Sample ($\times 10^{-20}$)								
	Helium Ion Irradiations				Cobalt-60 Irradiations				Ref. 11 (b)
	0.0[a]	1.21	3.74	5.54	0.0[a]	3.77	9.14	17.92	
H_2	.77	.76	.79	.76	.67	.55	.70	.67	
CH_4	.12	.12	.12	.12	.15	.18	.14	.15	
C_2H_6	~.008	.010	.009	.009	~.005	.007	.009	.008	
C_2H_4	<.01	.037	.017	.016	<.01	.039	.018	.013	
C_2H_2	~.01	.003	.009	.008	trace	trace	.002	.001	
C_3H_8	~.039	.034	.031	.031	~.099	.083	.075	.085	
C_3H_6	~.29	.24	.23	.23	~.26	.17	.14	.09	
C_3H_4[c]	.006?	?	?	.006	?	?	?	?	
$isoC_4H_{10}$	~1.04	.90	.91	.87	~2.80	2.32	2.43	2.37	
C_4H_8[d]	< .48	.46	.45	.42	<.26	.23	.20	.15	
$n\ C_4H_{10}$	0.0	.14	.13	.14	0.0	.42	.48	.45	
$isoC_5H_{12}$	>.07	.068	.071	.059	>.03	.029	.028	.035	
$isoC_5H_{10}$	~.003	.003	.002	.001	~.002	.002	.001	.0005	
CO	.15	.15	.14	.15	~.22	.31	.16	.12	
CO_2	3.5	3.51	3.51	3.46	4.2	3.93	4.25	4.24	5.9

(a)Observed yields extrapolated to zero dose and corrected for the presence of impurity. Values uncertain.
(b)Average of three Cobalt-60 irradiations. Energy input not given.
(c)Method of analysis used will not distinguish between isomers of C_3H_4.
(d)Analysed as mixture of isobutene and normal butenes, but reported as isobutene, uncorrected.

Table VIII

Methyl Isobutyl Ketone

Hundred Electron Volt Yields of Volatile Products (G Values)

Product	Electron Volts Absorbed per cc of Sample ($\times 10^{-20}$)							
	0.0[a]	2.40	5.74	8.27	0.0[a]	4.86	13.36	~20.6
H_2	.90	~.8	.90	.91	.70	.72	.62	.66
CH_4	.43	~.5	.42	.43	.58	.57	.62	.55
C_2H_6	.065	.065	.063	.065	.034	.034	.033	.033
C_2H_4	.027	.029	.026	.026	.022	.022	.021	.022
C_2H_2	.009	.009	.006	.010	.004	.003	.005	?
C_3H_8	.032	.032	.031	.031	.083	.082	.092	.081
C_3H_6	.52	.51	.52	.51	.82	.73	.62	.51
C_3H_4[b]	.016	.016	.016	.015	.010	.008	.005	.006
iC_4H_{10}	.27	.27	.27	.27	.56	.54	.51	.47
iC_4H_8	.23	.22	.21	.21	.15	.14	.12	.10
iC_5H_{12}	.13	.13	.13	.13	.08	.08	.08	.08
CO	.47	~.6	.46	.48	~.38	.31	.28	.22

Products detected but not measured quantitatively: C_8H_{18}, C_7H_{16}, CH_3CHO, $CH_3CO\ CH_3$, CH_2CO.

(a) Extrapolation of observed yields to zero dose. See Figure 12.

(b) Method of analysis will not distinguish between $H_2C{=}C{=}CH_2$ and $HC{\equiv}C{-}CH_3$.

Table IX

Isopropyl Acetate

Hundred Electron Volt Yields of Volatile Products (G Values)

Product	Electron Volts Absorbed per cc of Sample ($\times 10^{-20}$)													
	Helium Ion Irradiations						Cobalt-60 Irradiations							
	0.0[a]	1.40	2.00	4.27	6.33	Ref.95 (b)	0.0[a]	1.52	5.46	9.86	14.14	Ref.96 (c)	Ref. 72 (d)	(e)
H_2	.88	.86	.83	.81	.80	.87	.76	.73	.66	.56	.61	.83	.63	.51
CH_4	.98	.97	.99	.95	.95	.94	1.85	1.83	1.69	1.68	1.58	2.20	1.55	.95
C_2H_6	.59	.59	.60	.59	.58	.59	.34	.33	.33	.34	.32	.393	.23	.29
C_2H_4	.05	~.05	.042	.048	.029	.022	.04		.042	.022	.032		--	--
C_2H_2	.023	.021	.024	.022	.028	.027	.002		.002	?	.003		<.01	.02
C_3H_8	.15	.15	.15	.15	.15	.15	.43	.41	.41	.39	.35	1.13	.16	.15
C_3H_6	.82	.80	1.28	.75	.74	.77	.78	.60	.38	.25	.21	.60	.04	.19
C_3H_4[f]	.028	.024	.032	.028	.026	.020	.008		.007	.006	.006			
iC_4H_{10}	.26	.26	.24	.23	.23	.25	.15		.15	.14	.13	.19	.04	.10
iC_4H_8	.024	.024	.024	.022	.022	.024	.011		.010	.008	.010		<.01	
CO_2	.79	.79	.80	.79	.78	.80	.76	.75	.78	.78	.75	1.0	.52	.59
CO	1.19	1.21	1.18	1.13	1.14	1.18	1.02	.85	.57	.47	.47	1.20	.35	.75
CH_3CHO	1.5	1.44	1.35	1.34	1.25	1.6	1.42		1.17	1.01	.88		.08	.13
$i\text{-}C_3H_7OCH_3$	.19	.20	.16	.17	.16	.25	.15		≥.16	.14	.14			

Products detected but not measured quantitatively: C_6H_{14}, CH_3COCH_3.

(a) Extrapolation of observed yields to zero dose. See Figure 13.
(b) 28 Mev helium ions. Extrapolation to zero dose of four runs between 1.1×10^{20} and 58.6×10^{20} ev/cc.
(c) Cobalt-60 irradiations. Absorbed dose and number of runs unknown.
(d) Cobalt-60 irradiations. Two runs between 177×10^{20} and 267×10^{20} ev/cc.
(e) 1-Mev electrons (nominal energy). Two runs between 198×10^{20} and 305×10^{20} ev/cc.
(f) Method of analysis will not distinguish between $CH_3\text{-}C{\equiv}CH$ and $CH_2{=}C{=}CH_2$.

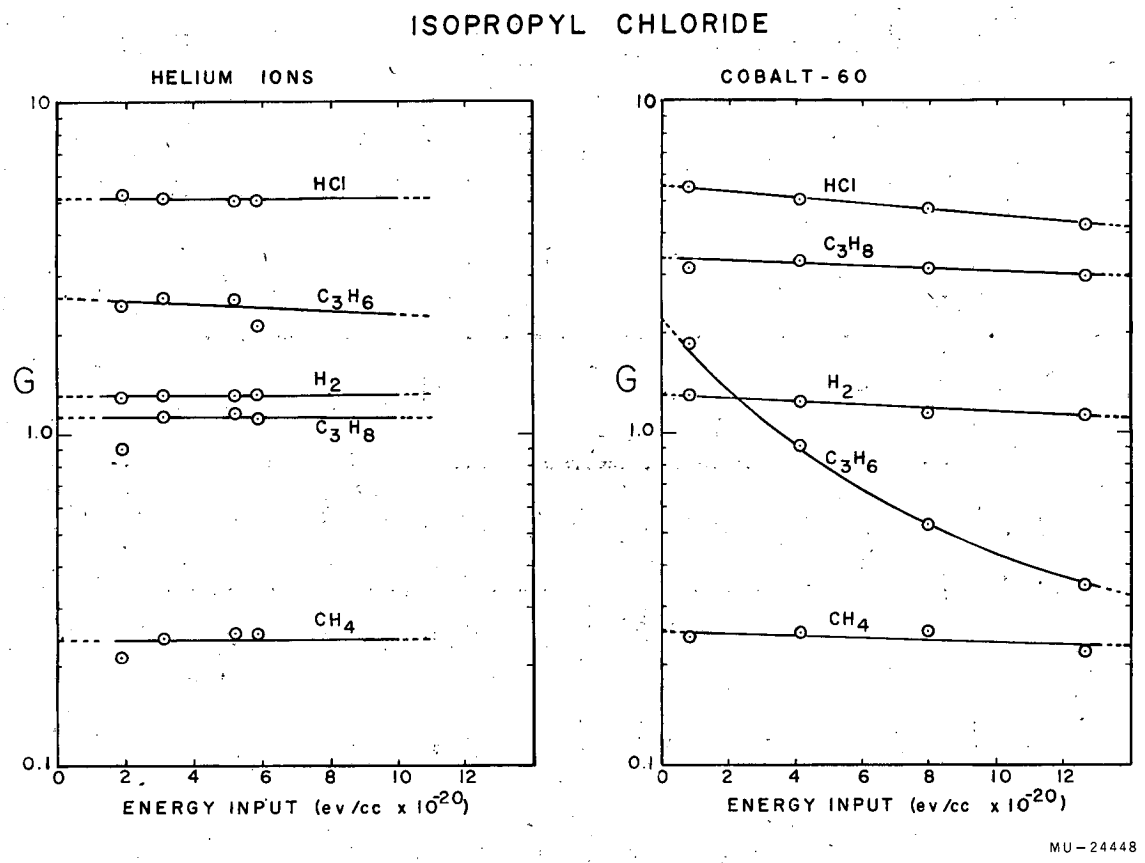


Fig. 6. Product yields as a function of total energy input from the irradiation of isopropyl chloride.

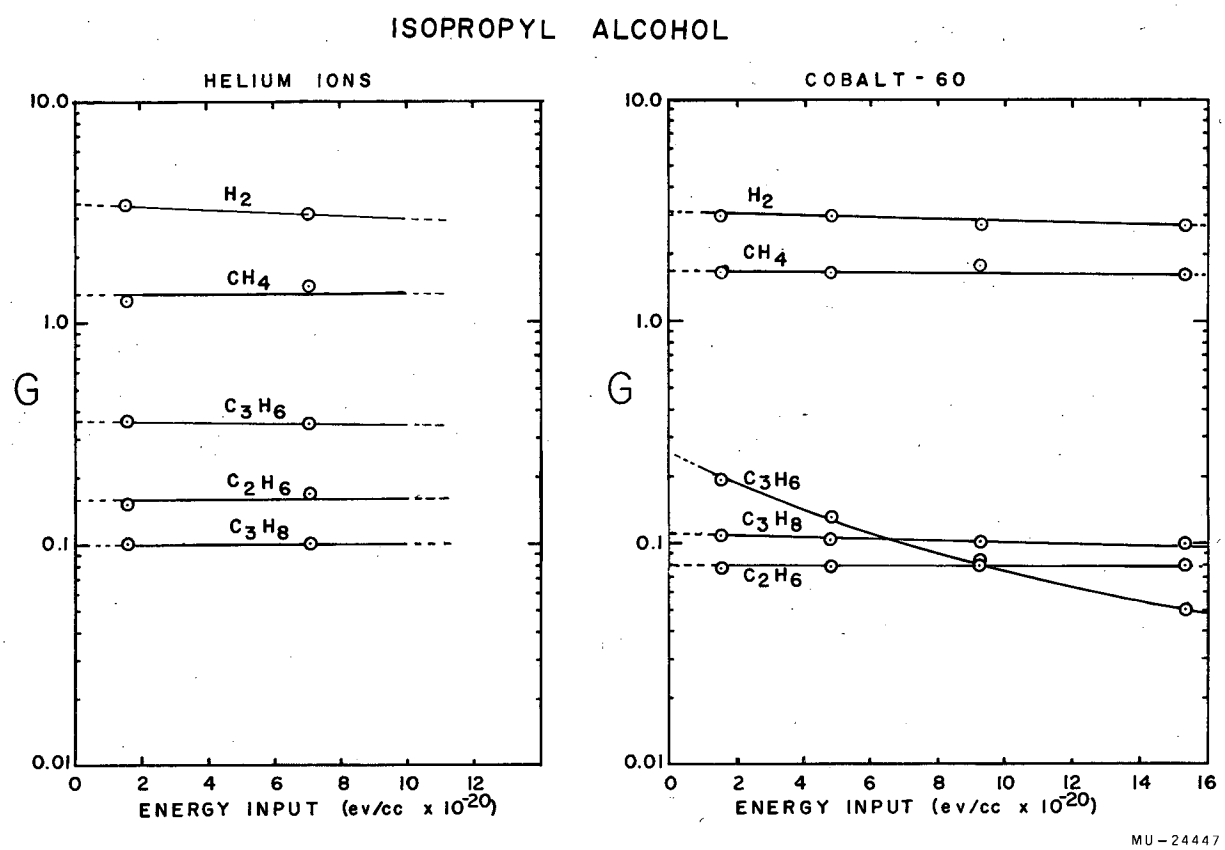


Fig. 7. Product yields as a function of total energy input from the irradiation of isopropyl alcohol.

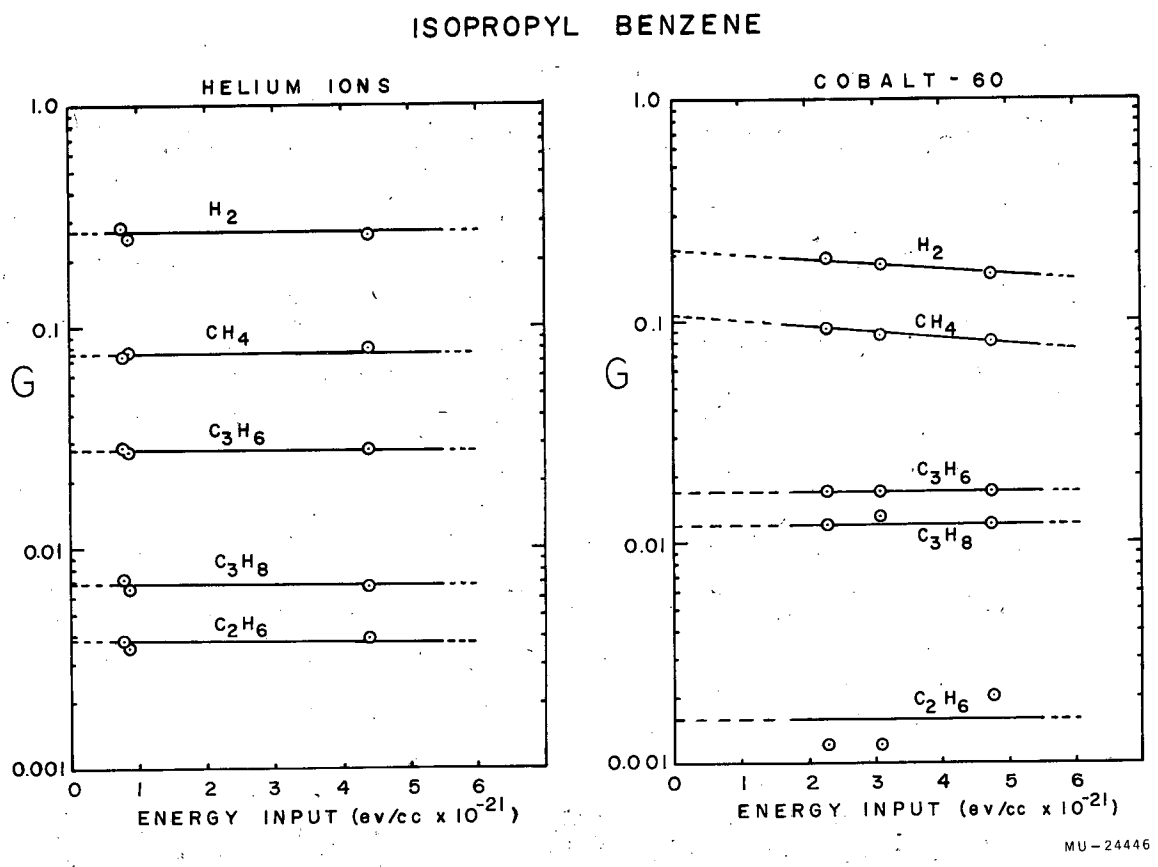


Fig. 8. Product yields as a function of total energy input from the irradiation of isopropyl benzene.

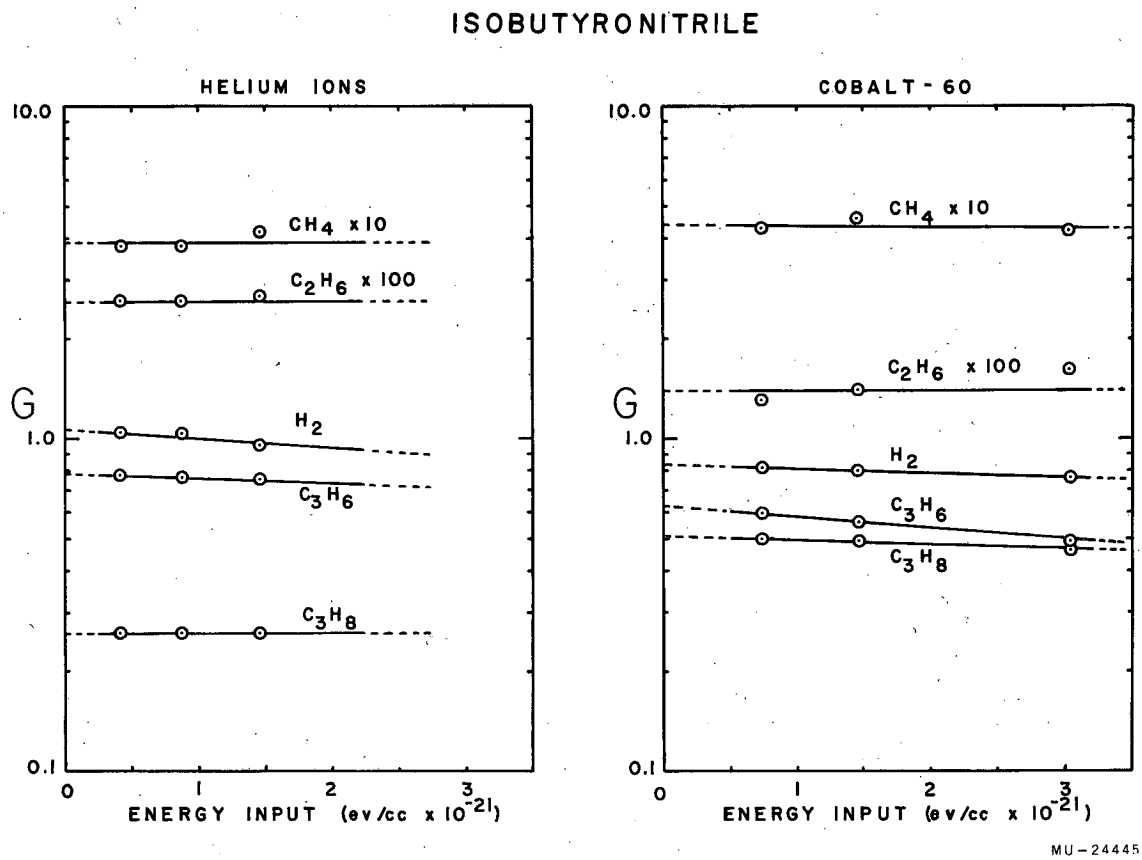


Fig. 9. Product yields as a function of total energy input from the irradiation of isobutyronitrile.

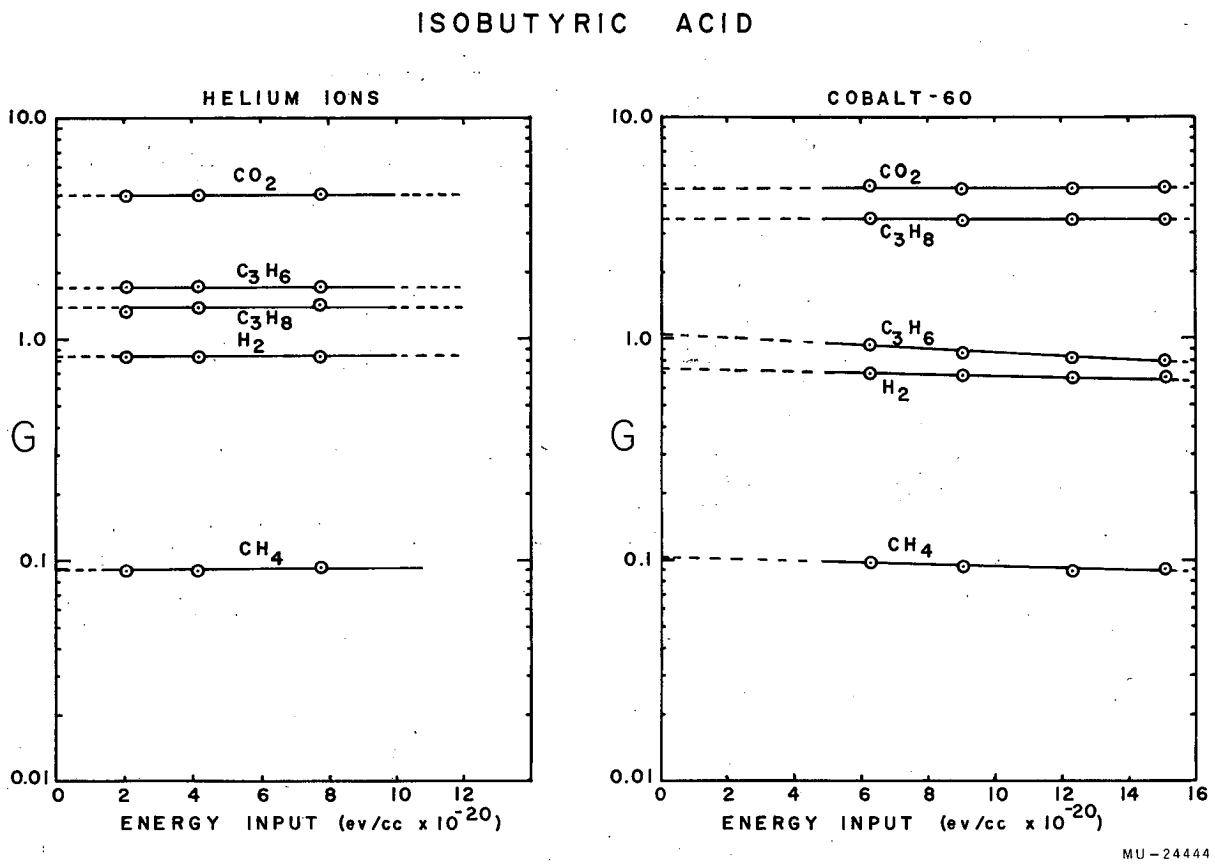


Fig. 10. Product yields as a function of total energy input from the irradiation of isobutyric acid.

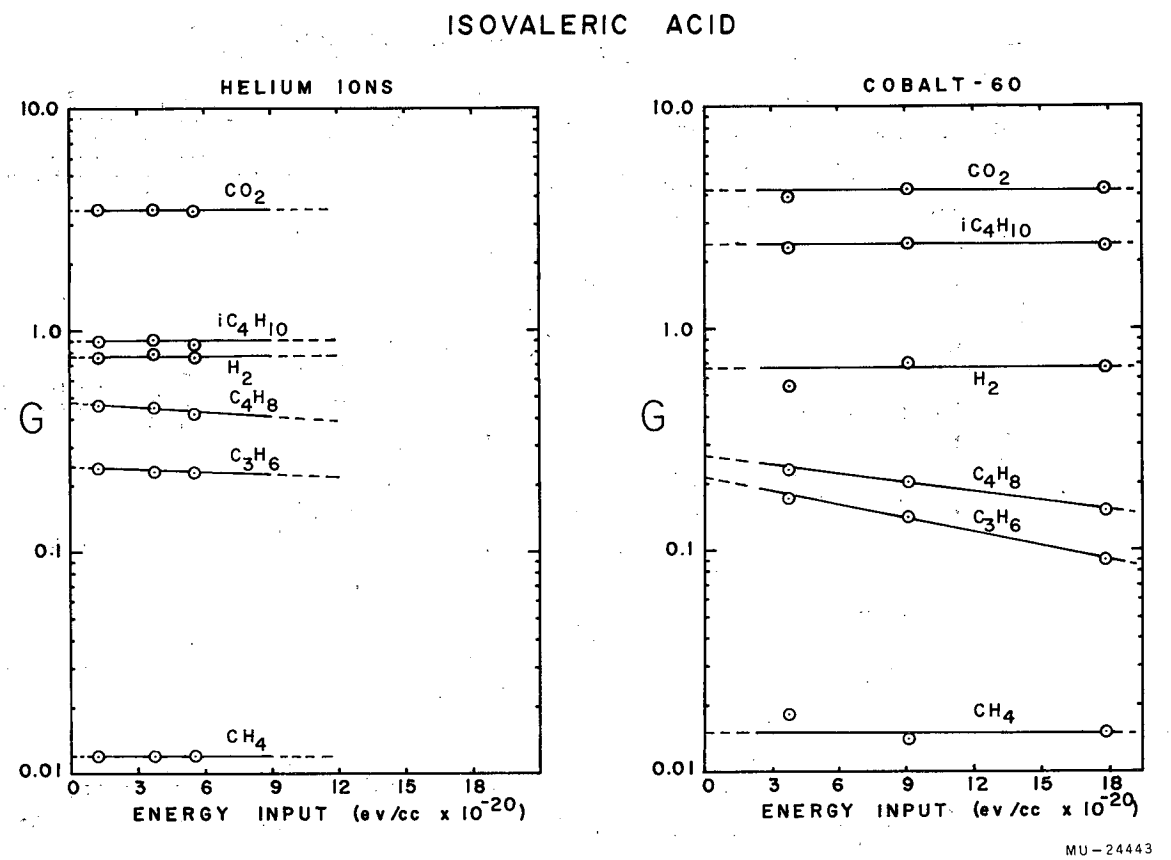


Fig. 11. Product yields as a function of total energy input from the irradiation of isovaleric acid (uncorrected for contribution from impurity).

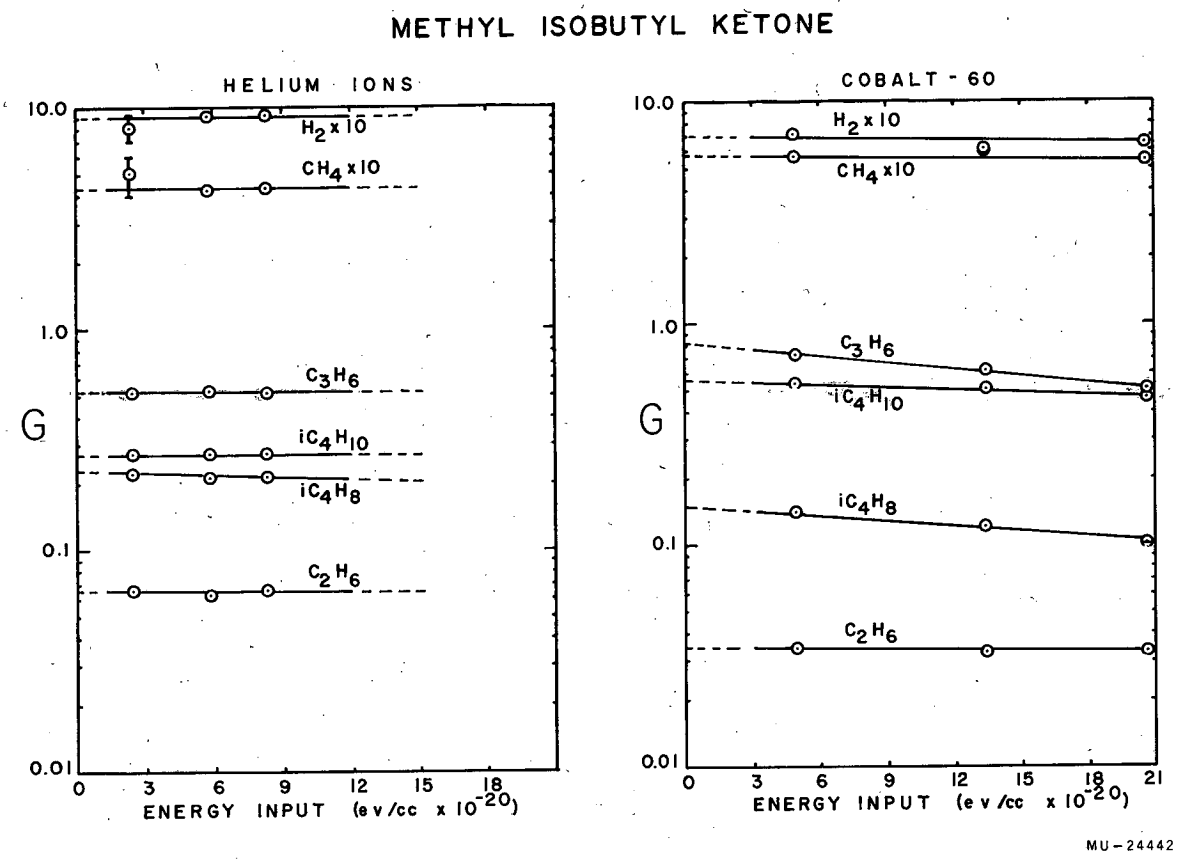


Fig. 12. Product yields as a function of total energy input from the irradiation of methyl isobutyl ketone.

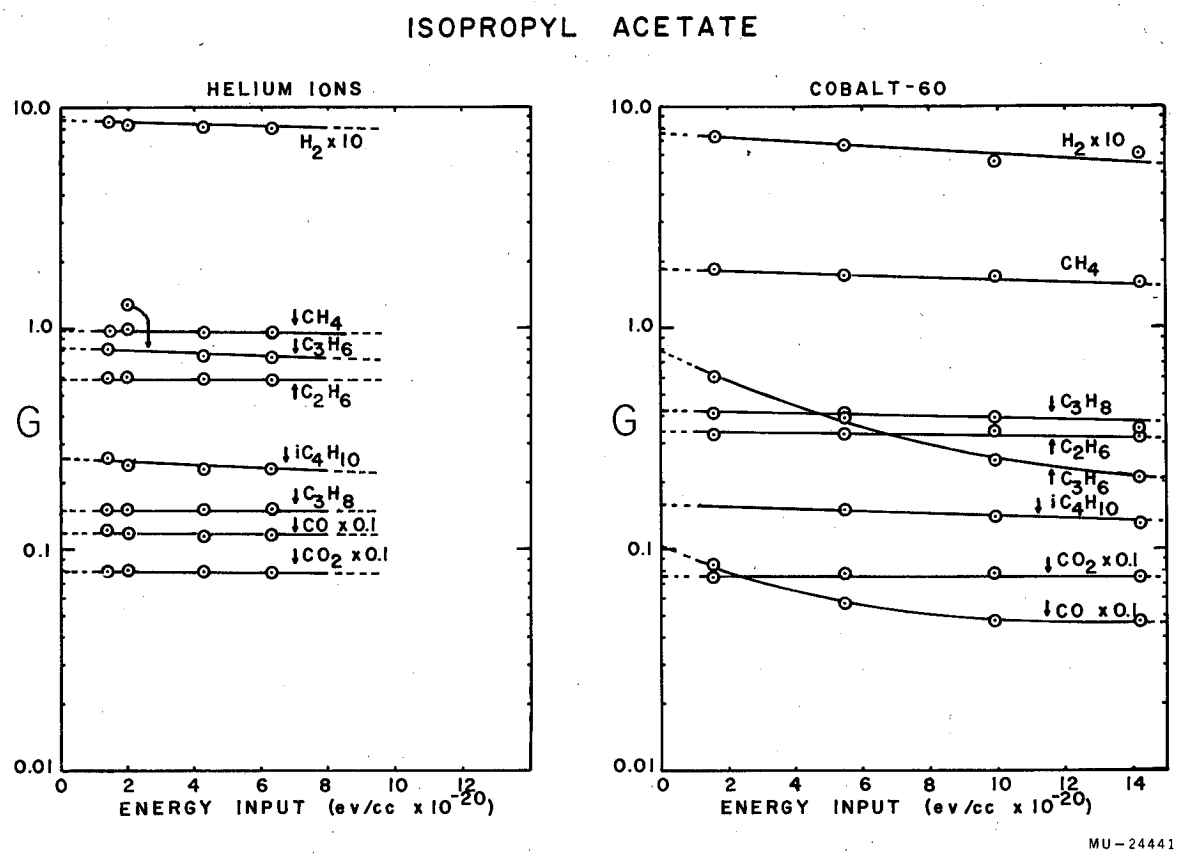


Fig. 13. Product yields as a function of total energy input from the irradiation of isopropyl acetate.

Table X

Summary of G Values (Extrapolated to Zero Energy Input)

Product	isopropyl chloride		isopropyl alcohol		isopropyl benzene		isobutyronitrile		isobutyric acid		isovaleric acid		methyl isobutyl ketone		isopropyl acetate	
	He^{++}	Co^{60}	He^{++}	Co^{60}	He^{++}	Co^{60}	He^{++}	Co^{60}	He^{++}	Co^{60}	He^{++}	Co^{60}	He^{++}	Co^{60}	He^{++}	Co^{60}
H_2	1.31	1.31	3.48	3.08	.27	.21	1.06	.84	.84	.73	.77	.67	.90	.70	.88	.76
CH_4	.24	.25	1.35	1.68	.075	.108	.39	.44	.091	.102	.12	.15	.43	.58	.98	1.85
C_2H_6	.010	.003	.16	.079	.0038	.0016	.026	.014	.01	$\leqslant$.005	~.008	~.005	.065	.034	.59	.34
C_3H_8	1.14	3.38	.10	.11	.0069	.012	.26	.51	1.40	3.47	~.04	~.1	.032	.083	.15	.43
C_3H_6	2.68	~2.16	.37	.25	.028	.017	.79	.63	1.71	1.04	~.29	~.26	.52	.82	.82	.78
iC_4H_{10}	.040	.02	.050	.028	.001	.0005	.045	.020	.055	.035	~1.04	~2.8	.27	.56	.26	.15
iC_4H_8	.002	.002	.007	.002	.0002	.0001	.010	.005	.008	.005	<.48	<.26	.23	.15	.024	.011
iC_5H_{12}											>.07	>.03	.13	.08		
CO			.04	.03					.33	.42	.15	.22	.47	~.38	1.19	1.02
CO_2									4.46	4.78	3.5	4.2			.79	.76
HCl	5.13	5.55														

For the gamma irradiations, the energy input depended on the length of irradiation, the volume of the liquid sample, and the electron density of the liquid. The dose rate was known, in ev/ml/min, for different volumes of the Fricke dosimeter. The energy input for each sample was calculated by multiplying the volume of liquid in the ampoule by (a) the dose rate, in ev/ml/min, for that volume of Fricke solution, (b) the duration of irradiation in minutes, and (c) the ratio of the electron density of the target liquid to that of the 0.8 N H_2SO_4 solution used in the dosimeter. When this energy input is known, the G values may be calculated by the above formula.

Reliability of Data

In this work no measurements were repeated with all the experimental conditions remaining the same. There is therefore no way to assess the reliability of the results statistically. Possible sources of error are outlined below, and their effects on the accuracy of the data are estimated.

For the cyclotron irradiations, the measurement of energy input was very reliable. Fluctuations of beam energy and errors in the measurement of charge deposition are estimated to be less than 2% in the irradiations performed for this work.

For the gamma irradiations, the measurement of energy input is less precise. However, errors stemming from inaccurate measurement of the volume of the target liquid, and from failure to reproduce the physical orientation of the target liquid with respect to the Co^{60} source from one irradiation to the next, are unlikely to exceed 5%.

In the separation process the possible source of error lies in failure to collect all of a given product. Consideration of volatility and of the consistency of product yields among several samples indicates that there is probably no significant error from this source in the listed G values.

The measurement of the pressure and volume of the gas in each fraction is quite accurate except for the small amounts of gas produced in the very short irradiations. The assumption of ideal gas behavior during measurement is reasonable at the low pressures involved (usually less than a few centimeters of Hg). Additivity of partial pressures is assumed in calculating the percentage of each constituent in a mixture of gases.

Mass-spectroscopic analyses yield very accurate results for a product that is present in reasonably high yield and has a distinctive fragmentation pattern. For products that border on trace amounts the uncertainty of analysis is much larger, but is normally not in excess of a factor of two. When a mixture of products contains gases whose fragmentation patterns resemble one another, an uncertainty is introduced into the relative yields of these products. In these cases the ambiguities were resolved by supplementing the mass-spectroscopic analyses with vapor-phase chromatography, as described in the section on Instrumental Analysis.

Several products showed dependence of yield on total dose. The reliability of the extrapolations made in these cases is discussed in the next section.

Effect of Total Energy Input

It has been established that G values can show a marked dependence on total energy input.[27] There are two possible mechanisms for this effect. Either the products formed during irradiation are capable of de-exciting excited states of the solvent molecule which would otherwise lead to the formation of measured products, or the products react readily with the unstable intermediates produced by decomposition of the solvent molecules, thereby preventing them from forming measured products. The experiments in this work were not designed to distinguish between these mechanisms. It seems significant, however, that substances that are known to react readily with radicals--C_3H_6,[28,29] CH_3CHO,[29] CO[30,31] --- are the only products whose G values show a strong dependence on total energy input.

In the He^{++} irradiations the effect of changing energy input is small. For products whose yields decrease as the energy absorbed in the sample increases, the G values measured for several values of absorbed energy are extrapolated to zero energy input. (See Figs. 6 through 13.) This extrapolated yield is considered to be the fundamental product yield, unaffected by secondary reactions, and is reported as such in Table X. When there is no systematic effect of total energy input on product yield, the average of the values obtained is considered to be the fundamental G value.

In the gamma irradiations the effect of total energy input on G values is much more pronounced. For the yields of products capable of acting as radical scavengers, the change of G value with total dose is so high in some cases as to make the extrapolation to zero dose

difficult and subject to inaccuracies. It is not clear why the effect of total energy input should be so large in the gamma irradiations and relatively small in the helium-ion work.

If the difference between He^{++} irradiations and Co^{60} irradiations were small, and were the same for all the substances irradiated, it could be explained by the fact that in the He^{++} irradiations fewer radicals escape from the particle track into solution where they may react with dissolved products. Another possible explanation for a small and uniform difference in the effect of total energy input is that the shaking of the cyclotron targets permits rapid escape of radical-scavenging products into the free volume above the liquid, while in the Co^{60} targets equilibrium between dissolved gaseous products and the expansion volume is more slowly attained.

The effect of increased dose is so pronounced in the gamma irradiations that these explanations are inadequate. In addition, it will be seen from Figs. 6 through 13 that there is a rough correlation between the volatility of the substance being irradiated and the effect of total energy input on the yield of the affected products. The decrease in, e.g., $G_{C_3H_6}$ with increasing energy input is most severe in isopropyl chloride (vapor pressure at room temperature $\approx$ 50 cm of Hg) and least important in isopropyl benzene and the acids (vapor pressure at room temperature $<$ 1 mm of Hg). This is evidence of radiation-induced reactions taking place in the gas volume in the gamma cells.

The energy absorbed in the gas volume is much less than that absorbed in the liquid, owing to the smaller density of the gas and

to the smaller radiation flux at larger distances from the cobalt pellets (see Fig. 4). This is counteracted, however, by the fact that the concentration of scavenger is much higher in the gas volume than in the liquid.

All the effects observed could be accounted for by high-efficiency radiation-induced reactions in the gas volume. Chain reactions, involving molecules of the starting material and molecules of the products that show the strong dependence on total energy input, would cause all the effects observed. Another possibility is the occurrence of ion-molecule reactions. The cross sections in the gas phase for some of these reactions exceed the collision cross section between molecules.[32]

Precedents for these types of reaction are not lacking. With respect to the products from isopropyl chloride, for example, the gas-phase photo-addition of HCl to ethylene at room temperature was found by Raley, Rust, and Vaughan to occur readily by a chain process.[33] The gas phase radiation-induced addition of HBr to propylene was found by Armstrong and Spinks to occur with high efficiency; they proposed that chain processes and ion-molecule reactions were responsible for the addition.[34] Analogous processes may be postulated to cause disappearance of products in the other substances affected.

These gas-phase reactions would not be important in the He^{++} irradiations. In these experiments the beam of particles is completely absorbed in the liquid, and the radiation flux to which the gas volume is exposed is negligible.

Whatever the cause of this change of G value with total energy input, the problem remains of establishing the fundamental G value,

unaffected by secondary reactions. It is not certain that extrapolating the observed values to zero energy input gives reliable values when the effect is so large as it is in several gamma irradiations. This is the only method available, however, and it is the one adopted. The extrapolated G values are listed in Table X.

The data presented graphically in Figs. 6 through 13 are shown on semilog plots so that a wide range of G values may be displayed together. Valid extrapolations may not be made on logarithmic plots for curves whose slopes differ appreciably from zero, and in these cases the extrapolated values in Table X are not obtained from the plots in Figs. 6 through 13. Instead, the extrapolation is made by plotting millimoles/ml of product against energy input in ev/ml. A typical example is shown in Fig. 14. If there were no change of G value with energy input, the plot would be a straight line and its slope would be proportional to the G value. If the G value depended on total dose, the plot would be a curve and its initial slope would be proportional to the initial G value--the value unaffected by secondary reactions. The advantage of this method of extrapolation is that an extra point is added to the measured points: at zero dose the number of millimoles of product formed is, of course, zero.

The reliability of these extrapolations depends on the extent to which the curve departs from the initial slope. For products only mildly affected by the total energy input, the accuracy of the extrapolations should be within the limits of error imposed by other uncertainties in the experiments. When product yields were severely affected

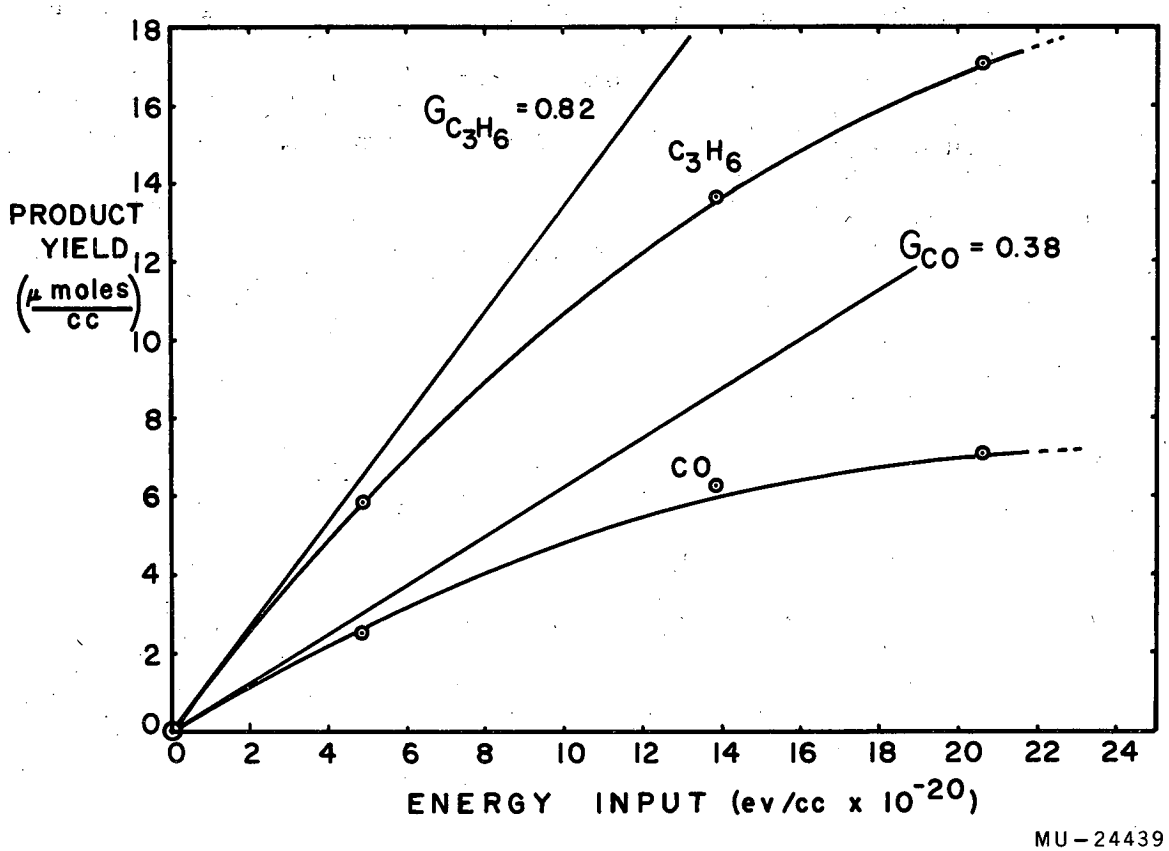


Fig. 14. Derivation of zero-dose G values for methyl isobutyl ketone by measurement of initial slopes.

by energy input, extra irradiations at low doses were performed to make the extrapolation more reliable. This was the case with isopropyl alcohol and isopropyl acetate. The extrapolations of yields for these compounds are probably valid. In the case of the γ-ray irradiation of isopropyl chloride, the concentration of propylene reached a steady state in the longer irradiations. The extrapolation depends only on the two values corresponding to the lowest absorbed energies. It should be considered to yield only an approximate G value.

DISCUSSION

I. General

The nature of the radiation-induced decomposition of each compound studied in this work is determined by measuring the stable products formed, and inferring from these products the primary bond cleavages and rearrangements that occurred under the influence of the radiation. The decomposition patterns of the eight compounds studied, as determined by this procedure, are presented in the succeeding sections. In order to illumine the principles that govern the interpretation of the experimental results, the possible processes by which ionizing radiation can cause chemical change are first outlined in this section.

Interaction of Radiation with Organic Liquids

Gamma Rays

Essentially the only interaction of Co^{60} γ rays with these organic liquids is the production of Compton electrons.[35] These primary Compton electrons are produced at the same rate in all parts of the irradiated liquid. At the dose rates used in this work the Compton electrons are formed at the rate of approx. 3×10^{12} e^-/ml/sec. The primary electrons are high-energy electrons, with a mean energy of about 750 kev.[35] They excite and ionize molecules and in these liquids excitation occurs about twice as often as ionization.[36] When ionization occurs secondary electrons are produced. These secondary electrons are mainly of low energy, and are capable of ionizing or exciting only a few more molecules. Their path lengths are very short, and the result is a series of clusters--called "spurs"--of ionization and excitation

along the path of each Compton electron. At the beginning of the path of the average primary electron, the average distance between spurs is about 5000 A.[35] As the Compton electron loses energy the density of ionization along its path grows larger, and when the average Compton electron has expended 99% of its orginal energy the distance between spurs is approx. 280 A.[35] In these liquids the average path length of the Compton electrons is approx. 4 mm.

A few of the secondary electrons ($\lesssim$ 5%) are formed with an energy greater than 100 ev. These higher-energy secondaries (called delta rays) branch out from the original path, forming a new series of spurs. The average distance between these δ rays is approx 10^5 A at the start of the path of the average Compton electron.[35]

The energy deposited in the liquid by the γ rays is spread throughout the liquid by the Compton electrons and the δ rays. The result is that the whole liquid during irradiation is laced with paths which consist of a succession of small clusters of ionization and excitation.

Helium ions

Helium ions cause ionization and excitation directly, and do so almost continuously along their path. The secondary electrons produced in the ionizations cause small clusters of ionization and excitation, just as in the gamma irradiations. The densely ionizing helium ions, however, produce these spurs about 20 A apart at the beginning of a track, and even more closely at the end of a track.[35] Because a typical spur just after formation has a diameter on the order of 10 A,[36] the clusters are formed so close to one another that they begin to overlap.

Again a few secondary electrons possess an energy greater than 100 ev. These δ rays branch out from the track, forming more spurs, at an average spacing of about 1000 A.[35] The result is that the track of each helium ion consists of a continuous column of ionization and excitation which is extended perpendicularly to the track by the δ rays. The shape of the track very closely resembles, therefore, the volume of revolution of a feather.

Reactions of Species Formed by the Radiation

Ions

Magee and Samuel have calculated that most of the ions produced by irradiation of water are neutralized within 10^{-13} sec.[37] It is widely but not completely accepted that, to quote Burton, in organic liquids "it is unlikely that...the ions can survive as long as 10^{-13} sec."[38] The neutralized molecule possesses a large excitation energy, and undergoes the same reactions as molecules that experience this high degree of excitation from direct interaction with the radiation.

If ions escape rapid neutralization they may decompose into ionized and uncharged fragments, or may react with molecules of the starting material. In the irradiation of gases these ion-molecule reactions (e.g., $CH_3^+ + CH_4 = C_2H_5^+ + H_2$) are observed directly in the mass spectrometer.[39] However, such reactions seem unimportant or unnecessary to account for the formation of products in certain gas-phase radiolyses.[40] The results of this work can be explained with a system of free-radical reactions and molecular rearrangements. Possible contributions from ion-molecule reactions are not considered.

Excited molecules

Some of the excited molecules produced during the irradiation lose their excitation energy by processes not involving decomposition. In other excited molecules dissociations occur. These are complex processes, and their detailed examination is beyond the scope of this discussion. Simple heterolytic bond cleavages occur, producing free radicals. In the liquid phase, a cage is formed by the solvent molecules surrounding the free radicals, promoting recombination of the radicals.[41] Another decomposition that can occur in excited molecules is rearrangement into molecular products.

Reactions between two excited molecules are sometimes proposed to explain radiolysis products; in general, this type of reaction is not necessary to explain the products formed in this work, and is disregarded. Triplet excited states are diradicals, however, and the possibility exists that triplet states formed by the radiation may participate in reactions with normal free radicals.

Radicals

The reactions of free radicals are the subject of several reviews, and are summarized briefly here.[29,30]

Radicals react with other radicals by combination (e.g., $C_2H_5\cdot + C_2H_5\cdot = n\text{-}C_4H_{10}$) and by disproportionation (e.g., $C_2H_5\cdot + C_2H_5\cdot = C_2H_6 + C_2H_4$). Most combination reactions have essentially no activation energies; the activation energies of disproportionation reactions are small. Disproportionation reactions are interpreted as head-to-tail encounters between radicals.[29] The ratio of disproportionation to

combination is known for the encounters of many radicals in the gas phase. The ratio is higher for energetic radicals than for radicals of thermal energies.[29]

Radicals react with molecules by abstraction reactions (e.g., $CH_3\cdot + C_3H_8 = CH_4 + C_3H_7\cdot$) and, if the nature of the molecule permits, by addition reactions (e.g., $CH_3 + C_3H_6 = C_4H_9\cdot$). Abstraction reactions require activation energies, usually in excess of 5 kcal/mole. Addition reactions also require activation energies, but these are usually smaller than the activation energies required for competing abstraction reactions.[29]

Radicals can undergo thermal decomposition, or can decompose because of energy carried over from the primary process in which they are formed. Several unstable radicals are produced from the compounds studied in this work, and decomposition of these radicals probably occurs. For example, decomposition of i-C_3H_7CO and of i-C_3H_7COO radicals is a possible source of CO and CO_2 produced in the irradiation of i-C_3H_7COOH.

The hydrocarbon radicals produced from these compounds are stable at room temperature.[30,42] Decomposition of hydrocarbon radicals because of energy retained from the process of formation cannot be ignored. Energetic hydrocarbon radicals formed by other means have been found, however, to be de-excited by collisions before decomposition can occur, even when they are formed in the gas phase.[43] An upper limit may be placed on the extent of product formation by decomposition of hydrocarbon radicals. The isopropyl radicals may decompose in two ways:[30]

$$C_3H_7\cdot = C_3H_6 + H\cdot , \quad E_{act} \approx 38 \text{ kcal/mole};$$

$$C_3H_7\cdot = C_2H_4 + CH_3\cdot , \quad E_{act} \approx 20 \text{ kcal/mole} .$$

Ethylene is produced by other processes in these irradiations, yet its yield is still small for all the compounds studied. If decomposition of isopropyl radicals produces only small amounts of C_2H_4, it can produce only smaller amounts of C_3H_6. Because the stability of isobutyl radicals is similar to that of isopropyl radicals,[30] their decomposition also is disregarded as a source of C_3H_6.

Isomerization of free radicals has been observed in some work and not in other work. For a summary of radical isomerizations see reference 44. No isomerization was observed in this work. For example, the C_6H_{14} measured in the radiolysis in which i-C_3H_7 radicals were produced was all (within the limits of error of the analysis) 2,3-dimethyl butane.

Determination of Decomposition Patterns

Formation of the observed products can be explained by decomposition of the starting material to form molecular products and to produce free radicals which then react with one another and with molecules of the starting material to yield observed products. The original fragmentation of a molecule in radiation chemistry can involve any bond in the molecule. The relative likelihood of bond cleavage at different locations in the molecule can be inferred from decomposition of the

molecule by other forms of excitation. This information may be gleaned from thermochemical and photochemical investigations, and from mass spectrometric cracking patterns. Subsequent reactions of most of the free radicals thus formed also can be inferred from other sources.

The difference in yield between Co^{60} and He^{++} irradiations may be used to confirm the source of the observed products. The high excitation density in the He^{++} irradiations means that radical-radical reactions occur more often in these irradiations than in the Co^{60} irradiations. Products formed by combination and disproportionation reactions between radicals should show larger yields in the helium-ion irradiations. These reactions occur in the track between radicals from the same solvent cage or radicals produced from neighboring molecules. In the Co^{60} irradiations there is little interaction between radicals produced in different spurs, and the combination and disproportionation reactions that occur in the spurs should be less important in these irradiations. The radicals that are formed are therefore more likely to escape immediate reaction and to diffuse into the body of the liquid. Products formed by abstraction and addition reactions should therefore show larger yields in the Co^{60} irradiations.

Table X shows that this is generally the case. Methane, produced by abstraction reactions of methyl radicals, shows a higher yield in the Co^{60} irradiations in every case. Ethane, produced from combination reactions of methyl radicals, is higher in the He^{++} irradiations. Addition reactions always lead to products that were

not measured in this work, and it cannot be proved that they are favored in the Co^{60} irradiations.

The probability of one radical's encountering another in the He^{++} irradiations exceeds that in the Co^{60} irradiations by a certain ratio. The ratio of these probabilities should be the same in each of the compounds studied. Unless the difference in diffusion coefficients between large and small radicals causes deviations, it is to be expected that for products formed exclusively by radical-radical reactions, $G_{He^{++}}/G_{Co^{60}}$ should be the same for the formation of these products from each of the compounds studied.

Certain products may be assumed to result only from combination of radicals: C_2H_6; i-C_4H_{10} from compounds producing methyl and isopropyl radicals but no isobutyl radicals; i-C_5H_{12} from compounds producing methyl and isobutyl radicals but no isopentyl radicals. These assumptions are not contradicted by the available evidence. Ethane formed in the radiolysis of partially deuterated acetone or methyl acetate has the isotopic distribution of ethane produced only from combination of methyl radicals.[45,46] Dilution of these substances with different solutes causes changes in the radiolytic yield of ethane and in its isotopic distribution which would be expected if ethane were formed in the spurs by radical combination.[45]

Isobutylene may be assumed to result only from disproportionation reactions when it is formed in the radiolysis of compounds which produce i-C_4H_9 radicals and in which molecular rearrangement gives other products, rather than isobutylene. There is no experimental evidence bearing on this assumption.

For all these products which are putatively produced only by radical-radical reactions and whose yields are reliable enough to give valid comparisons, one finds $G_{He^{++}}/G_{Co^{60}} = 1.8 \pm .2$.

Molecular rearrangements are normally independent of the type of radiation employed. The rearrangement of an excited molecule in a unimolecular process should be unaffected by the surroundings of the excited molecule. There is an exception when the excited state is susceptible to quenching by radicals or by other excited species before it can undergo rearrangement. In this case less quenching and more rearrangement occurs in the Co^{60} irradiations.

Reactions Observed in This Work

The decomposition patterns obtained by applying these principles to the observed data consist of (a) a set of primary decompositions yielding radicals and molecular products, and (b) a set of secondary reactions which the radicals undergo. A list of these reactions for an idealized compound and a description of the characteristics of each reaction are given here so that they need not be repeated for each individual compound studied.

Primary Reactions

Reaction (I-1): $$i\text{-}C_3H_7X \rightsquigarrow H^{\cdot} + (\underset{R_1}{CH_3\text{-}CHX\text{-}CH_2^{\cdot}} \text{ or } \underset{R_2}{CH_3\text{-}\dot{C}X\text{-}CH_3}).$$

There are more primary C-H bonds to break, but the secondary C-H bond is weaker. There is no information from the experiments presented here that determines whether R_1 or R_2 is predominantly formed

from a given compound. The hydrogen atom, as the smaller fragment, is apt to carry off most of the dissociation energy which appears as translational energy of the fragments. In addition, since the energy is translational, the hydrogen atom loses it slowly. The small, energetic hydrogen atom thus readily escapes from the solvent cage. The observations that (a) abstraction by hydrogen atoms to give H_2 in the radiolysis of acetone and of methyl acetate is only slightly diminished by addition of radical scavengers,[46,47] and that (b) the isotopic ratio of the hydrogen produced in the radiolysis of partially deuterated acetone or methyl acetate corresponds to the ratio from athermal abstraction reactions,[43,48] support the probability that many of the hydrogen atoms produced in these radiolyses undergo reaction while they still possess considerable energy.

Reaction (I-2): $$i\text{-}C_3H_7X \rightsquigarrow CH_3\cdot + CH_3\text{-}\underset{R_3}{CHX}\cdot$$

Reaction (I-3): $$i\text{-}C_3H_7X \rightsquigarrow CH_3\text{-}\dot{C}H\text{-}CH_3 + X\cdot$$

If X is a single atom, I-1 through I-3 are the only bond cleavages that can occur. If X is a complex polyatomic group, other bond cleavages can occur in the functional group.

Reaction (I-4): $$i\text{-}C_3H_7X \rightsquigarrow C_3H_6 + HX$$

This reaction has been observed in the pyrolysis, photolysis, and mass spectrometry of some of the compounds studied, and has been postulated in radiolyses. See Section X for a detailed outline of the occurrence of this reaction.

Reaction (I-5): $i\text{-}C_3H_7X \rightsquigarrow H_2$ + product

Reaction (I-6): $i\text{-}C_3H_7X \rightsquigarrow CH_4$ + product

Since this work was begun, strong new evidence has been presented that these processes are of importance in gas-phase radiolyses.[49] It was already known that production of H_2 by a molecular process occurred in the gas-phase radiolysis of acetone but apparently not in the liquid-phase radiolysis.[45] This work does not distinguish among these and other processes yielding the same products, and molecular elimination of these products is not considered.

Secondary Reactions

Reaction (I-7): $H\cdot + i\text{-}C_3H_7X = H_2 + (R_1 \text{ or } R_2)$

Reaction (I-8): $H\cdot + i\text{-}C_3H_7X$ = addition product

The hot hydrogen atoms would be expected to undergo these reactions readily, although I-8 will not take place unless the molecules of starting material allow the addition of hydrogen atoms. Activation energies for abstraction from an alkane by a hydrogen atom are approx 9 kcal/mole.[29] Thermalized hydrogen atoms would be expected to give R_2 as a product. Where the nature of these radicals has been estalished, the formation of R_2 is indicated. For example, in the radiolysis of alcohols Newton and McDonell found only vic-glycols among the radiolysis products.[50] When molecules are susceptible of the addition of hydrogen atoms, the activation energy for addition is usually lower than the activation

energy for abstraction (see p. 55).

Reaction (I-9): $H^{\cdot}$ + radical = H_2 + product

Reaction (I-10): $H^{\cdot}$ + radical = combination

Reaction I-10 has essentially no activation energy, and I-9 has a very small activation energy (E_{act} for disproportionation reactions of hydrogen atoms with alkanes is ≈ 1 kcal/mole in most cases[29]). These reactions occur for the most part in the particle track, where many hydrogen atoms are likely to possess enough translational energy to make this small difference in activation energy an unimportant influence on the competition between these two reactions.

All experimental evidence indicates that combination is a negligible reaction. If combination occurred often, the hydrogen yield would be lower in helium-ion irradiations than in Co^{60} irradiations. The reverse effect is observed. The failure of I-10 to occur may be due to steric factors, or because the energy of combination of the radical and the energetic hydrogen atom is too large to result in a stable combination product.

For compounds in which addition of hydrogen atoms to molecules of the starting material is possible, hydrogen atoms would react in the particle track to give H_2, or would escape into the bulk of the solution where they could either undergo abstraction reactions to give H_2, or disappear by addition reactions. The yield of H_2 would therefore be larger in helium-ion irradiations. This is the effect observed in this work.

Reaction (I-11): $CH_3^{\cdot} + i\text{-}C_3H_7X = CH_4 + (R_1 \text{ or } R_2)$

The activation energy for abstraction reactions by methyl radicals is less than approx 10 kcal/mole for alkanes.[29] It has been established that R_2 is produced when methyl radicals undergo abstraction reactions with isopropyl alcohol[51] and with hydrocarbons.[52]

The addition of radical scavengers reduces methane yields to very small values in the radiolyses of ketones and esters.[45,46,47] This indicates the importance of I-11 in pure organic liquids.

Reaction (I-12): $CH_3^{\cdot} + CH_3^{\cdot} = C_2H_6$

Reaction (I-13): $CH_3^{\cdot} + i\text{-}C_3H_7^{\cdot} = CH_4 + C_3H_6$

Reaction (I-14): $CH_3^{\cdot} + i\text{-}C_3H_7^{\cdot} = i\text{-}C_4H_{10}$

The ratio of I-13 to I-14 can be estimated from Trotman-Dickinson's compilations[29] to be approx 0.2 to 0.3.

Reaction (I-15): $CH_3^{\cdot} + X^{\cdot} = CH_4 + \text{product}$

Reaction (I-16): $CH_3^{\cdot} + X^{\cdot} = CH_3X$

CH_3X and the product of the disproportionation reaction are seldom completely measured among the volatile products. In these cases the occurrence of I-16 goes undetected, and a portion of the methyl radicals produced in I-3 is not measured.

Methyl radicals can react with radicals that are not listed in reactions I-11 to I-16: R_1, R_2, R_3, and so on. When this occurs there is a possibility that disproportionation reactions occur and CH_4 is produced. Otherwise the radicals combine, and the CH_3 radicals escape measurement. In aromatic compounds the possibility of addition of methyl radicals to molecules of the starting material cannot be excluded.[53]

The production of CH_3 radicals, and hence the yield of I-2, is measured by $G_{CH_4} + 2G_{C_2H_6} + G_{i\text{-}C_4H_{10}}$ plus G_{CH_3X} if CH_3X is measured. Addition reactions, and combination reactions that lead to high-molecular-weight products, escape measurement. The yield of $CH_3\cdot$ as calculated from the above product yields is therefore a minimum value. Except in compounds that are very susceptible of addition of methyl radicals, the unmeasured $CH_3\cdot$ would be expected to be larger in the He^{++} irradiations because the unmeasured combination products are formed in greater yield in these irradiations.

Reaction (I-17): $i\text{-}C_3H_7\cdot + i\text{-}C_3H_7X = C_3H_8 + (R_1 \text{ or } R_2)$

$i\text{-}C_3H_7\cdot + CH_3\cdot$ = (see I-13, I-14)

Reaction (I-18): $i\text{-}C_3H_7\cdot + i\text{-}C_3H_7\cdot = C_3H_8 + C_3H_6$

Reaction (I-19): $= C_6H_{14}$

The ratio of I-18 to I-19 is 0.5.[27]

When propyl radicals react with radicals not listed in reactions I-17 to I-19, disproportionation reactions produce C_3H_8 and C_3H_6, which are measured. Combination reactions, however, yield unmeasured product.

In measuring the production of isopropyl radicals, and hence the yield of I-3, it must be noted that part of the C_3H_6 is formed from isopropyl radicals and part is produced by molecular rearrangement via I-4. The production of $i\text{-}C_3H_7\cdot$ is given by $G_{C_3H_8} + G_{iC_4H_{10}} + (G_{\text{total } C_3H_6} - G_{\text{molecular } C_3H_6})$, plus $i\text{-}C_3H_7\cdot$ which disappears by addition to the starting material or by combination with other radicals to give measured product. It is probable that even more $i\text{-}C_3H_7\cdot$ escapes measurement than

$CH_3\cdot$ because the dimer of i-$C_3H_7\cdot$ is not measured among the volatile products. Again, more i-$C_3H_7\cdot$ escapes measurement in the helium-ion irradiations than in the cobalt-60 irradiations.

The reactions that X· undergoes are the common combination, disproportionation, and abstraction reactions of radicals. In some compounds X· is such that it decomposes. It will be shown that this can result in an ambiguity in the yield of the primary reactions as determined by the above method.

R_1, R_2, R_3, and other radicals must be considered differently from the above radicals. They are not only produced in the track by the primary decomposition of the molecule, but also may be produced in the body of the solution by abstraction reactions. When this occurs, R_1 and R_2 cannot undergo fruitful abstraction and are constrained to diffuse until they meet another radical--the most likely being another R_1 or R_2 formed in the body of the liquid. The predominant fate of these radicals is thus the formation of high-molecular-weight products, and the experiments reported here shed no light on reactions involving these radicals.

Other Reactions

Certain products are formed in small yield by these irradiations. It is reasonable to assume that they are partially formed by reactions similar to those above. For example, a possible source of ethylene from all these compounds is $CH_3\cdot + CH_3\cdot \rightarrow C_2H_6^* \rightarrow C_2H_4 + H_2$,[30] where * designates an excited molecule.

High-energy processes may contribute to formation of these minor products. For example, in the irradiation of isopropyl benzene $G_{C_2H_2}$,

although very small, is larger than $G_{C_2H_6}$ and $G_{C_2H_4}$. This acetylene is probably formed by high-energy disintegration of the benzene ring. A source of ethylene mentioned above is the reaction $i\text{-}C_3H_7\cdot^* \rightarrow C_2H_4 + CH_3\cdot$. Although the small observed yields of ethylene show that this is an unimportant process, it is a possible source of part of the observed ethylene.

No attempt is made in subsequent discussion to account for these minor products when the data do not indicate a possible mode of formation.

II. Isopropyl Chloride

Previous Radiolyses

Wiley et al. irradiated isopropyl chloride with Co^{60} γ rays.[44,54] They found $G_{HCl} = 4.7 \pm .6$, and $G_{isomerization}$ was zero. They also studied n-propyl chloride, and found that Co^{60} irradiation caused isomerization by a chain reaction. They do not report product yields, but state that the products formed correspond to bond cleavage at the C-Cl bond, with minor products resulting from breaking of other bonds. They imply that no propylene was detected.

Dismukes and Wilcox irradiated the butyl chlorides with Co^{60} γ rays, and report that decomposition proceeded by bond cleavage at the C-Cl bond.[55] They did not detect butene as a product, but it is not clear whether their analytical methods would separate butene from other products.

The radiolysis of other halides is summarized in reference 55. The main result of irradiation is bond cleavage at the carbon-halogen

bond. In addition to bond cleavage in the radiolysis of alkyl iodides, Willard et al. postulate unimolecular elimination of HI from excited molecules;[56] Hamill et al. explain olefin formation by bimolecular reactions between excited molecules.[57]

Decomposition Pattern

The product yields observed in these experiments can be explained on the basis of the following series of reactions. The general characteristics of the reactions are summarized in section I.

Reaction (II-1): $CH_3\text{-}CHCl\text{-}CH_3 \rightsquigarrow H^{\cdot} + (CH_3\text{-}\underset{R_1}{CHCl}\text{-}\dot{C}H_2^{\cdot}$ or $CH_3\text{-}\underset{R_2}{\dot{C}Cl}\text{-}CH_3)$

The hydrogen atoms produced in this reaction abstract from molecules and radicals to give H_2. The possibility that a hydrogen atom will abstract a chlorine atom from an isopropyl chloride molecule to give HCl is very small, and is disregarded.[30]

Because no addition of H atoms to isopropyl chloride is possible, the yield of II-1 is therefore given by G_{H_2}. The measured yield of II-1 equals 1.3 for both He^{++} irradiations and Co^{60} irradiations.

Reaction (II-2): $CH_3\text{-}CHl\text{-}CH_3 \rightsquigarrow CH_3^{\cdot} + CH_3\text{-}\underset{R_3}{CHCl}^{\cdot}$

These methyl radicals undergo the reactions of methyl radicals outlined in Section I. The yield of methane, which is produced mainly by abstraction reactions, is only slightly higher in the Co^{60} irradiations than in the helium-ion irradiations. In the other compounds

irradiated in this work, the yield of methane is substantially higher in the γ irradiations than in the He^{++} irradiations. It is not clear why isopropyl chloride should show a different effect.

The measured methyl radicals are given by $G_{CH_4} + 2G_{C_2H_6} + G_{iC_4H_{10}} + G_{CH_3Cl} = 0.33$ for He^{++} irradiations and 0.32 for Co^{60} irradiations. Since most of the radicals produced in the track are isopropyl radicals and chlorine atoms, with which methyl radicals react to give measured products, the disappearance of methyl radicals by reactions in the track to give unmeasured products should be small. In the body of the solution the methyl radicals react to give CH_4, which is measured. Unmeasured $CH_3\cdot$ is therefore quite small, and the yield of II-2 is slightly greater than 0.33 for helium-ion irradiations and 0.32 for Co^{60} irradiation. The near equality of these yields lends support to the belief that little $CH_3\cdot$ escapes measurement.

Reaction (II-3): $CH_3\text{-}CHCl\text{-}CH_3 \rightsquigarrow i\text{-}C_3H_7\cdot + Cl\cdot$

This reaction is the major result of radiolyses of other alkyl halides. In the mass-spectral cracking pattern the main peaks correspond to breaking of the C-Cl bond. The products measured in this work indicate that II-3 is the predominant mode of dissociation in the radiolysis of isopropyl chloride.

The isopropyl radicals undergo the reactions listed in Section I. The extent of II-3 as measured by the production of isopropyl radicals is given by $G_{C_3H_8} + G_{iC_4H_{10}} + (G_{C_3H_6} - 1.5)$, because the yield of C_3H_6 formed by molecular rearrangement is calculated below to be 1.51. Thus the yield of $i\text{-}C_3H_7\cdot$ is > 2.4 for He^{++} irradiations and > 4.1 for γ

irradiations. Less of the original i-$C_3H_7\cdot$ production is measured in the He^{++} irradiations because of the importance of dimerization of the isopropyl radicals in these irradiations.

The extent of II-3 may also be measured by the yield of products formed by reactions of chlorine atoms. Chlorine atoms are very reactive. They readily abstract hydrogen from the molecules of starting material. The activation energy for hydrogen abstraction by chlorine atoms from hydrocarbons is approx 1 kcal/mole.[29] Abstraction reactions by chlorine atoms from alkyl chlorides to give Cl_2 have not been observed.[30] Chlorine atoms that escape the track, therefore, yield HCl, a measured product.

Reactions of chlorine atoms in the track should also produce mainly HCl. Because abstraction reactions from radicals occur more readily than abstraction reactions from molecules, and because Cl atoms undergo abstraction reactions even with molecules so easily, the ratio of disproportionation to combination in encounters of chlorine atoms and other radicals should be quite high.

Thus nearly all the Cl atoms formed react to produce HCl, and G_{HCl} can therefore be used to measure the extent of (II-3). The contribution of HCl from molecular rearrangement must not be counted, and the small yield of CH_3Cl can be added. Therefore one finds for the measured Cl atoms $(G_{HCl} - 1.5) + G_{CH_3Cl}$, or 3.7 for He^{++} and 4.1 for Co^{60} irradiations, respectively. Because the proportion of Cl atoms disappearing by combination with radicals should be small, the yield of II-3 should be only slightly greater than 3.7 and 4.1 for the two types of radiation.

The minimum measured yield of II-3 is 4.1, as measured in the Co^{60} irradiations for both $Cl^{\cdot}$ and $i\text{-}C_3H_7^{\cdot}$ production. It is reasonable to assume that the occurrence of II-3 is the same in both He^{++} and Co^{60} irradiations, but that in the He^{++} work less of the radical production results in measured products. A yield of greater than 4.1 is therefore assigned to II-3 for both types of radiation.

Reaction (II-4): $CH_3\text{-}CHCl\text{-}CH_3 \rightsquigarrow C_3H_6 + HCl$

Thermal excitation of isopropyl chloride causes this molecular rearrangement, as outlined in Section X. It is therefore to be expected that rearrangement may occur during the radiolysis of this compound. The large yield of C_3H_6 in relation to the other C_3 products in the He^{++} irradiations indicates formation of propylene by processes not involving propyl radicals, but this is not a measure of the quantity of propylene formed by these processes. The yield of molecular rearrangement is measured as outlined below. The method and its validity are discussed in Section X.

The ratio between the yield of propylene from He^{++} irradiations and that from Co^{60} irradiations is a measure of the proportion of propylene formed by molecular rearrangement. If all the propylene formed in the irradiation of a given compound is produced by molecular rearrangement, the yield is normally the same for both types of radiation. When isopropyl radicals are formed by irradiation of the compound in question, propylene is produced by disproportionation reactions of these radicals. The portion of the yield attributable to radical-radical disproportionation reactions is approx 1.8 times as large in

the He^{++} irradiations as in the Co^{60} irradiations (see Section I). This makes it possible to separate the contributions from each process.

Assuming that the formation of propylene from rearrangement is the same in both He^{++} and Co^{60} irradiations, and letting G_{disp} stand for the yield of propylene from disproportionation reactions in the γ irradiations, one has

$$He^{++}: \quad G_{rearrangement} + 1.8\, G_{disp} = M,$$
$$Co^{60}: \quad G_{rearrangement} + G_{disp} = N,$$
$$G_{disp} = \frac{M-N}{0.8}.$$

The yield of propylene from disproportionation reactions in the He^{++} irradiations and the yield from rearrangement may then be easily calculated.

For isopropyl chloride the calculation of the proportion of the propylene yield due to molecular rearrangement is as follows: Let G_{disp} = the yield from disproportionation reactions in the Co^{60} irradiations. Then

$$He^{++}: \quad G_{rearrangement} + 1.8\, G_{disp} = 2.68$$
$$Co^{60}: \quad G_{rearrangement} + G_{disp} = 2.16$$
$$0.8\, G_{disp} = 0.52$$
$$G_{disp} = 0.65$$

The yield of propylene from radical disproportionation reactions in the He^{++} irradiations is $1.8(0.65) = 1.17$, and the yield of propylene from rearrangement is calculated to be 1.51. The reliability and

accuracy of this value is discussed in Section X, where the factors affecting the validity of this method of calculation are examined.

Summary

The radiolytic decomposition of liquid isopropyl chloride occurs mainly by rupture of the C-Cl bond. This behavior is in agreement with results obtained from other halides. The C-Cl bond is weaker than the primary C-H bonds by approx 15 kcal/mole, weaker than the secondary C-H bond by a somewhat smaller amount, and probably weaker than the C-C bonds by several kcal/mole.[29] Although other radiolytic results show that bond strengths form a precarious basis from which to make predictions of reaction probabilities, in the case of isopropyl chloride it appears that cleavage of the weakest bond is the predominant mode of dissociation of the molecule.

The yield of products corresponding to cleavage of the C-H bond greatly exceeds the yield of products corresponding to cleavage of the bonds between the methyl groups and the substituted carbon. This tendency is noted in every compound studied in this work and in most other radiolyses.[58] It is possible that the C-H bonds are more susceptible to cleavage than the C-C bonds. The opposite trend would be predicted from the relative C-C and C-H bond energies. It may be that the H atoms escape the solvent cage and form measured products, whereas the $CH_3^{\cdot}$ radicals produced by C-C bond cleavage are confined by the solvent cage and tend to undergo recombination reactions. There is no way to determine from these experiments which of the two possibilities is responsible for the predominance of C-H bond cleavage.

Molecular rearrangement into C_3H_6 and HCl is an important mode of decomposition. This reaction is discussed in detail in Section X.

The results obtained by Wiley et al. are in reasonable agreement with the results of this work. They report a G_{HCl} of 4.7, which is substantially less than my value of 5.6; their measured yields of HCl show considerable scatter, and were obtained from irradiations totaling higher absorbed doses than those used in this work. Reference to Fig. 6 shows that when less energy is absorbed by the sample, G_{HCl} is larger than for irradiations totaling larger absorbed doses.

III. Isopropyl Alcohol

Previous Radiolyses

Newton and McDonell irradiated a series of aliphatic alcohols, including isopropyl alcohol, with 28-Mev helium ions and measured the products formed.[50] Some of their G values are listed in Table III. Their hydrocarbon and glycol yields indicated that the main mode of decomposition was bond cleavage at the carbinol carbon, with C-H bonds affected more than C-C bonds. High olefin yields led them to propose molecular rearrangements to give water plus olefin. Newton determined that G values decrease at high absorbed doses in the He^{++} irradiation of ethanol.[26] Strong and Burr measured G values for H_2 and CH_4 production in the Co^{60} irradiation of isopropyl alcohol.[48] Adams, Baxendale, and Sedgwick reported G values for these two products for Co^{60} irradiations with and without the presence of radical scavengers.[59] See Table III.

Burr subjected several deuterated ethanols to Co^{60} irradiation.[60] He interpreted his results to mean that hydrogen was produced by radical

processes only, involving production of hydrogen atoms by bond rupture at the carbinol carbon and abstraction by these atoms from the OH group (82%) and the CH_3 group (18%) to give H_2. Alternative interpretations of his experimental results are discussed below.

Meshitsuka and Burton irradiated methanol with Co^{60} γ rays, using iodine as a radical scavenger.[61] They obtained higher G values from irradiation of pure methanol than previous workers, and attributed this to the use of impure methanol by the other workers. Their product yields were explained by free-radical processes, molecular rearrangement, and either energetic-atom processes or reactions between excited molecules.

Decomposition Pattern

Reaction (III-1): $$i\text{-}C_3H_7OH \rightsquigarrow H^{\cdot} + (CH_3\text{-}\overset{R_1}{C}HOH\text{-}CH_2^{\cdot} \text{ or } CH_3\text{-}\underset{R_2}{\overset{\cdot}{C}}OH\text{-}CH_3 \text{ or } i\text{-}C_3H_7\underset{R_4}{O}\cdot)$$

The radiolysis by McDonell and Newton[50] and by Burr[60] gave evidence of the formation of $R_2\cdot$. The mercury-sensitized photolysis of CH_3OD was studied by Phibbs and Darwent, who reported that the C-H bond was broken in the photolysis.[62] Later work by Porter and Noyes, however, who studied the direct photolysis of CD_3OH, was interpreted to show that the initial decomposition was the breaking of the O-H bond.[63] At short wave lengths these workers detected cleavage of the C-O bond.

Recently the Hg-sensitized photolysis of CD_3OH and $(CD_3)_2Hg$ at low pressures in a flow system was reported by Pottie, Harrison, and Lossing.[64] These workers find no formation of $\cdot CD_2OH$, but only of $CD_3O^{\cdot}$. They interpret the earlier work in which the C-H bond was

reported broken as being confused by the reactivity of the methoxy radicals formed; that is, that the initial decomposition in the earlier work was $CH_3OH \longrightarrow CH_3O^{\cdot} + H^{\cdot}$, but that this was followed so quickly by reaction of the extremely reactive methoxy radical ($CH_3O^{\cdot} + CH_3OH = CH_3OH + {}^{\cdot}CH_2OH$) that the initial decomposition was obscured.

Confirmation of this interpretation was reported at the most recent meeting of the American Chemical Society.[65] Knight and Gunning studied the Hg-sensitized photolysis of ethanol in the presence of NO and found ethyl nitrite, proving the formation of the ethoxy radical.

The formation during radiolysis of only vic-glycols, as determined by McDonell and Newton,[50] can be interpreted as production of R_4, followed by rapid abstraction at the carbinol carbon (a) by the isopropoxy radical to give isopropanol and R_2, and (b) by the hydrogen atom to give H_2 and R_2. The R_2 radicals then dimerize to give vic-glycols. The isotopic distribution in Burr's radiolysis of deuterated ethanols (see above), which he interprets to indicate production of hydrogen atoms by bond cleavage at the carbinol carbon followed by abstraction of the hydroxyl carbon, may be interpreted as the reverse: cleavage of the O-H bond to give hydrogen atoms which then abstract from the carbinol carbon. This seems more likely, in view of the bond energies involved: abstraction of hydrogen would be expected to occur at the C-H bond (approx 90 kcal/mole) rather than at the O-H bond (101 kcal/mole).[66]

In view of these findings, the main decomposition of isopropanol by III-1 will be considered to produce R_4. The production of at least small quantities of R_4 is shown by the production of $i\text{-}C_3H_7OCH_3$ and of $(i\text{-}C_3H_7)_2O$ in these radiolyses.

The R_4 radicals, in addition to undergoing abstraction reactions to form R_2 radicals, react with other radicals. The ratio of disproportionation to combination is high for isopropoxy radicals,[66] and large yields of acetone may be expected from disproportionation reactions of isopropoxy radicals. Newton and McDonell find a G value of approx 2.0 for acetone production in the irradiation of isopropyl alcohol,[50] but a large part of this acetone may be formed by III-5.

The extent of III-1 is given by the yield of hydrogen atoms, which undergo abstraction reactions with molecules and radicals to yield H_2. The yield of III-1 is G_{H_2}, which is measured as 3.5 and 3.1 for He^{++} irradiations and Co^{60} irradiations, respectively. Hydrogen atoms would not be expected to undergo addition reactions with isopropanol. No explanation of the difference in yield for the two types of radiation can be advanced.

Reaction (III-2): $$i\text{-}C_3H_7OH \rightsquigarrow CH_3^{\cdot} + CH_3CHOH^{\cdot}_{R_3}$$

The extent of III-2 is given by the production of methyl radicals. The measured yield of methyl radicals is given by $G_{CH_4} + 2G_{C_2H_6} + G_{i\text{-}C_4H_{10}} = 1.72$ and 1.87 for the two types of radiation. The large concentration of R_2, R_3, and R_4 radicals in the track indicates that an appreciable quantity of methyl radicals escapes measurement because of combination with these radicals to give unmeasured products. Thus the extent of III-2 is > 1.72 for He^{++} and > 1.87 for Co^{60} irradiations. The smaller yield in the helium-ion irradiations is indicative of disappearance of methyl radicals by combination with large radicals.

The R_3 radicals would be expected to form CH_3CHO by disproportionation reactions. Newton and McDonell found a G value of 0.9 for CH_3CHO production in the He^{++} irradiation of isopropyl alcohol.[50]

Reaction (III-3): $i\text{-}C_3H_7OH \rightsquigarrow i\text{-}C_3H_7^{\cdot} + OH^{\cdot}$

This reaction is observed in photolyses, but is a minor contribution to the decomposition of the molecule.[63,64]

The production of isopropyl radicals is given by $G_{C_3H_8} + G_{i\text{-}C_4H_{10}} + (G_{C_3H_6} - 0.1) = 0.4$ for the He^{++} irradiations and 0.3 for the Co^{60} irradiations. Since appreciable numbers of isopropyl radicals disappear by combination, the extent of III-3 is > 0.4 for helium-ion irradiations and > 0.3 for γ irradiations. There is no apparent reason for the excess production of isopropyl radicals as measured in the helium-ion irradiations.

Reaction (III-4): $i\text{-}C_3H_7OH \rightsquigarrow C_3H_6 + H_2O$

This reaction occurs in the thermal decomposition of alcohols (see Section X). The yield of this reaction is calculated by the method described in the previous section:

$$He^{++}: \quad G_{rearrangement} + 1.8\, G_{disp} = 0.37$$

$$Co^{60}: \quad G_{rearrangement} + G_{disp} = 0.25$$

$$0.8\, G_{disp} = 0.12$$

$$G_{disp} = 0.15$$

The yield of propylene from disproportionation reactions in the He^{++} irradiations is 1.8(0.15) = 0.27, and the yield from rearrangement is 0.10.

Reaction (III-5): $i\text{-}C_3H_7OH \rightsquigarrow H_2 + CH_3COCH_3$

The occurrence of this reaction in the photolysis of isopropyl alcohol has been proposed.[67] However, newer work indicates the formation of isopropoxy radicals (see above) which disproportionate to give acetone, and Burr concluded that all the hydrogen produced by radiolysis of ethanol was formed by radical processes.[60] This reaction therefore is not considered.

Reaction (III-6): $i\text{-}C_3H_7OH \rightsquigarrow CH_4 + CH_3CHO$

The occurrence of this reaction cannot be confirmed or disproved by the experimental data, and it is not considered.

Reaction (III-7): $i\text{-}C_3H_7OH \rightsquigarrow H_2 + H_2C\overset{O}{\frown}\underset{H}{C} - CH_3$

This reaction explains the formation of 1,2 propylene oxide. An alternative process for the formation of this compound is the reaction

$2\ i\text{-}C_3H_7O\cdot = H_2C\overset{O}{\frown}CH\text{-}CH_3 + i\text{-}C_3H_7OH$.

Reaction (III-8): $i\text{-}C_3H_7OH \rightsquigarrow CO + 2CH_4$

This would be a high-energy process for the formation of CO. If it occurs, III-6 probably also occurs. The possibility that most of the CO observed is due to secondary decomposition--of CH_3CHO and CH_3COCH_3-- cannot be eliminated.

<u>Summary</u>

The radiolytic decomposition of liquid isopropyl alcohol occurs mainly through the production of hydrogen atoms and methyl radicals. Other work indicates that the hydrogen atoms are formed by rupture

of the O-H bond, but the results of this work do not shed light on the source of the H atoms.

Cleavage of the C-O bond is a minor contribution to the decomposition of isopropyl alcohol. Molecular elimination of H_2O occurs to a relatively small extent but part of the measured propylene is formed by this reaction.

G values measured in other work are listed in Table III. The values measured by McDonell and Newton agree rather well with the values found in this work when the decrease in G values with absorbed dose is considered. Their irradiations involved much higher absorbed doses than the irradiations in this work. The G values measured by Strong and Burr for Co^{60} irradiations show excellent agreement with the values found in this work, but the results of Adams et al. are quite different. No explanation can be advanced for the discrepancy.

IV. Isopropyl Benzene

Previous Radiolyses

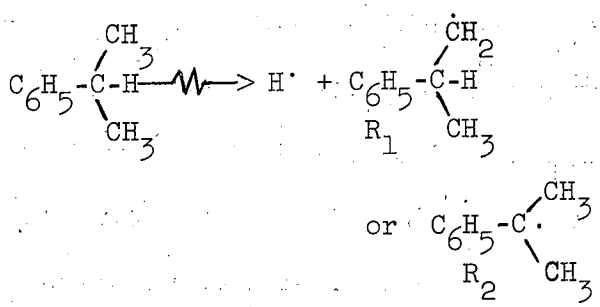
The irradiation of aromatic compounds gives very low product yields.[58] This is attributed to the ability of the conjugated system to absorb energy and to dissipate it without decomposition, and to the disappearance of radicals produced by the radiation through addition to the benzene ring.

The radiolysis of alkyl benzenes proceeds mainly by cleavage of bonds in the side group.[68,69] The most important bond rupture occurs β to the ring.[69]

Isopropyl benzene has been irradiated with helium ions by Newton,[70] by Sworski and Burton with neutrons and γ rays from a nuclear reactor,[71] by Sworski, Hentz, and Burton with electrons,[69] and by Kinderman with electrons.[72] The few products measured by these workers correspond to cleavage of the β bonds in the side chain. The G values from these investigations are listed in Table IV.

Decomposition Pattern

Reaction (IV-1):

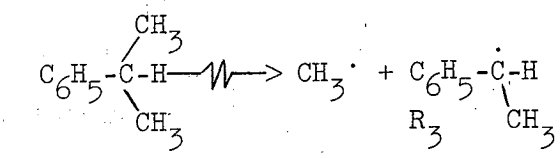


Sworski, Hentz, and Burton found that the yield of H_2 from the radiolysis and photolysis of alkyl benzenes decreased in the order ethyl benzene > isopropyl benzene > tert-butyl benzene.[69] This is the opposite order from what would be expected on the basis of the number of C-H bonds per molecule. The only interpretation is that C-H bond cleavage occurs predominantly at the β C-H bonds, and R_2 will be the radical most often formed in this reaction. Production of $H^{\cdot}$ from the ring is not considered, because radiolysis of benzene produces only small amounts of hydrogen.[58]

The R_2 radicals formed in this reaction cannot fruitfully abstract hydrogen from molecules, and so must diffuse in the liquid until they react with other radicals to give high-molecular-weight products. The hydrogen atoms, on the other hand, can undergo several reactions. They can abstract from molecules to give H_2 plus R_1 or R_2, they can add to

isopropyl benzene molecules, and they can disproportionate with radicals to give H_2. Hardwick has found that the competition between abstraction and addition, when hydrogen atoms react with isopropyl benzene molecules, favors addition.[73] Therefore the yield of hydrogen gives only the minimum yield of IV-1. The yield of IV-1 is > 0.27 for He^{++} irradiations and > 0.21 for Co^{60} irradiations. The smaller yield in the Co^{60} irradiations testifies to the occurrence of addition reactions.

Reaction (IV-2):



The extent of this reaction is measured in the usual way by the production of methyl radicals. The measured methyl radicals are given by $G_{CH_4} + 2G_{C_2H_6} + G_{i\text{-}C_4H_{10}} = 0.084$ for He^{++} irradiations and 0.112 for Co^{60} irradiations. Because addition to the benzene ring[53] and disappearance by reaction with other radicals are possible fates of the methyl radicals, the yield of II-2 > 0.08 for helium-ion irradiations and > 0.11 for Co^{60} irradiations. The larger yield in the Co^{60} irradiations indicates that more methyl radicals disappear by combination reactions than by addition.

Reaction (IV-3): $i\text{-}C_3H_7\text{-}C_6H_5 \rightsquigarrow C_6H_5\cdot + i\text{-}C_3H_7\cdot$

In the Hg-sensitized photolysis of toluene, rupture of the C-H bonds and of the bond between the methyl group and the ring were observed.[74] Photolysis of other alkyl benzenes showed, in addition to cleavage of the bonds β to the ring, a minor contribution from rupture of the bond between the ring and the side chain. Hentz and Burton attributed these two processes to different excited states.[68]

The yield of IV-3 is measured in the usual way by the yield of products formed from isopropyl radicals. The yield of IV-3 is greater than 0.03 for both types of radiation.

Reaction (IV-4): $i\text{-}C_3H_7\text{-}C_6H_5 \rightsquigarrow C_3H_6 + C_6H_6$

This reaction is calculated by the method described in Section II:

$$He^{++}: \quad G_{rearrangement} + 1.8\, G_{disp} = 0.028$$
$$Co^{60}: \quad G_{rearrangement} + G_{disp} = 0.017$$
$$0.8\, G_{disp} = 0.011$$
$$G_{disp} = 0.014$$

The yield of propylene from disproportionation reactions in the He^{++} irradiations is 1.8 (0.014) = 0.025, and the yield from rearrangement is 0.003.

Reaction (IV-5): $i\text{-}C_3H_7\text{-}C_6H_5 \rightsquigarrow$ unsaturated hydrocarbon fragments from the ring.

This reaction is the probable source of the many unsaturated hydrocarbons formed in the radiolysis of this compound.

<u>Summary</u>

The radiolysis of liquid isopropyl benzene proceeds mainly by cleavage of C-H bonds, presumably of the C-H bond β to the ring. Addition to the ring of the hydrogen atoms produced by this process causes a portion of this reaction to go unmeasured. Cleavage of the C-C bonds in the side group is also important. Not only is this result contrary

to what would be expected from the relative bond strengths in the molecule (the C-C bonds have a dissociation energy of approx 61 kcal/mole, whereas the β C-H bond energy is 74 kcal/mole),[29] but the prediction that the weak bonds of this molecule would rupture easily and give high G values would also be in error. The low product yields measured in the present work can be attributed to the influence of the aromatic ring.

Bond rupture between the ring and the side chain is minor. Contribution to the propylene yield from molecular rearrangement is small in isopropyl benzene.

The G values obtained in this work agree reasonably well with results obtained by the other investigators listed in Table IV.

V. Isobutyronitrile

Previous Investigations

Nitriles have been irradiated by Bouby and Chapiro[75] and by Dainton et al.[76] Both investigations measured radical production from nitriles by adding radical scavengers. It was found that measured radical production is smaller in nitriles than in most other organic liquids. Because nitriles may themselves act as radical scavengers, the meaning of these observations is not certain.

Decomposition Patterns

The primary reactions are listed below, together with their yields as determined by measurement of products containing the radicals produced in each primary reaction. These yields are only minimum yields because of the addition of radicals to the molecules of starting material.

Steacie and co-workers found that hydrogen atoms and methyl radicals produced in the photolysis of acetonitrile added to the nitrile molecules.[77] The study of the photolysis was made extremely difficult by this addition. Some of the addition products were identified in later work on the photolysis of CF_3CN.[78]

Reaction (V-1): $$i\text{-}C_3H_7CN \rightsquigarrow H^{\cdot} + (\underset{R_1}{CH_3\text{-}CHCN\text{-}CH_2^{\cdot}} \text{ or } \underset{R_2}{CH_3\text{-}CCN\text{-}CH_3})$$

Production of $H^{\cdot}$ is observed in the photolysis of acetonitrile.[76] The yield of V-1 is probably substantially greater than 1.04 for the He^{++} irradiations and 0.84 for the Co^{60} irradiations, respectively. The lower measured yield in the Co^{60} irradiations is caused by addition reactions.

Reaction (V-2): $$i\text{-}C_3H_7CN \rightsquigarrow CH_3^{\cdot} + CH_3\text{-}CHCN^{\cdot}$$

The yield of this reaction, determined in the usual way, is greater than 0.49 for both types of radiation.

Reaction (V-3): $$i\text{-}C_3H_7CN \rightsquigarrow i\text{-}C_3H_7^{\cdot} + CN^{\cdot}$$

Cleavage of the bond between the alkyl group and the CN group is observed in the photolysis of acetonitrile.[77] Some of the products found in this work (e.g., CH_3CN) indicate formation of CN radicals. The yield of this reaction is greater than 0.67 for He^{++} irradiations and 0.61 for Co^{60} irradiations.

Reaction (V-4): $$i\text{-}C_3H_7CN \qquad C_3H_6 + HCN$$

The largest peak in the mass spectral cracking pattern of isobutyronitrile corresponds to a rearrangement of the molecule ion to

propylene ion and, by inference, HCN. The yield of V-4 may be calculated by the method outlined in Section II:

$$He^{++}: \quad G_{rearrangement} + 1.8\, G_{disp} = 0.79$$

$$Co^{60}: \quad G_{rearrangement} + G_{disp} = 0.63$$

$$0.8\, G_{disp} = 0.16$$

$$G_{disp} = 0.20$$

The yield of propylene from disproportionation reactions in the He^{++} irradiations is 1.8 (0.20) = 0.36, and the yield of propylene from V-4 is therefore 0.43.

Summary

The radiolysis of liquid isobutyronitrile is complex because of addition reactions. G values for gaseous products are low, perhaps because of disappearance of radicals by addition reactions and perhaps because the C≡N group has a protective effect on the molecule similar to the protective effect of the benzene ring in aromatic molecules.

Cleavage of the three types of single bond in the molecule appears to occur to comparable extents, although the product formed in highest yield is H_2. Molecular rearrangement to HCN and C_3H_6 is also important.

VI. Isobutyric Acid

Previous Radiolyses

There have been many exploratory studies of the radiolysis of aliphatic acids, especially of the long-chain acids. Reference 58 summarizes these investigations. The main reaction observed is

decarboxylation, forming CO_2 and the hydrocarbon corresponding to the alkyl group of the acid.

Johnsen has measured CO_2 yields for ten aliphatic acids (see Table VI) and has measured other product yields from acetic and propionic acids.[11] Garrison et al. have irradiated aqueous solutions of acetic acid with helium ions,[8b] Newton has irradiated pure acetic and propionic acids with helium ions,[8a] and Burr has exposed deuterated and tritiated acetic acids to Co^{60} radiation.[79] In all these investigations the main products formed were CO_2 and the appropriate hydrocarbon, but the authors differ on the mechanism of formation of these and other less important products.

Decomposition Pattern

Because the substituent group in isobutyric acid can itself undergo decomposition, it is not sufficient to consider only reactions of radicals which come from the isopropyl group as was done in the discussion of the four previous compounds. Reactions of ·COOH and $i\text{-}C_3H_7COO\cdot$ must also be considered. Different processes for the production of hydrogen atoms, of CO_2, and of $i\text{-}C_3H_7$ radicals are possible. The data will not unambiguously indicate the relative importance of these processes; conjectures are made below regarding their relative importance, but the subject is not treated completely.

Reaction (VI-1): $i\text{-}C_3H_7COOH \rightsquigarrow H\cdot + (\underset{R_1}{CH_3}\text{-}CH(COOH)\text{-}CH_2\cdot$ or $CH_3\text{-}\underset{R_2}{\dot{C}}(COOH)\text{-}CH_3)$

Ausloos and Steacie investigated the photolysis of CH_3COOD and determined that at room temperature hydrogen atoms are produced only by

the analogs of VI-2 and VI-3a, but that at higher temperatures some of the hydrogen atoms are produced by the analog of VI-1.[80] From the knowledge gained about hydrogen production in the other compounds studied in this work, it may be assumed that VI-1 contributes a portion of the hydrogen atoms produced during the irradiation. There is, however, no way to determine this contribution from the data, and this reaction is disregarded. In this discussion the CO_2 and the hydrogen atoms are considered to be produced by the two following sets of reactions:

Reaction (VI-2): $i\text{-}C_3H_7COOH \rightsquigarrow i\text{-}C_3H_7COO\cdot + H\cdot$

Reaction (VI-2a): $i\text{-}C_3H_7COO\cdot \xrightarrow{R_4} i\text{-}C_3H_7\cdot + CO_2$

This reaction has been proposed for production of CO_2 in the photolysis of acetic acid.[80] The ratio of VI-2a to VI-2 depends on the stability of the isobutyrate radical, and there are no firm conclusions that may be drawn about its stability. Jaffe, Prosen, and Szwarc calculate that decomposition of this radical is exothermic by 13 kcal/mole,[81] but Steacie states that decomposition of the acetate radical involves an activation energy of 40 to 70 kcal/mole.[30] Levy and Szwarc found that decomposition of acetate radicals at 65° C occurred readily in some solvents and only to a moderate extent in others (including aliphatic acids).[53] Fry, Tolbert, and Calvin found that acetate radicals decomposed to a moderate extent in acetic acid at 85° C.[82]

Reaction (VI-3): $i\text{-}C_3H_7COOH \rightsquigarrow i\text{-}C_3H_7\cdot + \cdot COOH$

Reaction (VI-3a): $\cdot COOH \xrightarrow{R_5} CO_2 + H\cdot$

This reaction has also been proposed in the photolysis of acetic

acid by Ausloos and Steacie[80] and by Burton,[83] although the latter author subsequently modified his endorsement of the reaction.[84] The main peak in the mass-spectral cracking pattern of isobutyric acid corresponds to formation of the $i\text{-}C_3H_7^+$ ion.

Again, the ratio of VI-3a to VI-3 depends on the stability of the COOH radical. Some old experiments by West and Rollefson indicate that it is unstable at room temperature toward decomposition by VI-3a,[85] and Ausloos and Steacie postulate this reaction in the photolysis of acetic acid.[80]

It will be noted that VI-2a and VI-3a are equivalent reactions. The net reaction in both cases is $i\text{-}C_3H_7COOH = i\text{-}C_3H_7\cdot + CO_2 + H\cdot$. This net reaction may itself occur, but it would be indistinguishable from VI-2a and VI-3a, and is not considered.

Reaction (VI-4): $i\text{-}C_3H_7COOH \rightsquigarrow i\text{-}C_3H_7CO\cdot + \cdot OH$

Reaction (VI-4a): $R_6 \longrightarrow i\text{-}C_3H_7\cdot + CO$

This reaction was observed in the photolysis of acetic acid.[80] The ratio of VI-4a to VI-4 depends on the stability of the isobutyryl radical. There is evidence from the gas-phase photolysis of esters and ketones that a fraction of the acyl radicals formed in the decomposition of these molecules possesses excess energy which causes them to decompose immediately after formation.[86-89] Ausloos and Murad determined that in short-wave-length photolysis of pentanone-2 most of the acyl radicals are decomposed by energy carried over from the primary process.[88] Although photolysis in the liquid phase seems to reduce the proportion of the acyl radicals that decompose immediately,[87,90] the acyl radicals

can decompose thermally. The thermal stability of acyl radicals decreases as the size of the radical increases.[30] Although acetyl radicals do not decompose thermally at room temperature, Masson finds that n-C_3H_7CO radicals have a very low thermal stability.[91] These considerations indicate that most of the i-C_3H_7CO radicals formed eventually produce CO. The detection of small amounts of i-C_3H_7CHO in these radiolyses indicates, however, that some isobutyryl radicals react without decomposing.

The problem of determining the relative importance of these main decompositions cannot be solved with the information available. Minimum yields for some of the reactions can be determined, and the approximate yields for combinations of the reactions can be designated.

The yield of VI-4 and VI-4a seems relatively low. The yield of VI-4a is measured by G_{CO}, which is 0.33 for He^{++} irradiation and 0.42 for Co^{60} irradiation. The smaller value for the He^{++} irradiations presumably stems from reaction of i-C_3H_7CO radicals with other radicals before they can undergo decomposition to give CO. The yield of VI-4 is probably only slightly greater than 0.33 for He^{++} irradiations and 0.42 for Co^{60} irradiations, because of the instability of the i-C_3H_7CO radicals.

The yield of CO_2 is an exact measure of the combined extent of VI-2a plus VI-3a. The sum of the yields of these reactions is therefore 4.5 for He^{++} and 4.8 for Co^{60} irradiation. Reaction of the R_4 or R_5 radicals before they can decompose will occur more often in the He^{++} irradiations, and G_{CO_2} would be expected to be smaller in these irradiations.

The combined yield of VI-2 and VI-3 will therefore be greater than 4.5 for the He^{++} irradiations and 4.8 for the Co^{60} irradiations. The data will not support any conjecture as to the relative importance of VI-2 and VI-3.

Another means for the examination of these yields is measurement of the production of $i\text{-}C_3H_7$ radicals. The yield of $i\text{-}C_3H_7$ is measured in the usual way, by $G_{C_3H_8} + G_{iC_4H_{10}} + (G_{C_3H_6} - G_{molec.\ rearrang't})$ = 3.0 for the He^{++} irradiations and 4.3 for Co^{60} irradiations. In the radiolyses of isobutyric acid a large portion of the total yield of "diisopropyl" (2,3-dimethyl butane) was measured. Addition of the $i\text{-}C_3H_7$ radicals which are measured as 2,3 dimethyl butane to the yields of $i\text{-}C_3H_7\cdot$ measured above gives values of 4.0 and 4.9 for the measured production of isopropyl radicals in He^{++} and Co^{60} irradiations, respectively. Because isopropyl radicals disappear by production of unmeasured hexane and by combination with other radicals, the total yield of isopropyl radicals is greater than 4.0 for He^{++} irradiations and 4.9 for Co^{60} irradiations. This is in good agreement with the yield measured from CO_2 formation, above.

The yield of isopropyl radicals from VI-4a is measured directly by the yield of CO, which is 0.3 for He^{++} irradiations and 0.4 for Co^{60} irradiations. The combined yield of VI-2a plus VI-3 is therefore greater than 3.7 for He^{++} irradiations and 4.5 for Co^{60} irradiations. This is in rough agreement with the minimum values for the yield of VI-2a plus VI-3a as measured by CO_2 production.

The production of hydrogen atoms by the above processes is not measured by the yield of H_2. In the primary reaction scheme above, formation of a CO_2 molecule is necessarily accompanied by production of a hydrogen atom. In addition, hydrogen atoms may be produced by VI-1 and VI-2 without CO_2 formation. The minimum production of hydrogen atoms is therefore 4.46 for He^{++} irradiation and 4.78 for Co^{60} irradition. The actual production of hydrogen atoms can be expected to be larger.

In these irradiations, however, only a yield of 0.84 and 0.73 for He^{++} and Co^{60} irradiations, respectively, of these hydrogen atoms appears as H_2. The fate of the other hydrogen atoms is uncertain. Hydrogen yields in the radiolyses of other short-chain fatty acids are similar to those observed in this work,[78] and it is doubtful that experimental error is responsible for the discrepancy. This disappearance of hydrogen atoms was also noted by Ausloos and Steacie in the photolysis of acetic acid.[80] They attribute it to some unknown process forming H_2O.

Addition of hydrogen atoms to the carboxyl system of the acid is a possible explanation for the disappearance of $H^{\cdot}$. The addition of hydrogen atoms to the carbonyl group of acetone was observed by Burr.[48] Ausloos and Trumbore are unable to account for most of the thermal hydrogen atoms formed in the radiolysis of methyl acetate, and suggest that hydrogen atoms add to the carboxyl group.[46]

It is possible that addition of hydrogen atoms to acids is followed by a reaction that produces water. The occurrence of this

reaction would resolve another discrepancy in the radiolyses of aliphatic acids. The yields of water in these radiolyses are much larger than the CO yield. If the water were formed only by abstraction reactions of the OH· radicals produced in VI-4, it would be necessary to attribute to the isobutyryl radical a stability which other experiments indicate it does not possess (see above).

Disappearance of the hydrogen atoms could be explained by combination reactions with other radicals. These reactions do not seem to occur in the radiolyses of other compounds studied in this work.

Molecular production of CO_2, not proceeding via formation of $i\text{-}C_3H_7\cdot$ and H·, would also explain the failure to detect the hydrogen atoms. Molecular elimination of CO_2 was found, however, to be a very minor reaction in the radiolysis[11,79] and photolysis[80] of acetic acid. Moreover, if C_3H_8 were formed by molecular elimination of CO_2, the yield would be expected to be the same for both types of radiation. $G_{C_3H_8}$ is found instead to be much larger in the Co^{60} irradiations than in the He^{++} irradiations, indicating formation of C_3H_8 from abstraction reactions of isopropyl radicals.

Although Garrison et al. found that methane yields from irradiation of aqueous acid were not significantly reduced by the addition of iodine, and attributed this result to the formation of methane by molecular rearrangement of the acetic acid,[8b] Burr has stated that methyl radicals produced in these experiments would yield methane by abstracting H from HI, which is formed in high yield by the irradiation.[79]

Reaction (VI-5): $$i\text{-}C_3H_7COOH \rightsquigarrow CH_3\cdot + CH_3\text{-}\underset{R_3}{\overset{\cdot}{C}}H\text{-}COOH$$

The yields of methyl radicals as measured in the usual way are

0.17 and 0.15 for irradiations with He^{++} and Co^{60}, respectively. The yield of VI-5 is greater than 0.17 for helium-ion irradiations and 0.15 for Co^{60} irradiations. When combinations with large radicals is the main fate of unmeasured methyl radicals, the measured yield is smaller in He^{++} irradiations than in Co^{60} irradiations. The opposite trend is observed here; perhaps methyl radicals also add to aliphatic acids (both Johnsen[11] and Garrison et al.[8b] found that 1/3 of the methyl radicals produced in the radiolysis of acetic acid were not measured among the volatile products).

Reaction (VI-7): $i\text{-}C_3H_7COOH \rightsquigarrow C_3H_6 + HCOOH$

The yield of this reaction may be calculated by the method outlined in Section II:

$$He^{++}: \quad G_{rearrangement} + 1.8\, G_{disp} = 1.71$$
$$Co^{60}: \quad G_{rearrangement} + G_{disp} = 1.04$$
$$0.8\, G_{disp} = 0.67$$
$$G_{disp} = 0.84$$

The yield of propylene from disproportionation reactions in the He^{++} irradiations is 1.8 (0.84) = 1.51, and the yield of propylene from VI-7 is therefore 0.20.

<u>Summary</u>

The radiolysis of liquid isobutyric acid proceeds mainly by bond cleavage at the carboxyl group. CO_2, isopropyl radicals, and H atoms may be produced directly or may stem from the intermediate production of isobutyrate radicals or COOH radicals. Decomposition at the carboxyl group also produces isobutyryl radicals.

Reactions in the alkyl system of the molecule are not important. A part of the propylene formed is produced by molecular rearrangement.

The product yields measured in this work are in agreement with yields observed in radiolytic decomposition of similar acids by most other workers. The one G value previously measured in the radiolysis of isobutyric acid is $G_{CO_2} = 14.4$.[11] (See Table VI.) This value is in extreme disagreement with the value found in this work, and indeed with G_{CO_2} measured for every other aliphatic acid investigated.[58] No explanation for this discrepancy can be advanced.

VII. Isovaleric Acid

Previous Radiolyses

See Section VI for an outline of experiments applicable to interpretation of the radiolysis of aliphatic acids. See Table VII for G values previously measured in radiolyses of isovaleric acid.

Decomposition Pattern

The decomposition pattern of isovaleric acid is analogous to that of isobutyric acid, which is outlined in Section VI. The first step in determining the contribution of each primary decomposition is to convert the product yields measured in the mixture of α-methyl butyric acid and β-methyl butyric acid to the product yields putatively obtained from pure β-methyl butyric acid. This conversion is recorded in Table VII. The corrected product yields are subject to uncertainties, and the yields of the reactions below are therefore also uncertain.

Reaction (VII-1): $i\text{-}C_4H_9COOH \rightsquigarrow H^{\cdot} + i\text{-}\dot{C}_4H_8COOH$

The yield of this reaction cannot be determined. See Section VI.

Reaction (VII-2): $i\text{-}C_4H_9COOH \rightsquigarrow i\text{-}C_4H_9COO^{\cdot} + H^{\cdot}$

Reaction (VII-2a): $\hookrightarrow i\text{-}C_4H_9^{\cdot} + CO_2$

Reaction (VII-3): $i\text{-}C_4H_9COOH \rightsquigarrow i\text{-}C_4H_9^{\cdot} + {}^{\cdot}COOH$

Reaction (VII-3a): $\hookrightarrow CO_2 + H^{\cdot}$

Co_2 yields show that the minimum extent of these combined reactions is 3.5 for He^{++} and 4.2 for Co^{60} irradiations, respectively. Because virtually no dimer of isobutyl radicals was measured in these experiments, the measured production of $i\text{-}C_4H_9^{\cdot}$ was so small that it sheds no light on the above processes.

Reaction (VII-4): $i\text{-}C_4H_9COOH \rightsquigarrow i\text{-}C_4H_9CO^{\cdot} + {}^{\cdot}OH$

Reaction (VII-4a): $\hookrightarrow i\text{-}C_4H_9^{\cdot} + CO$

The arguments in Section VI for the instability of the isobutyryl radical also hold for the isovaleryl radical. The yield of this reaction is probably only slightly larger than G_{CO}, which is 0.15 for He^{++} irradiations and 0.22 for Co^{60} irradiations.

Reaction (VII-5): $i\text{-}C_4H_9COOH \rightsquigarrow CH_3^{\cdot} + H_3C\text{-}\dot{C}H\text{-}CH_2\text{-}COOH$

The yield of this reaction is greater than 0.21 and 0.19 for He^{++} and Co^{60} irradiations, respectively. As in the irradiation of isobutyric acid, the yield is larger in the He^{++} irradiations.

Reaction (VII-6): $i\text{-}C_4H_9COOH \rightsquigarrow i\text{-}C_3H_7\cdot + \cdot CH_2\text{-}COOH$

This is the only reaction that occurs in the radiolysis of isovaleric acid which does not have its analog in the radiolysis of isobutyric acid. Its yield is determined by measuring products formed by isopropyl radicals. The yield of VII-6 is > 0.04 for He^{++} irradiations and > 0.10 for Co^{60} irradiations.

Reaction (VII-7): $i\text{-}C_4H_9COOH \rightsquigarrow C_3H_6 + CH_3COOH$

The largest peak in the mass-spectral cracking pattern of isovaleric acid corresponds to a rearrangement of the molecule ion to CH_3COOH^+ and, by inference, propylene. The yield of VII-7 may be calculated by the method outlined in Section II:

$$He^{++}: \quad G_{rearrangement} + 1.8\, G_{disp} = 0.29$$
$$Co^{60}: \quad G_{rearrangement} + G_{disp} = 0.26$$
$$0.8\, G_{disp} = 0.03$$
$$G_{disp} = 0.04$$

The yield of propylene from disproportionation reactions in the He^{++} irradiations is 1.8 (0.04) = 0.07, and the yield of propylene from VII-7 is therefore 0.22.

Summary

The radiolysis of liquid isovaleric acid is similar to that of isobutyric acid: mainly production of CO_2, $i\text{-}C_4H_9$ radicals, and hydrogen atoms, perhaps through unstable intermediates. Production of isobutyryl, isopropyl, and methyl radicals occurs to a lesser degree. Molecular rearrangement to propylene plus acetic acid is unambiguously detected,

because the small amount of isopropyl radicals formed in the decomposition cannot account for the yield of propylene. G_{CO_2} measured in this work is less than G_{CO_2} determined by Johnsen.

The relationship between product yields in the two acids follows the expected trend. Isovaleric acid decomposition resembles that of a hydrocarbon more than does isobutyric acid decomposition: the yield of CO_2 and of the hydrocarbon corresponding to the alkyl group is less in isovaleric acid, but the production of methyl radicals is larger. The CO yield is half as large in the isovaleric acid as in isobutyric acid; this change is in the expected direction but is much larger than would be expected. This change in CO yield may result from a difference in stability between isobutyryl and isovaleryl radicals.

VIII. Methyl Isobutyl Ketone

Previous Radiolyses

Burr found that the Co^{60} irradiation of acetone resulted mostly in the well-known photolytic decomposition into CH_3 and CH_3CO radicals, with the CH_3CO radicals decomposing part of the time to give CO. He found that addition of acetone to isopropanol decreased the radiolytic yield of H_2, and attributed this to the addition of hydrogen atoms to acetone.[48]

Ausloos and Paulson irradiated acetone, acetone-d_6, and mixtures of the two.[47] Their results corresponded to formation of methyl radicals from the acetone, plus minor reactions yielding other products. Methyl ethyl ketone and di-ethyl ketone also decomposed in this way. Ausloos diluted acetone, acetone-d_6, and mixtures of the two with other organic

compounds; the results still indicated that the main mode of decomposition involved formation of methyl radicals.[45]

Decomposition Pattern

Reaction (VIII-1): $i\text{-}C_4H_9COCH_3 \rightsquigarrow H\cdot + (\cdot C_6H_{11}O)$ R_1

The hydrogen atom probably comes from the isobutyl group because of the greater statistical probability, and because of the weaker secondary and tertiary C-H bonds. Ausloos observed larger yields of H_2 from the radiolysis of ketones containing secondary C-H bonds than from acetone.[47]

The yield of VIII-1 is given by the yield of H_2 which is 0.90 and 0.70 for He^{++} and Co^{60} irradiations, respectively. These are minimum yields for VIII-1, because addition of hydrogen atoms to the ketone is possible. Burr states that hydrogen atoms add to acetone in the radiolysis of mixtures of alcohol and acetone.[48] The fact that G_{H_2} is larger for He^{++} irradiations than for Co^{60} irradiations is an indication that addition takes place. The yield of VII-1 is > 0.90 for He^{++} irradiations and > 0.70 for Co^{60} irradiations.

Reaction (VIII-2): $i\text{-}C_4H_9COCH_3 \rightsquigarrow i\text{-}C_4H_9\cdot + CH_3CO\cdot$

Reaction (VIII-2a): $R_2 \longrightarrow CH_3\cdot + CO$

Reaction (VIII-3): $i\text{-}C_4H_9COCH_3 \rightsquigarrow i\text{-}C_4H_9CO\cdot + CH_3\cdot$

Reaction (VIII-3a): $R_3 \longrightarrow i\text{-}C_4H_9\cdot + CO$

The photolysis of ketones, and especially of acetone, has been studied extensively. It has been established that ketones dissociate

into alkyl and acyl radicals, and that the acyl radicals are susceptible to further decomposition.[92] Except for ketones with γ hydrogens, which can also undergo molecular rearrangement, this is the only important mode of ketone decomposition in photolysis.[93]

It will be noted that VIII-2a and VIII-3a are the same net reaction: $i\text{-}C_4H_9COCH_3 \rightsquigarrow i\text{-}C_4H_9\cdot + CO + CH_3\cdot$. This reaction may occur directly, in the original dissociation. There is no way to determine how much CO is produced directly and how much is produced by dissociation of acetyl and isovaleryl radicals, and this question is not considered.

The consensus of previous work indicates that VIII-3 is less likely to occur than VIII-2. In the vapor-phase photolysis of methyl ethyl ketone, Pitts and Blacet found that the decomposition occurred "mostly" by dissociation to ethyl and acetyl radicals,[94] and Ausloos found that 90% of the decomposition occurred by this path.[87] Ausloos and Murad found also that 90% of the radical formation from methyl n-propyl ketone resulted in $CH_3CO\cdot + n\text{-}C_3H_7\cdot$, and only 10% in $CH_3\cdot + n\text{-}C_3H_7CO\cdot$.[88] No production of $C_2H_5CO\cdot$ was observed in the radiolysis of methyl ethyl ketone by Ausloos and Paulson,[47] although it should be said that the reaction $C_2H_5COCH_3 \longrightarrow C_2H_5\cdot + CO + CH_3\cdot$ which these authors propose could easily occur through formation of propionyl radicals which subsequently decompose.

In addition, the isovaleryl radical appears to have very low stability toward thermal decomposition.[30,47,91] When VIII-3 does occur, VIII-3a is therefore likely to follow.

The yields of these reactions may be investigated by means of the measured production of CO, $CH_3\cdot$, and i-$C_4H_9\cdot$. The yield of VII-2a plus VIII-3a is measured directly by G_{CO}, which is 0.47 and 0.38 for the He^{++} and Co^{60} irradiations, respectively. It is not clear why the CO yield should be lower in the Co^{60} experiments. A suspicion immediately presents itself that the anomalous ratio for G_{CO} between the two types of radiation is connected with the anomalous ratio for molecular rearrangement between the two types of radiation, but it is difficult to suggest how this connection might occur.

The yield of measured $CH_3\cdot$, as determined in the usual way, is 0.69 and 0.73 for He^{++} and Co^{60} irradiations, respectively. The fact that there are few radicals with which $CH_3\cdot$ can combine to yield undetected products makes it probable that the actual production of $CH_3\cdot$ is only slightly larger than these measured values, and the near equality of the yield for the two types of radiation bears out this expectation. The number of CH_3 radicals produced by VIII-4 probably does not exceed the number disappearing by radical combinations. (See Section IX.)

The measured yield of isobutyl radicals is 0.63 for He^{++} and 0.79 for Co^{60} irradiation. The number of isobutyl radicals that escape measurement is probably large, because dimerization will result in unmeasured product and because the yield is substantially smaller in the helium-ion irradiations, in which dimerization is more likely.

Because the production of i-$C_4H_9\cdot$ seems to be larger than that of $CH_3\cdot$, VIII-2 probably occurs more often than VIII-3, although the production of acetyl radicals does not monopolize the decomposition

as it does in photolysis (see above). The combined yield of VIII-2 and VIII-3 is given by the yield of methyl plus isobutyl radicals less the contribution from VIII-2a and VIII-3a, as measured by the CO yield. The combined yield of VIII-2a plus VIII-3a is 0.47 for He^{++} irradiations and 0.38 for Co^{60} irradiations, and so the combined yield of VIII-2 plus VIII-3 is something larger than (0.69 + 0.63 - 0.47) = 0.85 for the He^{++} irradiations and (0.73 + 0.79 - 0.38) = 1.14 for the Co^{60} irradiations.

Reaction (VIII-4): $i\text{-}C_4H_9COCH_3 \rightsquigarrow CH_3^{\cdot} + CH_3\text{-}\dot{C}H\text{-}CH_2COCH_3$

This reaction is indistinguishable from the production of methyl radicals by the preceding reactions. It probably occurs only to a minor degree, and is disregarded (see Section IX).

Reaction (VIII-5): $i\text{-}C_4H_9COCH_3 \rightsquigarrow i\text{-}C_3H_7^{\cdot} + {}^{\cdot}CH_2COCH_3$

Only a small number of isopropyl radicals are produced, as evidenced by $G_{C_3H_8}$. The yield of isopropyl radicals is approx 0.1. This is an accommodating behavior on the part of the ketone, because if the large yield of propylene does not stem from propyl radicals, it must be produced by molecular rearrangement (see Section X).

Reaction (VIII-6): $i\text{-}C_4H_9COCH_3 \rightsquigarrow C_3H_6 + CH_3COCH_3$

This reaction occurs in the photochemical decomposition of methyl isobutyl ketone (see Section X). The second largest peak in the mass-spectral cracking pattern of methyl isobutyl ketone corresponds to a rearrangement to $CH_3COCH_3^+$ and, by inference, propylene. The yield of VIII-6 cannot be calculated by the method outlined in Section II,

because the assumption that the yield from molecular rearrangement is equal for both types of radiation fails for the ketone. Because the production of isopropyl radicals from the ketone is so small, the contribution of disproportionation reactions to the yield of propylene should be unimportant, and the yield of VIII-6 will be approximately 0.5 for the He^{++} irradiations and 0.8 for the Co^{60} irradiations.

Summary

The radiolysis of methyl isobutyl ketone proceeds mainly by bond cleavage at the carbonyl group. In this respect ketone radiolysis is similar to ketone photolysis. Dissociation to form acetyl and isobutyl radicals is favored over dissociation to form methyl and isovaleryl radicals. The acyl radicals are capable of undergoing further decomposition to yield CO plus an alkyl radical.

In addition to bond cleavage at the carboxyl group, production of hydrogen atoms occurs. Molecular rearrangement is unambiguously observed, but occurs more often in the gamma irradiations than in the helium-ion irradiations. Rupture of C-C bonds in the butyl group is apparently unimportant.

IX. Isopropyl Acetate

Previous Radiolyses

Newton and Strom irradiated isopropyl acetate with helium ions.[95] They measured products corresponding to bond cleavage at the carboxyl group. Kinderman used electrons and Co^{60} γ rays to decompose isopropyl acetate,[72] and Ausloos irradiated isopropyl acetate with Co^{60} γ rays.[96] G values from the above work are listed in Table IX.

Hummel measured 17 high-boiling products from the Co^{60} radiolysis of methyl acetate.[97] He found cleavage of all the bonds in the molecule, but primarily formation of methyl, methoxy, acetyl, and acetate radicals. Ausloos and Trumbore exposed CH_3COOCD_3 and CH_3COOCH_3 to Co^{60} radiation.[46] They found products corresponding mainly to bond cleavage at the carboxyl group. The isotopic distribution of ethane produced in these irradiations indicated that recombination of methyl radicals involved in great part radicals formed from the same molecule, which then reacted within the solvent cage. This effect was first proposed by Newton and Strom to explain the large yield of isobutane in the radiolysis of isopropyl acetate.[95] Co^{60} irradiation of methyl acetate in the presence of different solutes supports these observations.[45]

Decomposition Pattern

Reaction (IX-1): $$i\text{-}C_3H_7OCOCH_3 \rightsquigarrow H^{\cdot} + \underset{R_1}{(C_5H_9O_2^{\cdot})}$$

The high-molecular-weight products formed from radiolysis of methyl acetate indicate that C-H bond cleavage is about equally likely in either methyl group.[97] The main source of the hydrogen atoms from isopropyl acetate is probably the isopropyl group, taking into account bond strengths and statistical considerations.

There are other possible sources of hydrogen from isopropyl acetate. The isotope ratios of the hydrogen produced from gas-phase radiolysis of CH_3COOCD_3 indicate a contribution from molecular elimination of hydrogen.[46] Wijnen proposes that some of the hydrogen atoms

produced in the photolysis of isopropyl propionate are formed in the decomposition of isopropoxy radicals: $i\text{-}C_3H_7O\cdot = H^\cdot + CH_3COCH_3$.[86] These reactions cannot be distinguished in this work from IX-1, and their yields are included in the yield from IX-1. The yields of IX-1 as measured by G_{H_2} is > 0.88 for He^{++} irradiations and > 0.76 for Co^{60} irradiations. The larger yield in the He^{++} irradiations is indicative of the addition of hydrogen atoms to the ester. Ausloos and Trumbore suggest that hydrogen atoms add to methyl acetate.[46]

Reaction (IX-2): $i\text{-}C_3H_7OCOCH_3 \rightsquigarrow i\text{-}C_3H_7O\overset{O}{\overset{\|}{C}}\cdot + CH_3^\cdot$

Reaction (IX-2a): $R_2 \longrightarrow i\text{-}C_3H_7^\cdot + CO_2$

Reaction (IX-3): $i\text{-}C_3H_7OCOCH_3 \rightsquigarrow i\text{-}C_3H_7^\cdot + \cdot O\overset{O}{\overset{\|}{C}}CH_3$

Reaction (IX-3a): $R_3 \longrightarrow CH_3^\cdot + CO_2$

These reactions are proposed in the photolysis of butyl acetate[98] and methyl acetate,[99] and in the radiolysis of isopropyl acetate[95] and methyl acetate.[46] The extent of IX-2a and IX-3a depend on the stability of the acetate and the $i\text{-}C_3H_7\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\cdot$ radicals. The stability of the acetate radical is discussed in Section VI. The $R\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\cdot$ radical is considered to decompose to some extent at room temperature.[80,100]

It will be noted that IX-2a and IX-3a are the same net reaction, $i\text{-}C_3H_7OCOCH_3 \rightsquigarrow i\text{-}C_3H_7^\cdot + CO_2 + CH_3^\cdot$. These experiments will not determine directly whether CO_2 is produced by decomposition of R_2 and R_3, or by a primary decomposition into CO_2 plus alkyl radicals. The high yield of isobutane in these experiments indicates that combination of isopropyl and methyl radicals often occurs within the solvent cage,

before diffusion of the radicals. The isotopic distribution of ethane produced from radiolysis of CH_3COOCD_3 supports this interpretation.[46] Addition of scavenger has little effect on CO_2 yields from radiolysis of isopropyl acetate[95] and methyl acetate.[46] All this evidence indicates primary decomposition to give CO_2 directly, or at least a very rapid decomposition of the intermediate R_2 or R_3. Hummel finds, however, products from methyl acetate radiolysis which contain the analogs of the R_2 and R_3 structures, indicating that some of the radicals formed participate in reactions without decomposing.[97] All three processes probably contribute to the CO_2 yield, but it seems that most of the CO_2 is formed during or immediately subsequent to the initial decomposition of the molecule.

Reaction (IX-4): $\text{i-}C_3H_7OCOCH_3 \rightsquigarrow \text{i-}C_3H_7O^{\cdot} + CH_3CO^{\cdot}$

Reaction (IX-4a): $CH_3CO^{\cdot} \xrightarrow{R_4} CH_3^{\cdot} + CO$

Again, part of the CO yield may stem from a primary decomposition into $\text{i-}C_3H_7O^{\cdot}$, CO, and $CH_3^{\cdot}$. The stability of the acetyl radical is discussed in Section VI. Products that include the structure of the isopropoxy radical ($\text{i-}C_3H_7OCH_3$) and of the acetyl radical (CH_3CHO) have been measured in this work (see Table IX).

The relative importance of IX-2, IX-2a, IX-3, IX-3a, IX-4, and IX-4a can be examined by means of the yields of CO, CO_2, $CH_3^{\cdot}$, and $\text{i-}C_3H_7^{\cdot}$, but quantitative yields are determinable only for the reactions that yield CO or CO_2. Measurement in the usual way shows a yield for production of $CH_3^{\cdot}$ of > 2.4 for He^{++} irradiations and > 2.7 for Co^{60} irradiations. The measured yield of $\text{i-}C_3H_7^{\cdot}$ is > 0.5 for He^{++} irradiation.

and > 0.6 for Co^{60} irradiation. That the measured yields are nearly equal for the two types of radiation argues that unmeasured radical production is not large. The yield of CO_2 is 0.79 for He^{++} irradiation and 0.76 for Co^{60} irradiation; that of CO is 1.19 and approx 1.0 for He^{++} and Co^{60} irradiation, respectively.

The yield of IX-4a is equal to G_{CO}, which is 1.2 for He^{++} irradiation and approx 1.0 for Co^{60} irradiation. The combined yield of IX-2a and IX-3a is given by G_{CO_2}, which is less: 0.79 and 0.76 for He^{++} and Co^{60} irradiation, respectively. Because the acetyl radical is at least as stable at room temperature as R_2 or R_3, this is an indication that IX-4 occurs more often than IX-2 and IX-3 combined. Other radiolyses indicate that the analog of IX-4 is the most important mode of decomposition.[46,95]

Each molecule of CO or CO_2 produced requires that one methyl radical be formed. Since the measured production of methyl radicals is considerably larger than G_{CO} plus G_{CO_2}, the extra methyl radicals may be formed by IX-2 (the yield of IX-5 will be considered to add a small contribution to methyl radical formation, but not enough to account for the excess $CH_3^{\cdot}$ production). On the other hand, the measured yield of propyl radicals is not in excess of G_{CO_2}, and it is not necessary to postulate the occurrence of IX-3.

It appears, therefore, that the importance of the reactions is in the order IX-4 > IX-2 > IX-3. The main dissociation occurs at the bonds at either side of the > C=O group.

Reaction (IX-5): $i\text{-}C_3H_7OCOCH_3 \rightsquigarrow CH_3^{\cdot} + (\underset{R_5}{{}^{\cdot}C_2H_4OCOCH_3})$

The extent of C-C bond cleavage in the alkyl group of molecules

which contain the > C=O group, as measured by the formation of isopropyl radicals from isovaleric acid and from methyl isobutyl ketone, appears to be quite small. For this reason IX-5 is probably a much smaller source of methyl radicals than IX-2, IX-3a, and IX-4a. Newton proposes that excited isopropoxy radicals decompose to give $CH_3\cdot$ and CH_3CHO.[95] Again, this reaction cannot be distinguished from other sources of methyl radicals by the observations in these experiments. It is, however, a convenient explanation of the excess production of methyl radicals that is referred to above. Wijnen found that isopropoxy radicals formed in the photolysis of isopropyl propionate possessed considerable excitation energy.[86]

Reaction (IX-6): $i\text{-}C_3H_7OCOCH_3 \rightsquigarrow C_3H_6 + CH_3COOH$

This reaction occurs in photolysis and in the thermal decomposition of isopropyl acetate (see Section X). The yield of IX-6 may be calculated by the method outlined in Section II:

$$He^{++}: \quad G_{rearrangement} + 1.8\, G_{disp} = 0.82$$
$$Co^{60}: \quad G_{rearrangement} + G_{disp} = 0.78$$
$$0.8\, G_{disp} = 0.04$$
$$G_{disp} = 0.05$$

The yield of propylene from disproportionation reactions in the He^{++} irradiations is 1.8 (0.05) = 0.09, and the yield of propylene from IX-6 is therefore 0.73.

Summary

The radiolysis of liquid isopropyl acetate proceeds predominantly by bond cleavage at the carbonyl group. Dissociation of the alkyl C-O bond and formation of hydrogen atoms by cleavage of C-H bonds is also important. Molecular rearrangement to acetic acid plus propylene

has a high yield, but is less important than bond-rupture processes.

It is of interest to note that in the four compounds irradiated here which contain the > C=O group, the main mode of decomposition involves cleavage of one or both bonds to the carbonyl carbon. Whether this is because of the concentration of absorbed energy in the carbonyl electron system, or because of comparative bond strength within the molecule, is not determinable from these experiments. Another similarity among these compounds is that G_{H_2} is virtually the same for all four compounds. It would be imprudent to suggest that this is not fortuitous.

The G values measured in this work show excellent agreement with those measured by Newton and Strom, and good agreement with Ausloos' values for all products except propane. Kinderman's values are uniformly low, but his method of analysis would only measure a part of the soluble low-boiling products of irradiation.

X. Molecular Rearrangement

The compounds irradiated in this work can undergo various rearrangements to yield several molecular products. The only molecular rearrangement distinguishable by the present experiments from other processes is the reaction

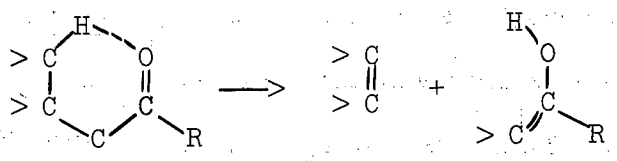
Reaction (X-1): $$i\text{-}C_3H_7X \rightsquigarrow C_3H_6 + HX.$$

This reaction has been suggested as a possible source of product during radiolysis (see below), but its occurrence as a result of irradiation has never been studied in itself.

Occurrence

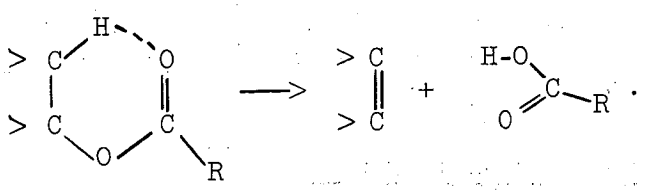
The above reaction has been widely observed. In addition to the usual formation of free radicals, the photochemical decomposition of ketones with hydrogen atoms γ to the carbonyl group proceeds through a rearrangement to form an olefin and a smaller ketone.[93,101,102] Methyl isobutyl ketone undergoes rearrangement to propylene and acetone as well as dissociating into free radicals.[93,103,104,105] This reaction has been shown to proceed by formation of a six-membered cyclic intermediate, followed by cleavage of the α C-C bond and formation of the enol form of the ketone:[88,106,107]

Reaction (X-2):



The photolysis of esters shows rearrangement to olefin plus acid when the ester has a hydrogen atom on the β carbon of the alkoxy group.[87,100,108,109] The photolysis of isopropyl acetate mainly produces propylene and acetic acid.[100] This reaction probably involves a six-membered intermediate also.[93,98]

Reaction (X-3):



Ausloos found products corresponding to molecular rearrangement in the photolysis of esters if either the alkoxy group or the acyl group had a structure capable of forming the six-membered intermediate.[100] Rearrangement might therefore be expected to occur in aliphatic acids that possess the proper structure. Molecular rearrangement occurs in the pyrolysis of

isopropyl acetate, and the kinetics of the reaction indicate a cyclic intermediate.[110] Rearrangement was proposed in the radiolysis of isopropyl acetate because of the excess of C_3H_6 production over that of C_3H_8.[95]

The thermal decomposition of chlorides and of secondary and tertiary bromides proceeds by molecular elimination of hydrogen halide.[111-114] The kinetics of these reactions show evidence of their being four-center reactions, involving polarized C-H and C-hologen bonds.[111-114] The radiolysis of alkyl iodides has been said to proceed in part by molecular elimination of HI,[56] although other workers propose other mechanisms for HI formation.[57] See Section II.

The thermal decomposition of tert-butyl and tert-amyl alcohols proceeds by molecular elimination of H_2O.[115] Catalytic dehydration of alcohols involves the hydrogen atoms β to the carbinol carbon.[116] Molecular elimination of H_2O was proposed in the radiolysis of alcohols.[50]

The fragmentation of ions in the mass spectrometer often proceeds via elimination of molecule-ions or of molecular fragments. Among the compounds studied in this work, molecular rearrangement is the main mode of decomposition of the excited parent ion in isobutyronitrile and in isovaleric acid. It occurs to a large extent in the ketone, and to a small degree in isopropyl benzene. It is not detected in the remaining compounds.

Method of Determination

Excitation of the molecules of several compounds by means other than ionizing radiation causes molecular rearrangement by Reaction (X-1), as outlined above. It is therefore to be expected that a similar rearrangement may occur during radiolyses of these compounds or of similar

compounds. The extent of this rearrangement may be calculated by comparing the yield of propylene from He^{++} irradiations with that from Co^{60} irradiations. This method of calculation is described in detail in Section II, p. 70. It is based on the observation that the yield of propylene from radical disproportionation reactions is 1.8 times as large in the helium-ion irradiations as in the Co^{60} irradiations. If it is also assumed that molecular rearrangement forms the same amount of propylene in both types of irradiation, and if G_{disp} stands for the yield of propylene from disproportionation in the Co^{60} irradiations, then

$$He^{++}: \quad G_{rearrangement} + 1.8\, G_{disp} = M$$

$$Co^{60}: \quad G_{rearrangement} + G_{disp} = N$$

$$G_{disp} = \frac{M - N}{0.8}$$

Several factors limit the accuracy of this method of calculation. The value of 1.8 for the ratio of yields is approximate. The calculation involves the subtraction of one large number from another. In addition, the extrapolation of observed propylene yields for the Co^{60} irradiation of several compounds may be in error (see Results).

The error in determining the yield of propylene from molecular rearrangement should be small, however, when M - N is small. And even though the absolute value of $G_{propylene}$ from rearrangement may be uncertain for several compounds, the relative importance of molecular rearrangement in the different compounds studied should not be affected by errors of the magnitude expected.

The validity of this method of calculation depends on two assumptions: that the yield of propylene from rearrangement is the same for He^{++} and Co^{60} irradiations, and that rearrangement and radical disproportionation are the only important sources of propylene.

The assumption of equality of yield for the two types of radiation can be tested for isovaleric acid and methyl isobutyl ketone, where the production of isopropyl radicals is so small that disproportionation reactions cannot be considered an important source of propylene. This assumption, hereafter referred to as the equality assumption, is obviously wrong for the ketone. The increase in $G_{C_3H_6}$ in the ketone for γ irradiations is attributed to deactivation by radicals of a relatively long-lived triplet-state intermediate that is responsible for at least part of the production of propylene. Such deactivation would be greater in He^{++} than in γ bombardments. Brunet and Noyes[93] and Ausloos and Murad[88] state that photochemically induced rearrangement of ketones occurs from either a singlet state or a short-lived triplet state, but excitation by low-energy electrons, as in radiation chemistry, can populate excited states that are forbidden for interactions with light quanta. Vapor-phase radiolysis of methyl isobutyl ketone in the presence of oxygen would help to resolve the question of the nature of the excited state which results in molecular rearrangement. In the absence of this information it can only be said that deactivation by radicals of a triplet state responsible for rearrangement is possible in the light of photochemical data, although not probable, and is an adequate explanation for the excess yield in the Co^{60} irradiations.

The equality assumption is correct in the case of isovaleric acid (and probably for the structurally similar isobutyric acid). There is no indication that this assumption is not correct for the ester. The probability is small that the simpler electronic systems in the chloride and the alcohol would allow extensive formation of a long-lived triplet state. The failure of the equality assumption in the ketone irradiations is therefore probably an isolated case, in which decomposition through a relatively long-lived triplet state can occur because of the special electronic nature of the carbonyl group.

The second assumption, that propylene is produced mainly by disproportionation and by rearrangement, is very probably true. The production of propylene from decomposition of isopropyl radicals is necessarily smaller than the production of ethylene, and so is not important (see Section I). It is unlikely that the production of propylene from decomposition of isobutyl radicals is more important than the production of ethylene from isopropyl radicals. The possibility of reactions such as

Reaction (X-4): $H\cdot + i\text{-}C_3H_7OCOCH_3 = \cdot C_3H_6OCOCH_3 + H_2$

Reaction (X-4a): $\cdot C_3H_6OCOCH_3 \rightarrow C_3H_6 + CH_3COO\cdot$

cannot be excluded, but it is extremely unlikely that such a radical as $\cdot C_3H_6OCOCH_3$ should be unstable at room temperature. No precedent for such a reaction has been observed in similar systems. The possibility of reactions between two excited molecules to give propylene would be subtracted by the method of calculation used, because the ratio of reactions between excited molecules for He^{++} and γ irradiations will be

the same as for radical-radical reactions. No precedent for this type of reaction has been observed.

The determination by Ausloos that addition of radical scavengers to isopropyl acetate only slightly decreased the yield of propylene[96] supports the proposal that propylene is formed by disproportionation reactions in the spurs and by rearrangement of an unscavengable excited state.

Results for Each Compound

The yield of propylene from molecular rearrangement is calculated for each compound in the section devoted to discussion of the decomposition of that compound. The results are summarized in Table XI.

Discussion

The results show that molecular rearrangement can be an important process in the radiolysis of organic liquids, and must be considered in the discussion of the mechanisms of radiolytic decomposition. It is difficult, however, to discern any systematic effect of the structure of each compound that will allow prediction of the importance of rearrangement in the radiolyses of other compounds.

The problem of correlating the structure of a compound with its tendency to undergo molecular rearrangement during irradiation is complicated by the fact that different compounds rearrange by different mechanisms. Rearrangement of ketones and esters (and presumably acids) would be expected to proceed by way of a six-membered cyclic intermediate. The ease of rearrangement will be determined by the ability of the oxygen to form a bond with the γ H atom, as well as by the strength of the C-C

Table XI.

Factors affecting molecular rearrangement

	Compound Studied							
	isopropyl chloride	isopropyl alcohol	isopropyl benzene	isobutyro-nitrile	isobutyric acid	isovaleric acid	methyl isobutyl ketone	isopropyl acetate
Yield of propylene	2.68; 2.16	.37; .25	.028; .017	.79; .63	1.17; 1.04	.29; .26	.52, .82	.82; .78
Yield of propylene from molecular rearrangement	1.5	0.1	0.003	0.4	0.2	0.2	0.5, 0.8	0.7
ΔH_{react} for molecular rearrangement (b) (kcal/mole)	+17 (119)	+13 (120)	+16 (15)	+31 (121)	+35 (122)	+35 (9)	+21 (123)	+8 (124)
Activation energy for molecular rearrangement (kcal/mole)	50.5 (110) (46 for t-BuCl) (112)	62 for t-BuOH (112)						45 (109)
Extent of molecular rearrangement in mass spectra (c)	~ 1% @ m/e 36	< 1% @ m/e 18	~ 4% @ m/e 78	~ 25% @ m/e 42	0.0 @ m/e 46	~ 20% @ m/e 60	~ 10% @ m/e 58	< 1% @ m/e 60
Electronegativity of functional group (Ref. 122)	+2.94	+1.55	+0.60	+3.64	+2.94			+2.4

(a) The first value given in each column is the yield from the helium ion irradiations; the second value is from the cobalt-60 irradiations.

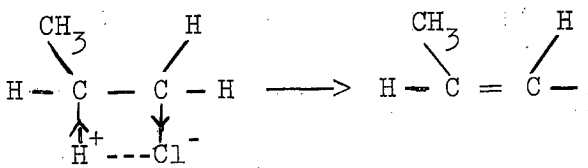
(b) ΔH_{react} is calculated from ΔH_f^o for each substance in the reaction $i\text{-}C_3H_7X = C_3H_6 + HX$. ΔH_f^o for C_3H_6 is obtained from reference (15). ΔH_f^o for HX is obtained from reference (125) except in the case of acetone, which is obtained from reference (126). The ΔH_f^o of $i\text{-}C_3H_7X$ is obtained from the references listed in the columns above.

(c) Except for the nitrile, the extent of molecular rearrangement is expressed as the percentage of the total ion spectrum which appears at the m/e value corresponding to the HX^+ ion. Propyl radicals are formed from every compound but isopropyl benzene and isobutyronitrile, and cracking of these isopropyl radials produces $C_3H_6^+$ ions, masking any contribution at m/e = 42 from molecular rearrangement. In no case, however, can this contribution at m/e = 42 from rearrangement exceed one or two percent of the total ion decomposition.

or C-O bond that is eventually broken. It is found that rearrangement occurs more readily in the photolysis of methyl n-butyl ketone than in methyl isobutyl ketone, presumably because of the weaker secondary C-H bonds involved in the cyclic intermediate.[104]

Rearrangements of halides or alcohols cannot proceed by such a mechanism. The proposed mechanism for thermal decomposition is

Reaction (X-5):



For this type of reaction the electronegativity of the substituent determines the extent of the rearrangement.

It should be noted that although methyl ethyl ketone and diethyl ketone do not undergo photochemically induced molecular rearrangement, the radiolyses of these compounds yielded small quantities of ethylene which could not be explained by radical disproportionation reactions.[47] It may be that radiation-induced rearrangements may involve five-membered cyclic intermediates, or other paths not available in photolyses.

There are several properties of the molecule which do not affect the relative importance of rearrangement processes. The overall heat of reaction for

Reaction (XI-1): $i\text{-}C_3H_7 \rightsquigarrow HX + C_3H_6$

does not influence the probability of rearrangement. See Table XI. The reaction is considerably more endothermic for the nitrile than for the alcohol or for isopropyl benzene, and yet the reaction is much more important for the nitrile than for the other two compounds. Mass spectra

may not be used to predict the likelihood of radiation-induced rearrangements. The two acids provide a convincing example. Rearrangement is of equal importance in the radiolysis of the two acids. The largest peak in the mass-spectral cracking pattern of isovaleric acid is produced by rearrangement of the parent ion to acetic acid ion plus, presumably, propylene, and yet no such rearrangement of the isobutyric acid ion occurs. This is an indication that the radiolysis of these organic liquids does not involve the reactions of ions, in accordance with the arguments in Section I.

The activation energies for the rearrangements are mainly unknown. Those few which are known are listed in Table XI. They seem to be a good indication of the probability of the reaction. Activation energies, however, are only reflections of more fundamental properties which allow rearrangement to occur more readily in some compounds than in others.

The electronic nature of the substituent influences the susceptibility of the molecule toward rearrangement, but this effect depends on the mechanism of rearrangement. In four of the compounds studied here, rearrangement by way of a cyclic intermediate is unlikely. The chloride and the alcohol cannot form a five- or six-membered ring, the stereochemistry of the nitrile prevents the formation of a cyclic form of the molecule, and the electronic nature of the isopropyl benzene does not permit intermediates such as those drawn above. For these four compounds Table XI shows that the extent of rearrangement depends on the electronegativity of the substituent.

The electronegativities listed in the Table are those compiled by Taft.[117] The values are based on the effect of substituents on the rate of reactions which depend on the electron density at the reaction center. They are substituent constants for aliphatic compounds similar to those compiled for aromatic compounds by Hammett.[118] They are in agreement with the qualitative scale of polarities developed by Ingold and other English organic chemists.[119] A close qualitative agreement can be shown to exist between these electronegativities and the inductive constants of Branch and Calvin.[119,120] A positive value for these electronegativities indicates electron-withdrawing power relative to the $-CH_3$ group.

The most electronegative group is the -CN group, followed by the -Cl atom. It is in these two compounds that rearrangement occurs in the largest fraction of molecules that decompose. The -OH group is considerably less electronegative, and rearrangement occurs only to a small extent in the alcohol. The phenyl group is least electronegative, and rearrangement in isopropyl benzene is insignificant.

This effect is easily understood if the rearrangement in these compounds is considered to occur by the intermediate listed on page 109. By analogy to rearrangement produced by other means, however, elimination of HX in the other four compounds must be considered to occur at least partly by a cyclic intermediate. No correlation between electronegativity and the extent of molecular rearrangement is evident in these compounds. The attraction of the γ H for the carbonyl oxygen determines the probability of formation of these intermediates. There is no quantitative measurement of this attraction that will permit its correlation.

It is to be expected, however, that the -OH group in the acids reduces the polarity of the > C=O group. Rearrangement is less important in the acids than in the other two compounds.

CONCLUSIONS

The information that these experiments provide regarding the specific mode of breakdown of each of the compounds studied is summarized at the ends of Sections II-IX. Free-radical reactions and molecular rearrangements are used to explain the observed product yields. In general, all the bonds in a given molecule are susceptible to rupture induced by the radiation. In each compound one or two modes of bond cleavage predominate, depending on the nature of the functional group in the molecule.

Product yields from any given compound are different for He^{++} irradiations and for Co^{60} irradiations. When a product is formed by radical-radical reactions, its yield should be larger in the He^{++} irradiations than in the Co^{60} irradiations. The experimental results verify this prediction. Products that would be expected to be formed by radical-radical reactions are not only found in larger yields in the He^{++} irradiations, but also the ratio of $G_{He^{++}}/G_{Co^{60}}$ for these products has a nearly constant value. Products that are considered to be formed by radical-molecule reactions are measured in higher yield in the Co^{60} irradiations, again in agreement with expectation.

Molecular rearrangement of the type $i\text{-}C_3H_7X \longrightarrow HX + C_3H_6$ has been shown to occur to a varying extent in all these liquid-phase radiolyses. In several compounds this molecular rearrangement is such an important source of product that this process cannot be ignored in discussions of the processes by which products are formed during radiolysis. The extent of radiation-induced rearrangement in any given

molecule depends on the electronic nature of the molecule and on the nature of the intermediate state through which the rearrangement occurs. These experiments indicate that rearrangement occurs most readily in compounds containing the most electronegative functional groups, unless formation of cyclic intermediates provides an alternative path by which the rearrangement may proceed.

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