1960

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Recommended Citation

Kivel, Joseph, "Gamma radiolysis of carbon-14 labeled isobutane " (1960). *Retrospective Theses and Dissertations*. 2649.
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GAMMA RADIOLYSIS OF CARBON-14 LABELED ISOBUTANE

by

Joseph Kivel

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1960

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I. INTRODUCTION

The effects of radiation on hydrocarbons were investigated as early as 1924. Mund and Koch (1) in France studied the alpha particle irradiation of methane. Shortly thereafter Lind and Bardwell (2) observed the effect of alpha particles in ethane and later extended their studies to include many of the hydrocarbon gases (3).

The present approach to understanding the fundamental processes of radiation chemistry was formulated by Eyring, et al. (4) in 1936, and, although their theory has been modified by further investigations, many of the observable effects can be explained by their postulates.

Since the original investigations, many compounds have been studied. The radiation chemistry of water has been studied by many investigators, and the mechanisms by which the radiation products are formed are believed to be understood. However, for most chemical systems, the mechanisms are very difficult to determine. The effects of radiation on the hydrocarbons are still not completely understood. Until 1953 there were relatively few investigations on this subject. Analysis of the gaseous radiation products was tedious until the new technique of gas chromatography was utilized. Gas chromatography markedly reduced analysis time and effected excellent resolution in most cases. Since 1953 the number of reports on the radiation chemistry of organic compounds has increased enormously. Many of the more recent reports have been concerned with the mechanisms involved in the formation of products. Various techniques, such as analysis of mass spectra, deuterium labeling of compounds, and reactions with scavengers, especially radioactive iodine, have yielded a greater knowledge of the fundamental effects of radiation.

The addition of an 1800 curie cobalt-60 source to the facilities available at Iowa State University has made it feasible to undertake radiation chemistry studies. It was believed that a further contribution to the understanding of the mechanisms involved in the radiation of hydrocarbons could be obtained by irradiating a carbon-14 labeled compound. If the hydrocarbon could be obtained or prepared so that the tagged atom replaced each of the various carbon atoms in the molecule, a study of the products formed would be valuable in explaining these mechanisms.

Kokes, Tobin and Emmet (5), Evans and Willard (6), and Wolfgang and Rowland (7) recently have developed methods for separation of radioactive compounds by gas chromatography. These developments, plus the accessibility of commercially available carbon-14 labeled hydrocarbons, have helped to make the present investigation possible. Recent studies by Lampe (8) and Hamashima _et al._ (9) on neopentane indicated the value of investigating a similar compound, such as isobutane.

II. REVIEW OF THE LITERATURE

A. Interaction of Radiation with Matter

1. Distribution of radiation

Radiation effects can be conveniently divided into effects of ionization and electronic excitation and effects of atomic displacement. Atomic displacement effects occur primarily in solids, and do not contribute to the radiation chemistry of the light hydrocarbons. Only the effects of transfer of energy to the recoil electron, leading to ionization and excitation, will be considered.

When a gamma or X-ray interacts with a molecule the most common phenomena is the ejection of a Compton electron. The electron produced travels several hundred molecular diameters before it comes to rest (10), either to discharge a positive ion or to form a negative ion. Many ionizations and excitations occur along the track of the electron. If the Compton electron does not give enough energy to the particle "hit" to cause ionization, it produces excitation, and the excited molecule produced does not differ from the excited molecules observed in photochemistry.

It can be shown that the energy of the electron is about evenly distributed between excitation and ionization. When a one Mev gamma ray undergoes a Compton process, the mean energy of the Compton electron is about 440 kv. Since most gases require 30-35 ev to produce an ion pair, this electron may produce about 15,000 additional ionizations and 30,000 to 45,000 excitations. Actually the electron itself produces only about 4,000 ionizations, but the energetic secondary electrons produce an average of about three ionizations each. The single atom affected by the gamma ray makes a negligible contribution to the total chemical change. Most of the ionization in irradiated systems, therefore, is caused by the relatively slow secondary electrons, which are able to remove valence electrons only. Ionization of the inner shells is relatively unimportant.

The primary reactions of radiation chemistry generally are considered as being

$$A \xrightarrow{\gamma} A^{+} + e \tag{1}$$

and

$$A \xrightarrow{\gamma} A^{*} \tag{2}$$

where A^{*} represents any excited state of A, and the symbol $\xrightarrow{\gamma}$ has the meaning "under the influence of radiation, yields". These processes are independent of whether the cause of the reaction has been the primary Compton electron, the gamma ray, the secondary electron, or the charged positive ion. The excited state of A^{*} may vary, depending on the method of excitation. The fate of these species will now be considered.

2. Fate of the electron

The primary and secondary electrons will usually become thermalized and react with a positive ion to form excited neutral species.

$$e + A^+ = A^* \qquad (3)$$

In certain cases the electrons react with neutral molecules, probably by resonance absorption to produce negative ions.

$$e + \underline{A} = \underline{A}^- \qquad (4)$$

Negative ion formation is unlikely, except when the A molecule possesses a low-lying vacant orbital and can capture a thermal electron, as is the case for NO, O_2, and NO_2, or when the electron affinity of X in the reacting molecule RX is greater than the RX bond. In the latter case, RX reacts with the electron to yield R and X^-, as in the case of halogens or hydroxides.

The negative ion may break up into a smaller negative ion plus either a radical or a small molecule. It may react with the solvent in a liquid system, or it may react with a positive ion in a neutralization reaction.

3. Fate of the positive ion

When a molecule is hit by ionizing radiation, any part of the molecule may be ionized. The charge may be distributed throughout the molecule or it may be localized in a group or atom; the latter case leads to selective chemical effects. The molecule ion may also be produced in a variety of different excited states, both stable and unstable.

In most molecules the charge is not localized. It assumes a normal probability distribution very rapidly (11). Vibrational energy is nearly always produced when a molecule is ionized because the lowest potential function of the ion will not, in general, have exactly the same equilibrium configuration as that of the molecule. Furthermore, excited states of the ion are produced and vibrational energy is created during internal conversion processes. Thus, an ion frequently has enough vibrational energy to produce dissociation or rearrangement. Such an ion, unless it has been deactivated by collision, wanders through all configurations consistent with its energy and potential function, until it passes through one of the activated states which leads to reaction products. Possible reactions of positive ions are:

(a) Neutralization by reaction with an electron.

(b) Formation of a smaller ion and a radical.

(c) Formation of a smaller ion and molecule.

(d) Production of a second excited state by imparting some of the energy acquired in the collision process to adjoining molecules (e.g., as polarization energy).

(e) Ionization transfer. Consider a mixture of A and B with A having the greater ionization potential. Then

$$A^+ + B = A + B^+ + \text{energy}. \qquad (5)$$

(f) Neutralization with a negative ion.

(g) Ion-molecule reactions. Ion-molecule reactions only occur when there is a large collision cross section and a negligible activation energy. They are noted particularly in gases at higher pressures. The reaction may be considered as

$$A^+ + A = F + G^+ \,. \qquad (6)$$

These reactions occur primarily for small molecules. Examples of ion-molecule reactions are

$$CH_4^+ + CH_4 = CH_3 + CH_5^+ \qquad (7)$$

and

$$CH_4^+ + CH_4 = C_2H_6^+ + H_2 \,. \qquad (8)$$

4. Neutralization reactions

In 1936, Eyring *et al.* (4) applied modern ideas of chemical kinetics and molecular structure to radiation chemistry. Before the publication of the Eyring, Hirschfelder, and Taylor theory, it had been assumed that the ions originally produced entered into reactions as ions. They suggested that before any chemical process involving the ion could occur, the ion would be discharged with the production of an excited molecule. However, if the ion is not discharged within one molecular vibration period, it may undergo a reaction as an ion.

Neutralization of a gaseous ion by a free electron releases nine to fifteen ev and tends to yield excited free radicals, although direct decomposition by elimination of small molecules such as hydrogen or methane may be important. Large polyatomic molecules are expected to give a variety of products. However, if a polyatomic ion, A^+, is neutralized by a negative ion, B^-, the most likely products are excited states of A and B.

5. The excited state

Major emphasis in radiation chemistry is placed on the study of the excited state and the radicals produced by it. Most of the radiation products are formed through the intermediate A^*, where A is the starting material.

The excited molecules formed either directly or through ionization and neutralization undergo all photochemical processes including dissociation into atoms, radicals or ultimately into stable molecules. The variety of excited states accessible in radiation chemistry is much greater than in photochemistry, and consequently the variety of processes is much greater.

Excited states of molecules which result from very fast (primary) particle impacts are principally singlet states.

The effects of slow secondary electrons are qualitatively different. States which differ in multiplicity from the ground state may also be excited with high probability. Triplet state excitations are to be expected and should be formed in abundance, since their low excitation potential and high multiplicity favor them over singlet states in slow electron impact (12). These triplet states should be relatively important since their difference in multiplicity from the ground state tends to protect them from destruction by radiation and internal conversion. In general, triplet states undergo reactions that singlet states cannot undergo, since singlet states react rapidly.

6. Fate of excited molecules

Possible reactions of excited molecules are:

(a) Internal conversion to the ground state.

(b) Internal conversion to lower excited states.

(c) Emission of energy as luminescence.

(d) Excitation transfer. If the initial and final states of molecules A and B are closely coupled there may be transfer of energy between the two molecules. This reaction may be considered to be a process such as

$$A^* + B = A + B^* . \tag{9}$$

(e) Metathetical reactions. A typical metathetical reaction may be written as

$$2A^* = B + C \quad (10)$$

There may be possibilities of more complicated reactions involving two excited molecules of different reactants.

(f) Decomposition reactions. The excited molecule may decompose into smaller stable molecules or into free radicals.

7. Formation and fate of free radicals

Free radicals are frequently formed in radiation chemistry in many ways. Burton *et al.* (13) point out that free radicals are products of decomposition of excited molecules, by-products of ion formation, such as dissociative capture of an electron, products of ion-molecule reactions and of ion neutralization. They note that if two radicals having a common parent diffuse through the liquid there is a considerable probability that a reencounter will occur before a random distribution is attained. The probability of reaction on such a geminate reencounter is usually assumed to be unity. When bond rupture of ABCD to yield AB and CD is followed by simple recombination the yield may be considerably decreased.

8. Hot radical reactions

A hot radical has an energy content considerably greater than that characteristic of the temperature of the system. The excess energy of the hot radical will rapidly become distributed among the molecules of the whole system by two types of collisions. Collisions which simply reduce the energy of the hot radical are called moderating collisions; collisions which result in the formation of a recognizable product with the hot radical before it has lost much of its excess kinetic energy are called hot radical reactions.

The "splitting factor" is defined as the ratio of hot radicals undergoing reaction to hot radicals moderated. One can determine the splitting factor by introducing into the system a small proportion of a reagent which reacts very efficiently with the thermal radicals, but does not react with the hot radicals. This reagent is called a "sink".

B. Interpretation of Radiation Effects

1. Statistical and selective effects of radiation

In the interpretation of radiation effects, a limiting case to consider is the statistical nature of the radiation process. Studies of the hydrogen and methane yields in the radiolysis of saturated aliphatic hydrocarbons and their acids by Breger (14) and Schoepfle and Fellows (15) have shown that the ratio of hydrogen yield to methane yield for a number of different hydrocarbons is proportional to the ratio of the number of C-H bonds to the number of $C-CH_3$ bonds. This and other evidence has led to a statement essentially statistical in its nature by Burton (16) that, where special chemical restrictions can be neglected, nature and quantity of the products are determined by nature and number of parent groups in the molecule of the substance decomposed. This principle is useful as a sort of ideal behavior for a substance. However, as will be shown, chemical effects can rarely, if ever, be neglected.

The other limiting case to consider is the case of complete selectivity. This, of course, is typical of the results obtained in photochemistry. However, complete selectivity is never the case in radiation chemistry.

Many compounds exhibit varying degrees of selectivity. There is the well known case of the exceptional stability of aromatic compounds to radiation. Even in bombardment with very high energy particles there is a remarkable stability of aromatic compounds. Current investigations by Lang (17) have shown that for the synchrotron irradiation of cyclohexane and benzene by 47 Mev maximum energy gamma rays, the number and amount of low molecular weight compounds produced in benzene was considerably less than in cyclohexane. In mixed aliphatic-aromatic compounds such as toluene and ethyl benzene, the aliphatic part is preferentially decomposed.

Dewhurst (18), in a study of the branched chain alkanes, noted some degree of selectivity. By analysis of the intermediate molecular weight products of the radiolysis of these compounds, he found that the preferred site of scission was at the point of branching. For example, 2-methylpentane did not form any appreciable amounts of C_8 and C_{10} products;

a large yield of C_9 product was formed, corresponding to a cleavage into two C_3 fragments, which combined with the starting material. Similarly, in 2,2-dimethylbutane no C_9 compounds were formed, and the primary products were C_8 and C_{10} hydrocarbons, corresponding to a preferred cleavage into C_2 and C_4 fragments.

Investigations of the radiolysis of the alkyl halides by Gevantman and Williams (19), Schuler and Petry (20), Schuler and Hamill (21), and many others have shown that the carbon-halogen bond is broken more often than expected statistically.

2. Isotope effects

Isotope effects have been observed. Burr (22) has compared a series of deuterated ethanols, and has found a notable decrease in the hydrogen plus deuterium yield with deuterium substitution in the $-CH_2-$ group; however, the hydrogen plus deuterium yield is unaffected by deuterium substitution in either the CH_3- or $-OH$ groups.

3. Scavenger effects

There have been many investigations on the effects of addition of scavengers. A scavenger is a species that reacts rapidly and indiscriminately with all radicals. The most common scavengers used have been molecular iodine and diphenylpicrylhydrazyl.

In the application of scavengers, an indication of the stability of a species towards radiation can be obtained by measuring the amount of radicals produced. Dewhurst (23) added iodine and other scavengers to hexane and exposed the mixture to a high energy electron beam. The hydrogen yield, upon addition of any of these scavengers, decreased to the same value observed during the irradiation of pure hexane in the solid state. The portion of the yield unaffected by scavengers was attributed to intramolecular processes which produced hydrogen molecules. The scavengers only captured the hydrogen atoms produced in radical reactions.

4. Effects of temperature and physical state

The effects of temperature on the yield of radiation products has given information as to the mechanisms involved in their formation. Hot radical and ion-molecule reactions are not affected by temperature, whereas most other reactions are temperature dependent.

A study of the effect of temperature in the radiolysis of cyclohexane and neopentane by Hamashima *et al.* (9) showed little change in the methane yield and no change in the hydrogen yield in cyclohexane. Distinct effects were noted in neopentane. The increase in yield in neopentane was attributed to free radical reactions, whereas the residual yield in cyclohexane and neopentane was attributed to molecular processes.

5. Effects of radiation intensity

The energy of the interacting particle or ray determines the spatial distribution of energy absorption processes along the track of the secondary electron. Dewhurst and Winslow (24) compared the electron beam radiolysis for 800 kvp electrons and the cobalt-60 gamma ray radiolysis of liquid hexane. Since the Compton electrons from cobalt-60 gamma rays have an average energy of 600 kv, the chemical changes for the two modes of radiation should be similar; however, quantitative differences were observed. Generally, in the case of high energy radiation, the primary events are spaced at random and at great enough distances that they can be considered as being isolated from one another; however, at the higher dose rate obtained during the electron beam radiolysis there appeared to be interactions between spurs. A spur is defined as the region in which the energy from one primary event, e.g., interaction of a secondary electron with a molecule, is dissipated. The intensity of radiation must be taken into consideration only when there is interaction between spurs, and for any gamma source presently available initial yields may be considered as independent of dose rate.

6. Comparison of mass spectra and radiation

Useful comparisons can often be made between the data from mass spectra and from radiolysis. Burr (22), as previously noted on page 13, has compared the radiolysis products of a series of deuterated ethanols. The mechanism presented to account for hydrogen formation is similar to that deduced from mass spectra observations. Burr (25) has extended these observations to acetic acid, ethane and benzene, and has shown that mass spectra data can be used to determine the approximate amounts of products formed by radical and molecular processes.

Mass spectral data cannot be compared to radiolysis data when the formation of products by radiation is dependent on track density effects. Unimolecular decomposition of an excited or ionized molecule should be independent of track density, and for similar reasons independent of physical state, and should lend itself very nicely to comparison between the two methods.

7. Miscellaneous effects

Many approaches have been used in an attempt to understand the mechanisms involved in radiation chemistry. Williams and Essex (26), for example, have used an applied electric field for the isolation of various steps in gas phase reactions.

The radiolysis of mixtures of compounds has given much information as to the selective nature of a radiation process. Protection and sensitization have been observed in mixtures; the component with the lowest ionization potential should form relatively more positive ions, whereas the component with the lowest excitation potential will form relatively more excited states. Competition between the components occur, leading to radiation protection of one species by another. The radiolysis of mixtures is presently being investigated by industry to determine its commercial possibilities for the production of several types of compounds. In particular, the study of graft polymerization is being looked into extensively.

Studies using intermittent irradiation have been pursued. Using intermittent radiation, the concentration of intermediates is no longer built up to a steady value, which determines the rate of reaction.

Other approaches which have been used include examination, theoretically and experimentally, of the geometry of particle tracks, studies of pressure dependence in gaseous compounds, and energy transfer studies by addition of the rare gases to a gaseous system. However, the present state of radiation chemistry knowledge leaves much to be desired. A major breakthrough is needed. It is hoped that by continuing investigations of the various effects, the properties of materials exposed to radiation can be predicted.

It is suitable, at this point, to include a discussion of radiation dosimetry. However, due to the relationship between some of the literature of radiation dosimetry and the determination of radiation dose in this investigation, a separate section of the experimental procedure will be devoted to dosimetry.

III. EXPERIMENTAL TECHNIQUES

A. Preparation of Sample for Irradiation

1. Description of vacuum line

A vacuum line (Figure 1), consisting of a Duo-Seal vacuum pump attached to a 15 mm vacuum main (G_1), was subdivided into segments by stopcocks S_3 and S_9. Attached to the main were a cold trap, manometer, McLeod gauge, and four side arms containing four two mm bore stopcocks (S_7, S_8, S_{14}, S_{15}) and three 12/30 standard tapers. In addition, there was a connecting arm (G_8) containing a two mm bore stopcock (S_{13}) between a side arm and the McLeod gauge.

A McLeod gauge is usually employed for the measurement of low pressures, but since it is fundamentally a volume measuring instrument it can be usefully applied to gas analysis. The design of the McLeod gauge was similar to that recommended by Glascock (27), but was modified by incorporating a standard taper and a stopcock (S_{11}) onto the calibrated tube (G_5). These modifications made it possible to transfer the radioactive material directly from the calibrated tube to the irradiation vial.

2. Preparation procedure

The irradiation vial consisted of a 25 mm pyrex glass tube attached to a two mm bore vacuum stopcock. The tube was cleaned in concentrated nitric acid, washed several times

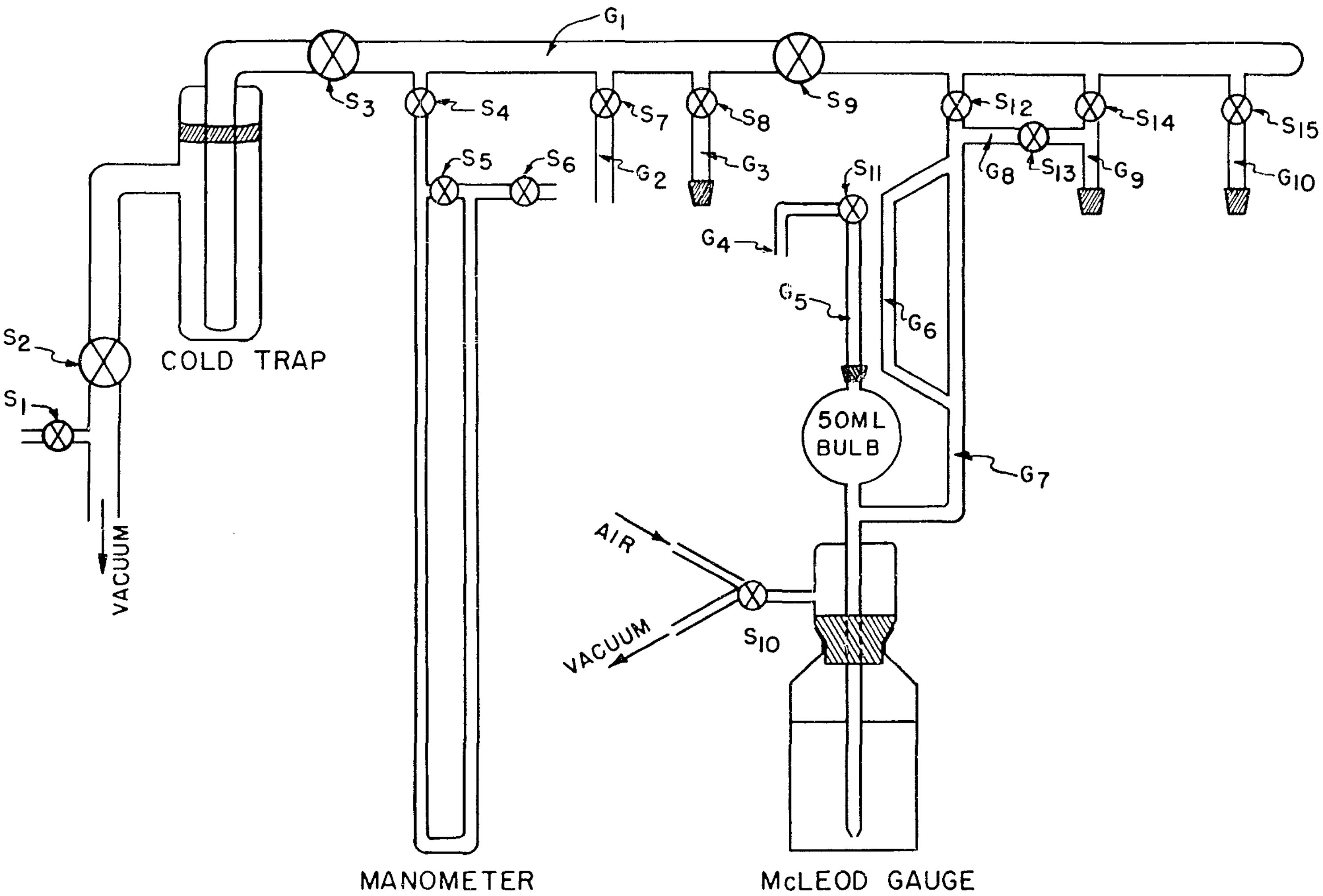

Figure 1. The vacuum line

with distilled water, and heated with a Bunsen burner while attached to the vacuum line to drive out any gases adsorbed on the surface of the glass.

A "lecture bottle" of Matheson Company "instrument grade" isobutane was attached to G_{10}. Analysis by gas chromatography revealed only a trace amount of n-butane; the isobutane was used without further purification.

The irradiation vial was attached at G_2 and the vacuum line was completely evacuated. Isobutane was added to the closed system to the desired pressure, as indicated by the manometer. If carbon-14 labeling was not desired, the vial was available for irradiation at this point.

To add the desired labeled compound, the irradiation vial was attached to the side arm (G_4) of the McLeod gauge calibration tube. The labeled compound was attached at G_9. The labeled compounds used in this investigation were Orlando Research, Incorporated isobutane-1-C^{14} and Research Specialties Company isobutane-2-C^{14}. The isobutane-1-C^{14} contained impurities of radioactive ethane, propane and isobutene. The isobutane-2-C^{14} contained traces of radioactive propane, n-butane and isobutene. The isobutene in the isobutane-1-C^{14} was the only impurity large enough to affect the results.

The system was again evacuated and the irradiation vial was immersed in liquid nitrogen. By adjustment of the appropriate stopcocks a calibrated amount of radioactive compound was transferred into the irradiation vial by way of the McLeod gauge.

B. Sample Irradiation

1. Radiation dosimetry

In general, gamma dose is measured in terms of energy absorbed per unit mass of the material absorbing the dose. If the absorbed energy is produced predominantly by the Compton effect, the amount absorbed is directly proportional to the number of electrons per gram of absorbing material. Cobalt-60 gamma radiation produces energy primarily by Compton processes.

A requirement for a system to be used for dosimetry studies is that it must be stable for a reasonable length of time before and after the irradiation. In addition, the system should have a low temperature dependence and must be free of complicating side reactions. Most dosimeters are useful only up to a certain maximum dose and dose rate. Generally the maximum total dose is inversely proportional to the radiation stability of the dosimeter. Ionization chambers have been found to be excellent dosimeters for gaseous systems, but are not very applicable for liquid systems (28). Calorimeters have also been used, as well as glass dosimeters consisting of glass containing silver or cobalt.

Chemical dosimeters have probably received the greatest amount of attention. The dose measurements for most chemical systems are based on a radiation-induced optical change in the system. Harteck and Dondes (29) used a nitrous oxide dosimeter for studies of high level beta and gamma rays and thermal neutrons. The calculation of the dose was based on the measurement of the nitrogen dioxide produced from the decomposition of nitrous oxide. The amount of nitrogen dioxide was measured colorimetrically. This system is especially useful for measurements of dose absorbed in gaseous systems. By adjustment of the gas pressure, a system similar in electron density to the desired system can be produced; direct determinations of dose absorbed in a gaseous system could be obtained by using this system. Unfortunately, the dose range for this system is 10^7 to 2×10^9 rads. Below 10^7 rads the amount of nitrogen dioxide produced is unmeasurable; above 10^9 rads the plot of reaction yield as a function of dose begins to depart from linearity. Another limitation of this system is that the production of nitrogen dioxide is dependent on the temperature and the dose rate even in the working range.

Many different dyes have been tried as dosimeters. The most successful dosimeters were halogenated hydrocarbon-dye indicators (30) and methylene blue indicators (31).

The ferrous-ferric sulfate indicator is the most widely used indicator, and is often used as a standard of dosimetry. This system obeys most of the requirements for a suitable dosimeter. The amount of ferric ion produced is measured spectrophotometrically, although there is a considerable dependence of the extinction coefficient on temperature. The most useful range of this dosimeter is from 10^3 to 4×10^4 rads; this range can be extended by using various techniques (32). The ferrous-ferric sulfate dosimeter will be discussed in more detail in the following section.

Above a dose of 10^5 rads the ceric-cerous sulfate system (28) is in wide use. The ceric sulfate is reduced to cerous sulfate and the cerous ion concentration is generally determined from the difference in ceric concentration before and after irradiation. The major drawback to using this system as a dosimeter is that the ceric sulfate solutions are susceptible to light, and significant changes can occur upon storage.

2. Dosimetry procedure

The ferrous-ferric sulfate dosimeter was used to determine the amount of radiation absorbed by the isobutane. The vials that were used to contain the isobutane were used in the dosimetry measurements in order to eliminate geometry effects.

The vials were cleaned by the same procedure as described for the preparation of isobutane for irradiation, and the experimental procedure described by Weiss *et al.* (32) was followed. Two grams of ferrous sulfate heptahydrate, 0.3 gram sodium chloride, and 110 milliliters of concentrated sulfuric acid were dissolved in sufficient distilled water to make five liters of solution. The sodium chloride was added to inhibit the oxidation of ferrous ion to ferric ion by any organic impurity that may have been present. The irradiation vial was then filled with this solution and lowered into the cobalt-60 source and the dosimeter was exposed to the gamma radiation for a measured amount of time. To correct for the exposure due to lowering and raising the irradiation chamber, and for bringing the source in contact with the irradiation vial, the vial was lowered, brought in contact with the cobalt-60 and raised. This procedure was repeated five times; the value obtained for the total exposure was divided by five to get the correction factor. The correction factor was subtracted from the value obtained for the dose.

The sample, after being taken out of the cobalt-60 irradiator unit, was analyzed for ferric ion by direct reading of the optical density (absorbency) by a Beckman Model DU Spectrophotometer with a wavelength setting of 305 mμ and a slit opening of 28μ . The extinction coefficient of the ferric ion was previously determined by measuring the absorbency of a 0.0002 M ferric ion solution.

3. Irradiation procedure

Samples were irradiated at the Iowa State University Veterinary Medicine Research Institute's cobalt-60 source. The source contained 1850 curies of cobalt-60 in mid-September, 1957. Figure 2 is a description of the cobalt-60

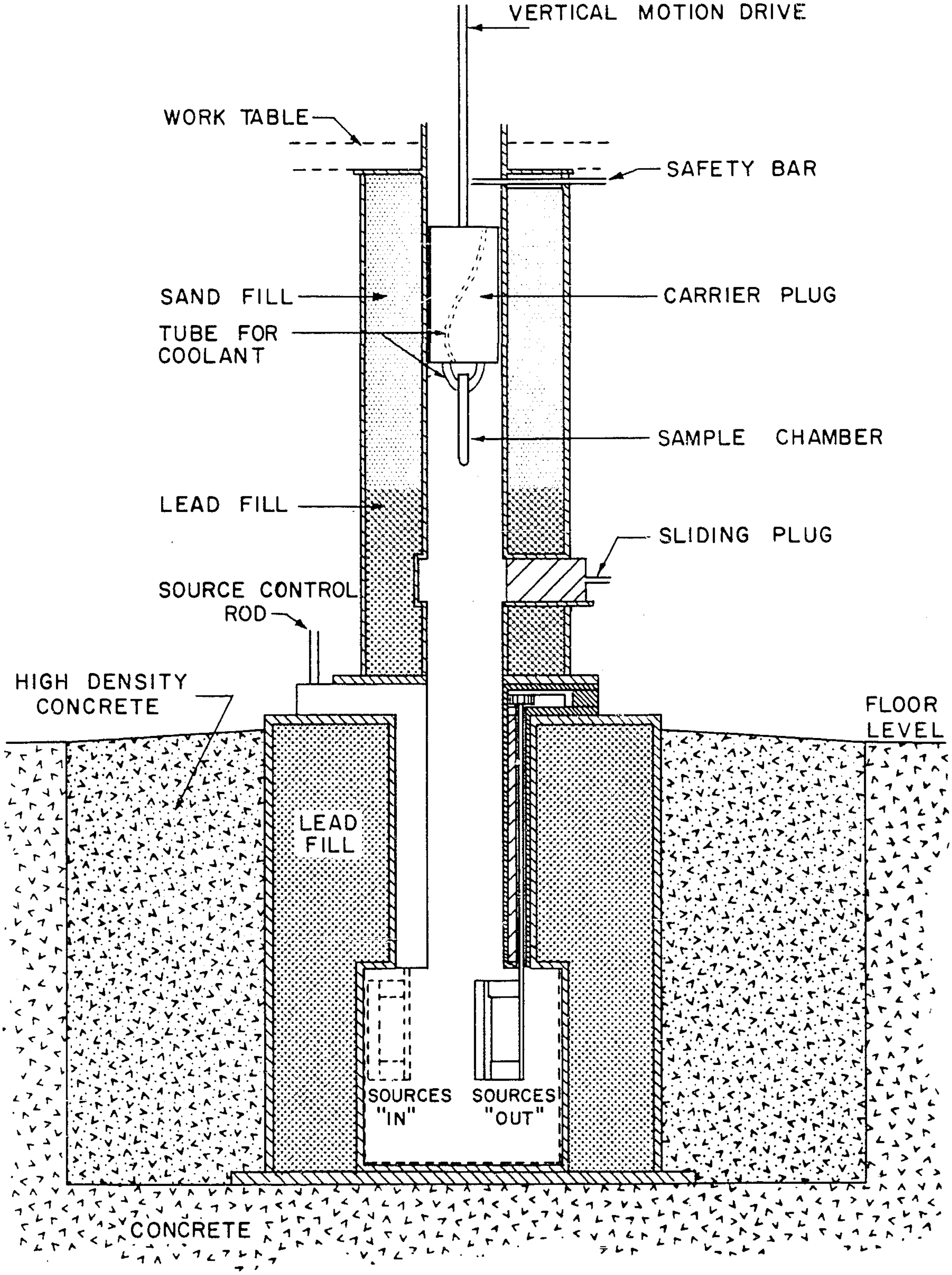

Figure 2. The cobalt-60 irradiator unit

irradiator unit, and shows the cobalt-60 sources in two different positions.

The irradiation vial was placed in the sample chamber and lowered until it was parallel to the cobalt-60 sources. The sources were then brought to the "out" position, and the sample was irradiated for the desired length of time. A thermocouple, within the sample chamber during the irradiation, actuated and controlled the temperature of circulating fluid reservoirs; these reservoirs maintained the sample chamber and sample at the desired temperature within a tolerance of ± 0.2°C.

C. Sample Analysis

1. The gas chromatograph

A gas phase chromatograph, referred to as the GPC, designed by W. A. Stensland and R. G. Clark of this laboratory, was used to separate the desired products. The GPC is an instrument which can rapidly analyze substances that can be converted easily into the vapor phase. A schematic diagram of the GPC is shown in Figure 3.

The carrier gas, after passing through a low-flow rotameter, entered the GPC, passed through the reference thermal conductivity cell, and flowed through the sampling system, picking up the mixture to be analyzed. The mixture was resolved as it was carried through a packed column by the

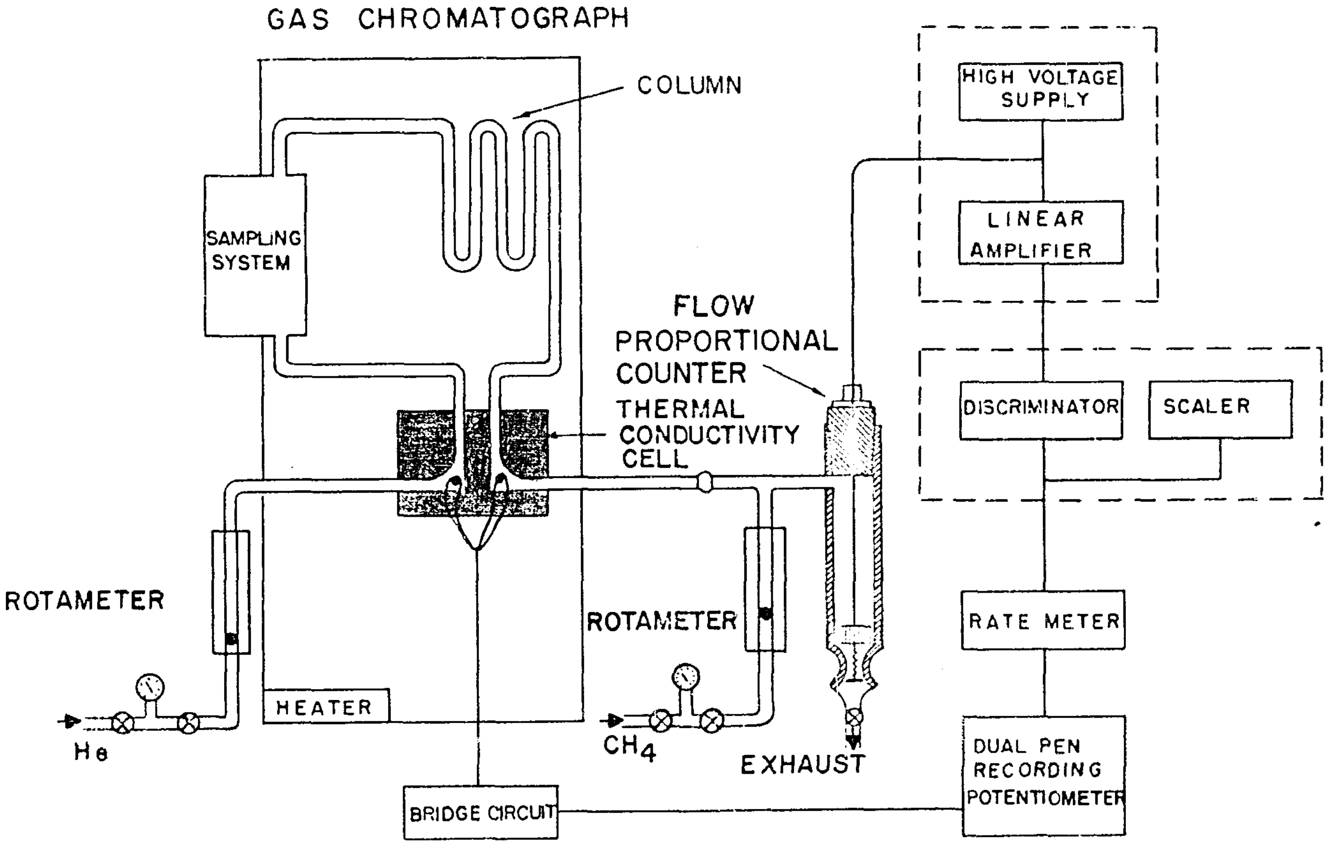

Figure 3. The analysis equipment

stream of carrier gas. If the column packing material was properly selected, the rate of adsorption and desorption of each component was different, and the individual components were fractionated as they moved through the column. The components emerging from the column appeared as separate "bands" of the pure vapor in the carrier gas. The amount of each component was determined by passing the gas stream through the other thermal conductivity cell, where the thermal conductivity of the component plus carrier gas was measured. The two thermal conductivity cells were set up in a Wheatstone bridge arrangement so that only the thermal conductivity due to the components other than the carrier gas was recorded.

Heating and cooling systems were incorporated into the GPC in order to analyze mixtures at temperatures up to 200°C. The heating system consisted of a cycling heater and a steady heater, each having separate controls. Programmed temperature analysis, i.e., analysis in which there is a linear increase of temperature with time, could be obtained by adjustment of the steady and cycling heater controls.

The components, after passing through the thermal conductivity cell, emerged from the GPC in a continuous stream. This gas stream was mixed with a regulated amount of methane. The gases were passed into a proportional counter where the amount of radioactivity in each component was detected.

2. The sampling system of the GPC

The sampling system is illustrated in Figure 4. Three

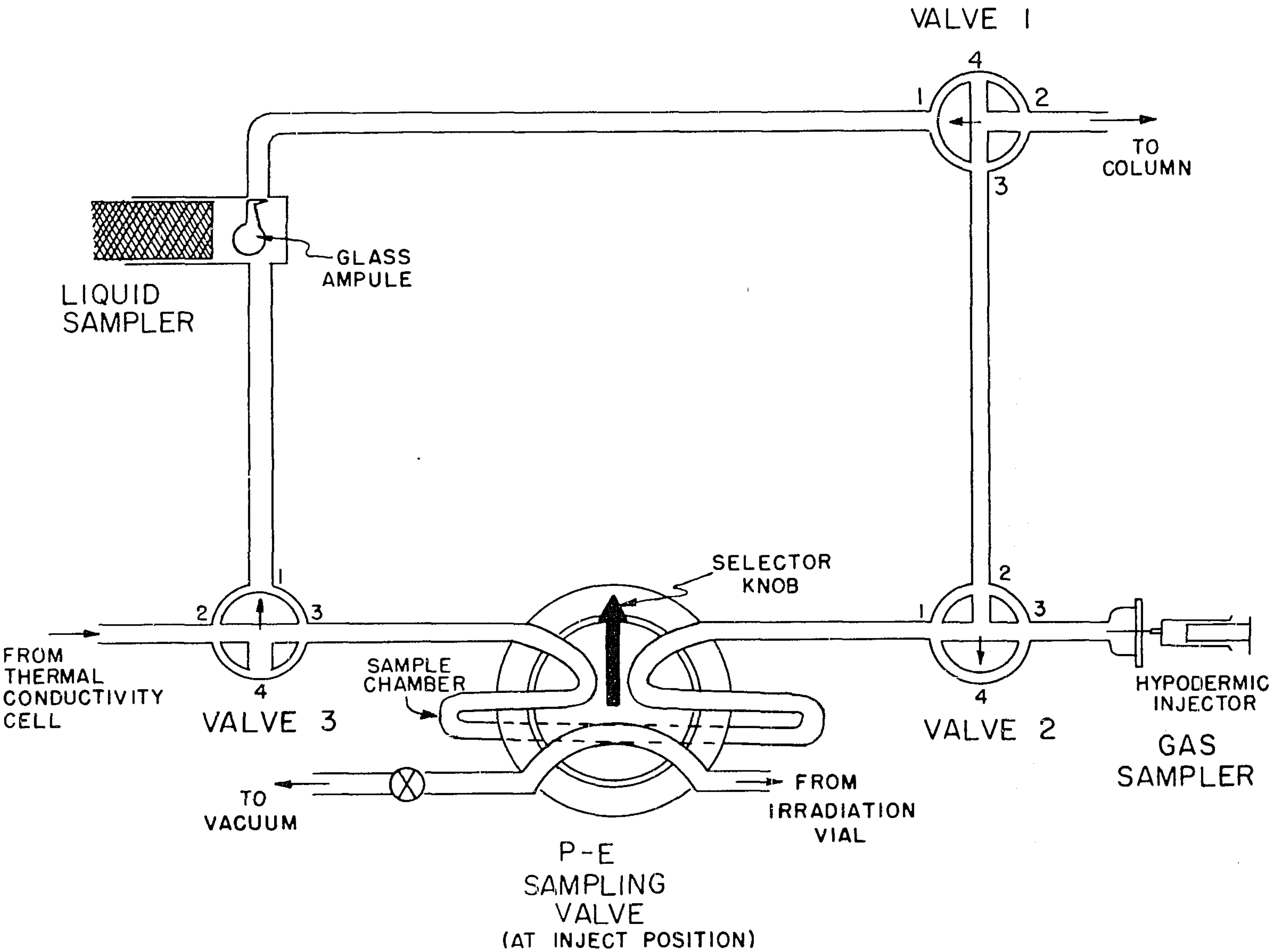

Figure 4. The sampling system of the gas phase chromatograph

methods of sampling were used. For preliminary investigations, and to determine elution times on a column, the "gas sampler" was used. The gaseous mixture was injected into the gas sampler by a hypodermic injector, previously setting the valves to the desired positions.

The "liquid sampler" was used in the analysis of isobutane irradiated in sealed, glass ampules. An irradiated ampule was placed in the chamber of the liquid sampler; the air in the sampler was flushed out. The ampule was crushed by pushing in the plunger of the liquid sampler. The gaseous components were swept into the column by the carrier gas. Using this method of sampling, only one sample was obtained from each ampule. The geometry of the cobalt-60 source was such that only two or three appropriate size ampules could be exposed to the same intensity of radiation for each irradiation. Therefore, using this sampling technique, only two or three analyses could be obtained from each lengthy irradiation.

The liquid sampler was of great use in determining the validity of the results obtained using the other sampling techniques; using the liquid sampler, there was no possibility of changing the concentration of radiation products by transfer from one chamber into another. The liquid sampler could, in addition, be used in the determination of the total amount of liquid, as well as gaseous, products produced during an irradiation.

The Perkin-Elmer Corporation sampling valve was used for the majority of the analyses. The sampling valve consisted of interchangeable sample chambers of one-quarter, one, five and 25 ml, which could be connected to either of two pairs of openings by turning the attached selector knob. Tubes leading from one pair of openings were connected to the glass tubing in the GPC. A tube, leading from one of the other two openings was connected to the vacuum line; the other opening was connected to the irradiation vial and a mixture of gases by a fourth tube. The selector knob could be set at two positions. At the first, or sample position, the sample chamber was connected to the vacuum line and irradiation vial. When the selector knob was in this position the sample chamber was evacuated. The stopcock on the irradiation vial was opened to allow a regulated amount of gas to flow into the chamber. If it was desirable for identification purposes to add a mixture of gases of the suspected radiation products, a Dewar flask containing liquid nitrogen was placed under the sample chamber and the gases were added. The mixture of gases consisted of Matheson Company methane, ethylene, ethane, acetylene, propane, propylene, propyne, butane, butene-1, isobutene and neopentane. In addition, Eastman Kodak Company pentane and isopentane, and Matheson Company butene-2 were occasionally used.

The selector knob was then turned to the second, or inject position, connecting the sample chamber to the GPC.

The sample was then flushed into the chromatographic column for analysis by the carrier gas.

3. Description of the chromatographic columns

The columns used for the analysis of the radiation products of isobutane are listed in Table 1.

Table 1. Chromatographic columns

Column liquid	Wt %	Solid support	Mesh size	Column length
silica gel	100	self	14-20	10 ft
activated charcoal	100	self	35-48	15 ft
decane	40	celite	48-65	12 ft
ethylacetoacetate	40	celite	48-65	12 ft
hexadecane	40	celite	48-65	15 ft
Mixed columns				
decane-	30	chromosorb	30-60	11 ft
activated charcoal	100	self	35-48	2 ft
dimethylsulfolane-	40	celite	28-35	16 ft
diisodecylphthalate	40	celite	28-35	6 ft

The silica gel column was prepared by packing a six mm inside diameter pyrex glass spiral with Fisher Company silica gel. The column was heated at about 150°C for several hours; during this time helium flowed through the column, removing any material adsorbed on the surface of the silica gel. The silica gel column was especially useful for the separation of ethane from ethylene and their subsequent analysis. Analysis of higher molecular weight radiation product could not be obtained using this column, thus severely limiting its use.

The charcoal column was prepared by packing another pyrex spiral with activated charcoal obtained from the Mallinckrodt Chemical Works.

The other columns were prepared using Johns-Mansville Company celite 22 as the solid support. The celite was prepared by pulverizing a brick of it and sieving the powder for the desired mesh. A mixture of hydrochloric acid and water was added while stirring the celite, and the solution was heated to boiling. The material was washed thoroughly with distilled water and dried. The dry celite was fired in a muffle furnace at 1000°C for several hours.

The decane column was prepared by pouring the decane directly onto the celite and stirring until the celite had a uniform color. The mixture was allowed to reach equilibrium in a sealed container before it was packed. The same procedure was used for the preparation of the ethylacetoacetate column.

The remaining columns were prepared by dissolving the liquid phase in excess acetone and adding the desired amount of treated celite. The acetone was removed by careful evaporation. The final traces of acetone were removed by placing the mixture in a vacuum dessicator. The column was then packed.

The decane, ethylacetoacetate and hexadecane columns separated most of the radiation products. However, only the hexadecane, because of its low vapor pressure, maintained its separating ability after prolonged usage. This column was especially useful for the separation and subsequent determination of propane and propylene.

Two mixed columns were prepared. A two-stage column consisting of eleven ft decane on Wilkens Company chromosorb and two ft activated charcoal, was used to separate hydrogen, air, methane and isobutane. A three-way stopcock was fitted between the two segments of the column so that by adjusting the stopcock, the isobutane could be transferred directly from the decane segment to the thermal conductivity cell, whereas the other components passed through both segments of the column. The elution times of hydrogen, air, methane and isobutane on this column are presented in Table 2.

The dimethylsulfolane-diisodecylphthalate column was prepared according to the specifications given by Fredericks and Brooks (33); this column was used for the majority of the analyses. It could not separate ethane and ethylene, or isobutene and butene-1, but gave excellent resolution of the other one to five carbon atom hydrocarbons.

4. The counting system

The radiation products, after emerging from the column,

Table 2. Elution times using the decane-charcoal column

Carrier flow rate - 20 ml/min argon

Temperature - 26°C

Component	Decane segment	Decane and charcoal
Hydrogen	3.4 min	4.0 min
Air	3.4	5.4 min
Methane	3.6	11.7 min
Isobutane	31.8	undetectable

were mixed with a regulated amount of methane and flowed into a flow-proportional counter similar in design to that of Wolfgang and Rowland (7). The proportional counter is illustrated in Figure 3. The optimum size of the counter chamber was found to be 20 ml. The nature of the center wire did not affect the quality of the results. When a three mil stainless steel center wire was used the operating voltage was generally about 3000 volts; using a two mil tungsten wire the operating voltage was about 2300 volts. The operating voltage was also dependent on the ratio of helium to methane in the counting gas mixture. As this ratio increased, the operating plateau length increased. The quality of the results was not affected by a change in ratio, as long as the ratio remained constant during the course of the analysis.

The flow-proportional counter was connected to a RCL pulse amplifier containing a high voltage supply and a linear amplifier, and to a Nuclear-Chicago Model 162 scaler containing a discriminator. The output of the scaler was fed into a Nuclear-Chicago Model 1615-A ratemeter and the counting rate was recorded by one pen of a Bristol dual-pen recording potentiometer; the other pen recorded the thermal conductivity changes caused by the passage of the radiation products through the thermal conductivity cell. A block diagram of the counting equipment is included in Figure 3.

5. Analysis

Samples of .25 and one ml of hydrogen, methane and isobutane were analyzed on the decane-charcoal column to determine the number of molecules of each corresponding to a unit of area of the recorded thermal conductivity peak. Argon was used as the carrier gas for these observations and for the subsequent determinations of hydrogen and methane yields. The irradiation vial was attached to the sampling valve and the sampling procedure previously described was employed. A constant flow rate of twenty cc/min argon was used for the hydrogen and methane studies. Although the flow of argon could be maintained constant for short periods of time, it was impossible to keep it at the identical value for more than two successive analyses. However, the relative thermal conductivity response of isobutane, methane and hydrogen remained constant over flow rates of 15-25 cc/min.

The procedure for the determination of the amounts of radioactivity in the radiation products was identical to the procedure used for the hydrogen and methane studies except that helium replaced argon as the carrier gas. The helium was usually maintained at a flow rate between 15 and 25 cc/min. As the gas stream emerged from the chromatograph it was mixed with methane regulated at a flow rate of about 50 cc/min.

The number of counts corresponding to one unit of area of the activity peak was previously determined for each scale of the ratemeter. A cesium-137 source was placed alongside the proportional counter, and the total number of counts was recorded by the scaler. The area under the recorded activity or thermal conductivity peaks was measured with a K & E planimeter to obtain the counts corresponding to an area unit.

IV. EXPERIMENTAL RESULTS

A. Dosimetry Measurements

The molar extinction coefficient of ferric ion was determined to be 2193 at 21.2°C. Ferrous sulfate solutions were irradiated for 60, 90, and 120 seconds in the irradiation vials. The absorbency of these samples was determined. The absorbency was corrected for the optical density of the spectrophotometer cells, and for the difference in temperature of the observation from 21.2°C. In addition, a correction factor was applied to account for the exposure due to the lowering and raising of the irradiation chamber, and for bringing the sources in contact with the irradiation vial. The value of 15.45 ferric ions produced by 100 ev of energy absorbed by the ferrous sulfate solution, as described by Schuler and Allen (34), was used to calculate the dosage. A value of 12,637 ± 110 rad/min was obtained for the dose rate in the solution on November 20, 1959. A rad is defined as the unit of absorbed dose and is equal to 100 ergs/gram. Correction for the electron density difference between the solution and the isobutane gave a value for the dose rate in isobutane as 13,395 ± 117 rad/min on the same date. This value does not include any correction for the difference in effects in the solution and the gas due to the secondary electrons produced by the interaction of the gamma rays with the glass sides of the irradiation vial.

B. Hydrogen and Methane Studies

The thermal conductivity response of hydrogen, methane and isobutane was measured. One unit of area on the planimeter corresponded to 5.71×10^{15} molecules of hydrogen, 2.78×10^{16} molecules of methane or 1.56×10^{17} molecules of isobutane at 0°C and 745 mm pressure at a flow rate of 20.0 cc/min argon through the decane-charcoal column.

Irradiation vials containing isobutane at 745 mm pressure were irradiated for 930 min in the cobalt-60 irradiator unit. Samples were irradiated at -16°C and at ten degree temperature intervals between 0°C and 70°C. The areas of the Gaussian curve obtained by the chromatographic analysis were measured, and the G values of hydrogen and methane were calculated. The G value, or yield, is defined as the number of atoms, molecules or ions produced by 100 ev of energy absorbed by the system. As long as the flow rate remained constant throughout the analysis, the yields could be calculated. The hydrogen yield was obtained by applying the following calculations. By definition,

$$G(H_2) = \frac{H_2 \text{ molecules}}{Q/100} \qquad (11)$$

where

Q = dose in ev

$$H_2 \text{ molecules} = A_{H_2} \times T_{H_2} \times R_{H_2} \qquad (12)$$

where

A_{H_2} = planimeter measurement of the thermal conductivity peak area of hydrogen.

T_{H_2} = molecules of hydrogen equal to one unit of area on the planimeter.

R_{H_2} = ratio of hydrogen in the irradiation vial to the analyzed sample.

Since

$$R_{H_2} = R_{C_4H_{10}} = \frac{y \times 6.02 \times 10^{23}/58}{A_{C_4H_{10}} \times T_{C_4H_{10}}} \qquad (13)$$

and

$$Q = \frac{Q_r \times t \times y \times 100 \text{ erg g}^{-1} \text{ rad}^{-1}}{1.6 \times 10^{-12} \text{ erg ev}^{-1}} \qquad (14)$$

where

y = grams of isobutane in the irradiation vial.

Q_r = dose rate in rad/min.

t = minutes of irradiation.

Then

$$G(H_2) = \frac{1.66 \times 10^{10}\, A_{H_2} \times T_{H_2}}{Q_r \times t \times A_{C_4H_{10}} \times T_{C_4H_{10}}} . \qquad (15)$$

Table 3 shows the effect of temperature on hydrogen and methane yields in the radiolysis of isobutane. Each value is

Table 3. Hydrogen and methane formation; effect of temperature

Temperature	Irradiation	$G(H_2)$	$G(CH_4)$
-16°C	29	2.21 ± 0.09	1.29 ± 0.08
0°C	39	2.95 ± 0.05	1.37 ± 0.05
10°C	31	3.28 ± 0.07	1.42 ± 0.05
20°C	36	3.92 ± 0.07	1.70 ± 0.03
30°C	32	4.39 ± 0.09	1.90 ± 0.09
40°C	33	5.87 ± 0.04	2.33 ± 0.05
50°C	34,37	5.47 ± 0.09	3.31 ± 0.09
60°C	35,38	4.94 ± 0.09	3.27 ± 0.07
70°C	40	5.16 ± 0.05	3.31 ± 0.09

the average of a minimum of four determinations. The yields at 50°C and 60°C were each obtained by analyzing samples from two irradiations, whereas the other yields were obtained by analysis of samples from one irradiation. Figure 5 is a diagram of the results obtained for a sample irradiated at 40°C.

C. Carbon-14 Studies

Samples of isobutane-1-C^{14} at 745 mm pressure were irradiated at 20°C and -16°C. Two irradiations of 2160 min and 2091 min duration were made at the higher temperature, and one

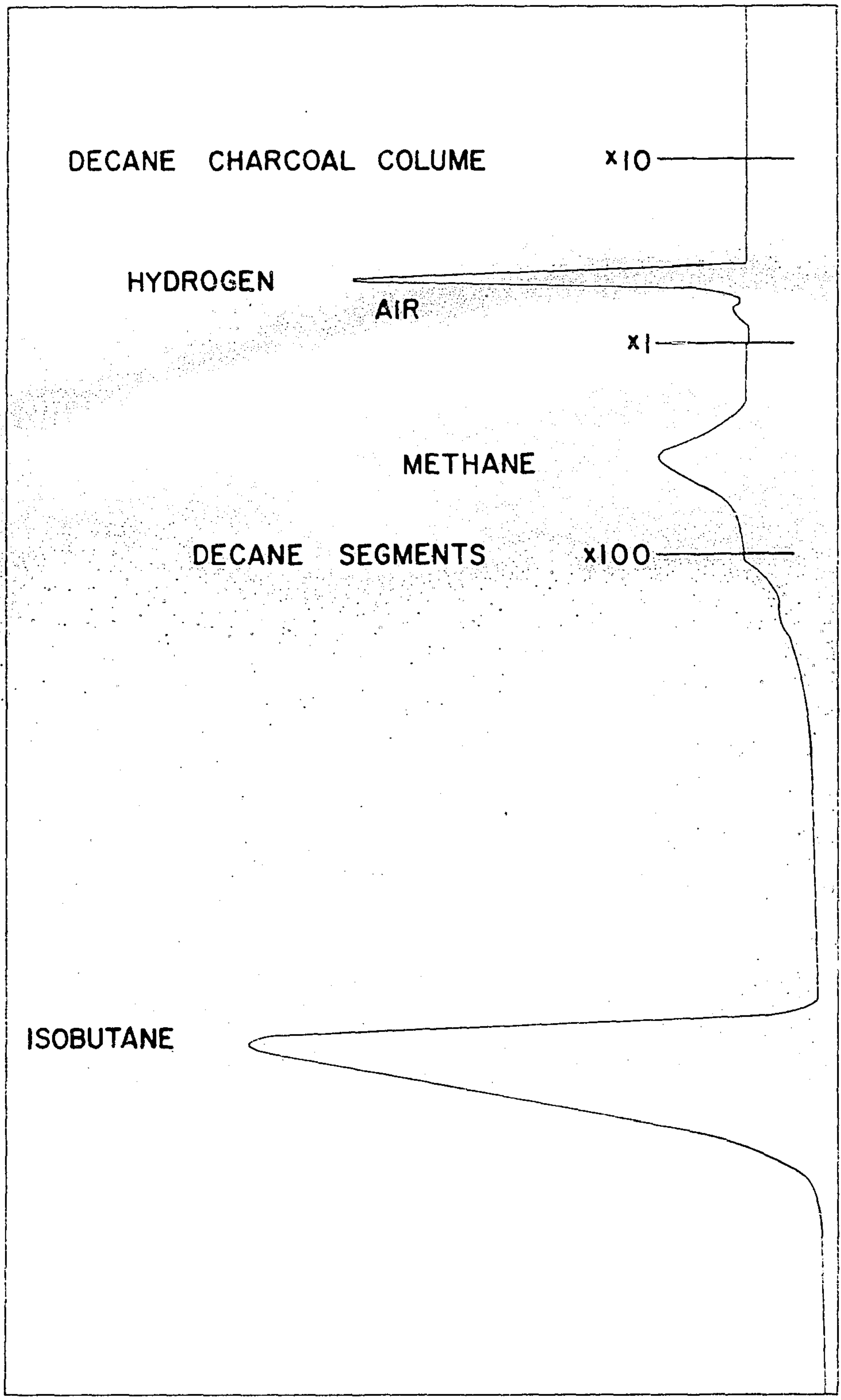

Figure 5. Analysis of isobutane irradiated at 40°C using the decane-charcoal column

irradiation of 2160 min was made at the lower temperature. The boiling point of isobutane is -10.2°C, and thus, both gaseous and liquid isobutane were irradiated. Samples of isobutane-2-C^{14} were also irradiated in the gaseous and liquid states. Two irradiations of 2094 min and 2126 min at 20°C, and one irradiation of 2070 min at -20°C were made using an initial isobutane pressure of 745 mm. In all six irradiations the irradiation vials were placed in the volume of the irradiator unit where the cobalt-60 field was uniform, and the cobalt-60 sources were placed in the identical positions, so that, neglecting the differences due to decay of the cobalt-60, the dose rate was the same.

The radioactivity disintegration rate of the gaseous components was measured by the ratemeter and recorded automatically on recording paper as the components passed through the flow-proportional counter. In addition, the counts in each component were measured by the scaler included in the counting circuit. The scaler data was especially useful in determining the activity of the isobutane, since the counting rate of the isobutane, in many cases, was considerably greater than that measurable by the ratemeter. The scaler provided an excellent check on the reliability of the total relative activity obtained by the planimeter measurement of the area under the Gaussian shaped curve.

The value obtained for the activity was not an absolute value, but was dependent upon the flow rate of helium carrier gas and the characteristics of the proportional counter. The absolute activity of each component was not determined since only relative activity measurements were required in the calculations of the yields.

The number of determinations of the yield of each of the radiation products varied widely. This number depended in part upon the nature of the column used in the determinations. The majority of the analyses were made using the dimethylsulfolane-diisodecylphthalate column; acetylene, ethylene, and ethane could not be separated from each other on this column, and as a consequence, the number of determinations of the yield of these components was less than the number of determinations of a component that could be separated. An example is cited below. In the analysis of propane yield at 20°C from isobutane-2-C^{14}, sixteen determinations were obtained, whereas the acetylene yield in the identical series of analyses could only be determined three times. The number of determinations is partially reflected in the size of the experimental error included alongside the value obtained for the yield. The size of the experimental error also reflects the efficiency of separation from other components that interfere in its determination.

Table 4 is a comparison of the activity yields obtained by irradiation of the two isotopes of isobutane in the liquid and gaseous phases. The values are expressed in units which are proportional to the G value, but reflect the differences

Table 4. Effect of physical state and carbon-14 position on activity yields

Temperature	20°C	-20°C	20°C	-16°C
Physical state	gas	liquid	gas	liquid
Labeled position	2-C^{14}	2-C^{14}	1-C^{14}	1-C^{14}
Compound	Activity yield (G_a)			
methane	0.00	0.00	0.64 ± 0.12	0.42 ± 0.11
acetylene	0.22 ± 0.06	0.30 ± 0.06	[a]	[a]
ethylene	0.24 ± 0.04	0.24 ± 0.06	0.20 ± 0.06	0.16 ± 0.05
ethane	0.24 ± 0.04	0.15 ± 0.06	0.68 ± 0.18	0.44 ± 0.15
propyne	0.00	0.00	0.00	0.00
propylene	1.39 ± 0.25	0.72 ± 0.20	0.88 ± 0.18	0.50 ± 0.16
propane	3.61 ± 0.22	2.91 ± 0.36	2.51 ± 0.29	1.82 ± 0.36
isobutene	1.87 ± 0.19	0.79 ± 0.12	2.0 ± 0.6	1.0 ± 0.5
butene-1	0.00	0.00	0.00	0.00
butene-2	0.00	0.00	0.00	0.00
n-butane	1.02 ± 0.37	0.42 ± 0.11	0.85 ± 0.20	0.51 ± 0.06

[a] Not determined.

Table 4. (Continued)

Temperature	20°C	-20°C	20°C	-16°C
Physical state	gas	liquid	gas	liquid
Labeled position	2-C^{14}	2-C^{14}	1-C^{14}	1-C^{14}
Compound	Activity yield (G_a)			
neopentane	0.92 ± 0.12	0.45 ± 0.08	1.34 ± 0.25	0.75 ± 0.12
isopentane	a	a	0.37 ± 0.06	0.33 ± 0.05
n-pentane	0.00	0.00	0.00	0.00

in radioactivity measurements, although the G value is independent of the amount of radioactivity. The unit of measurement is defined as the "activity G value" and is denoted by G_a. The relationship between G_a and G yields of component i is expressed by

$$G(i) = G_a(i) \times f \tag{19}$$

where f is a constant equal to the ratio of the specific activities of isobutane to i. For example, if methane is formed by a methyl group, which after being split from the isobutane-1-C^{14} molecule, picks up a hydrogen, then the specific activity of carbon-14 in the methane is one-third that of the isobutane. The constant, f, then has a value of three.

The G_a values were obtained by applying the following calculations. By definition

$$G(i) = \frac{\text{molecules } i}{Q/100} \tag{16}$$

$$\frac{\text{molecules } i}{\text{initial molecules } C_4H_{10}} = \frac{d_i \times f}{D_t} \tag{17}$$

where

d_i = counts of component i.

D_t = total counts in the entire sample.

Then

$$\text{molecules } i = \frac{d_i \times f \times y \times 6.02 \times 10^{23}}{58\ D_t}\ . \qquad (18)$$

Substitution of Q from equation 14, page 40 into equation 16 gives

$$G_a(i) = \frac{G(i)}{f} = \frac{1.66 \times 10^{10}\ d_i}{Q_r \times t \times D_t}\ . \qquad (19)$$

The above equations were valid only if the assumption is made that there was no isotope effect due to substitution of C^{14} for C^{12}.

The total counts, D_t, was measured by adding the counts of all the radiation products to the counts of isobutane. Often, the total counts had to be estimated since several components were eluted from the column in a manner such that they could not be counted; however, about 98% of the total radioactivity of the gaseous products usually was contained in the isobutane, which always was measured; therefore, the error introduced by the estimate was small. An additional error was introduced by neglecting to add the amount of radioactivity in the products containing six or more carbon atoms to the total activity. The amount of activity in these components was also small compared to the activity in the isobutane, and no serious error was introduced by neglecting these activities.

In general, the amount of radioactive contaminant in the starting material was small enough that the slight correction factor involved was within the experimental error of the technique. However, the correction factor due to the radioactive impurity of isobutene in isobutane-1-C^{14} was considerably beyond the limits of the experimental error. This was reflected in the determination of isobutene yield.

Figure 6 shows the typical results obtained for the irradiation of isobutane-1-C^{14} at -16°C using a hexadecane column.

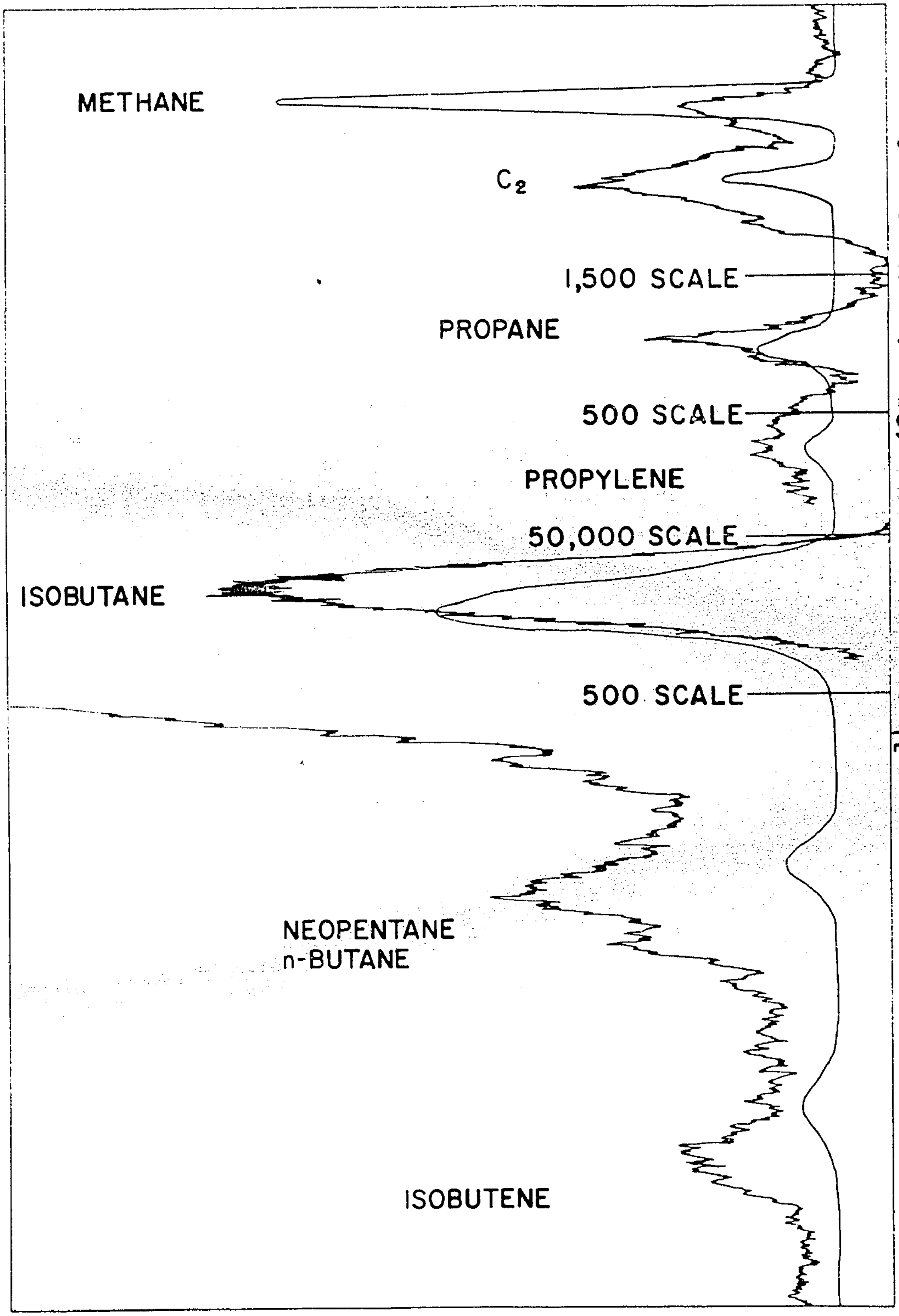

Figure 6. Analysis of isobutane-1-C^{14} irradiated at -16°C using the hexadecane column

V. DISCUSSION OF RESULTS

A. Hydrogen

Figure 7 is a plot of the dependence of the hydrogen and methane yields on temperature. This plot showed that the hydrogen yield was a function of temperature. The amount of hydrogen produced appeared to have a maximum value of 5.87 at 40°C. It is possible that other processes which compete for the hydrogen are coming into play above 40°C.

The value of $G(H_2) = 2.21$, obtained for the liquid state irradiation at -16°C can also be obtained by a straight line extrapolation of the gas phase irradiations between 0°C and 30°C. This is to be expected since the hydrogen radical is too small to remain trapped in a Franck-Rabinowitch cage (35) and therefore no dependence of phase should be expected.

A comparison of the hydrogen yield in isobutane with its published yield in other saturated hydrocarbons was made. Due to the great difference in method of irradiation, dose, dose rate, pressure, etc., these comparisons were only of a qualitative nature. It was found that the hydrogen yield was approximately independent of the dose rate, state of aggregation, and ionization density for unbranched hydrocarbons. These straight chain hydrocarbons had $G(H_2)$ values between 4.2 and 5.2 (3, 11, 18, 36, 37). The yield of hydrogen in hydrocarbons was essentially statistical in nature; as the branching

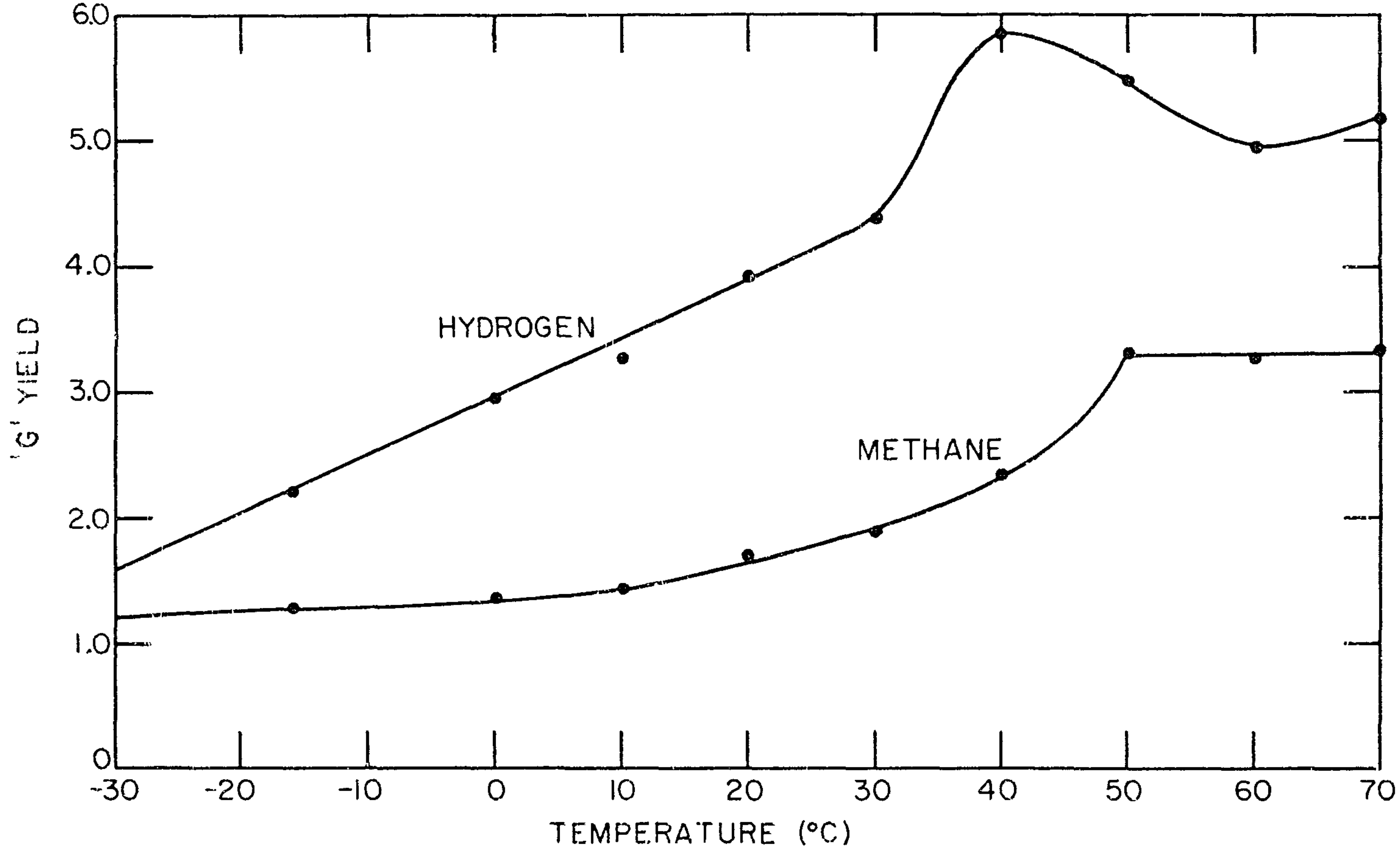

Figure 7. The dependence of hydrogen and methane yield on temperature

in the hydrocarbon increased the amount of hydrogen was found to decrease.

The value of $G(H_2) = 3.92$ obtained in this investigation at 20°C is in agreement with the general trend of decreasing hydrogen with increasing branching.

By extending the plot of $G(H_2)$ as a function of temperature to -30°C, a value of 1.6 ± 0.1 was obtained; this value is in excellent agreement with the value of 1.75 obtained by converting the yields of Keenan et al. (38), for the electron bombardment of liquid isobutane at -30°C and a total dose of 4.8×10^{24} ev, to G values.

There appeared to be a linear dependence of $G(H_2)$ with temperature below 40°C. However, it is possible that a limiting value of the yield could have been reached at a lower temperature than that obtained in this set of experiments.

The hydrogen yield that was temperature dependent can be attributed to free radical processes in which the hydrogen may have been formed in reactions such as

$$C_4H_{10} \xrightarrow{\gamma} C_4H_9 + H \qquad (20)$$

$$H + C_4H_{10} = C_4H_9 + H_2 \ . \qquad (21)$$

In addition, other molecules and radicals may have lost a hydrogen atom, which then abstracted and combined with another hydrogen.

The temperature independent process for the formation of hydrogen is probably a reaction such as

$$C_4H_{10} \xrightarrow{\gamma} C_4H_8 + H_2 \qquad (22)$$

although the possibility of reactions such as equation 20 involving hot radicals cannot be neglected. In addition, many other radicals or excited molecules may eliminate hydrogen atoms or molecules.

For unimolecular processes such as the reactions above, mass spectra data can give a good approximation of the extent of radical and molecular processes. It may be assumed that the ratio of the mass spectra peaks at m/e 's 56 and 57, corresponding to the loss of a hydrogen molecule and hydrogen radical, respectively, are indicative of the ratio of molecular to radical processes. The ratio of these peak heights is reported (39) to be 56/57 = 0.44/3.68, or a computed 89% attributable to the radical process. If the mass spectra data can be taken as valid for the radiation process, then a $G(H_2)$ value of only 0.5 can be attributed to the temperature independent process, and very little, if any, departure from linearity should be observed at the temperatures used in these experiments. The mass spectra observations suggest that the hydrogen was not formed by molecular or hot radical processes, but primarily by radical disproportionation reactions.

B. Methane

The yield of methane was found to be temperature dependent below 50°C. A maximum G value of 3.3 was observed above 50°C; a limiting value of $G(CH_4) = 1.2$ was obtained by extrapolation of the yield-temperature plot to -30°C. The low temperature value did not agree with the value of 0.63 obtained by Keenan et al. (38) at a total dosage of 4.8×10^{24} ev, but was in good agreement with their value of $G(CH_4) = 1.0$, obtained at a dosage of 6.0×10^{24} ev. The dose per gram of irradiated material used by Keenan et al. was a minimum of fifteen times the value used in this investigation, and thus, only qualitative comparisons could be made.

It was somewhat surprising that the $G(CH_4)$ value obtained for the liquid state irradiation falls on the same straight line as the G values in the gas. This may be indicative of an absence of a cage effect. A Franck-Rabinowitch cage (35) would cause increased recombination of radicals and lower the yield in the liquid state irradiation.

Table 5 is a comparison of the methane yield from isobutane with that from other saturated hydrocarbons as a function of the percentage of methyl groups in the hydrocarbon. The $G(CH_4)$ value in isobutane, observed in this investigation, is in agreement with the value expected on the basis of the ratio of CH_3-C bonds to total bonds.

The mechanisms for formation of methane may be considered

Table 5. A comparison of methane yields in saturated hydrocarbons

Compound	$100 \times \frac{CH_3\text{-}C \text{ bonds}}{C\text{-}C \text{ bonds}}$	$100 \times \frac{CH_3\text{-}C \text{ bonds}}{\text{total bonds}}$	$G(CH_4)$	Reference
neopentane	100	25	1.8	(8)
isobutane	100	23	1.7	this work
propane	100	20	1.2	(3)
ethane	100	14	1.0	(3)
2,2-dimethylbutane	80	21	1.2	(18)
n-butane	67	15	0.9	(11)
2-methylpentane	60	16	0.5	(18)
n-pentane	50	13	0.4	(36)
2-methylheptane	43	12	0.4	(18)
n-hexane	40	11	0.2	(18)
n-heptane	33	9	0.09	(37)
n-octane	28	8	0.08	(37)

as

$$C_4H_{10} \xrightarrow{\gamma} CH_3 + C_3H_7 \qquad (23)$$

$$CH_3 + C_4H_{10} = CH_4 + C_4H_9 \qquad (24)$$

and

$$C_4H_{10} \xrightarrow{\gamma} CH_4 + C_3H_6\ . \qquad (25)$$

The first mechanism is temperature dependent as long as hot radicals are not involved. If this is assumed to be the only reaction producing methane by a temperature dependent process, a G value of 3.3 - 1.2 = 2.1 can be attributed to it, and a G value of 1.2 is attributed to the temperature independent molecular process (reaction 25). Therefore, the molecular process contributes 1.2/3.3 = 36% of the total methane.

Analysis of mass spectra data (39) again may be applied. It may be assumed that the ratio of the mass spectra peaks at m/e's 42 and 43, corresponding to the loss of methane and methyl radical, respectively, are indicative of the ratio of molecular to radical processes. The ratio of these peaks is 42/43 = 36.7/100 = 27% molecular processes, which is in good agreement with the value of 36% calculated above.

In either of the two mechanisms postulated above, $G_a(CH_4)$ is expected to be zero when isobutane-2-C^{14} is used. This has been observed. $G_a(CH_4)$ should be one-third of $G(CH_4)$, i.e., f is three, using isobutane-1-C^{14} if the above mechanisms are valid. The value of $G(CH_4)$ = 1.70, obtained by thermal conductivity measurements is 2.65 times as great as the value of $G_a(CH_4)$ obtained by activity measurements. The ratio $G(CH_4)/G_a(CH_4)$ at -16°C was $1.29/0.42 = 3.07$. It appears that these mechanisms are valid for the production of methane from isobutane.

C. Acetylene, Ethylene and Ethane

Acetylene, ethylene and ethane were found to have almost identical G_a values at 20°C when isobutane-2-C^{14} was used. The sum of the activity yields of the C_2 products was independent of state, although the acetylene yield appeared to increase slightly at the expense of the ethane. It therefore appears that the C_2 product may be formed by a temperature independent process.

The activity yield of ethane was approximately tripled by substituting isobutane-1-C^{14} for isobutane-2-C^{14} in both the liquid and gas irradiations, although the ethylene yield decreased slightly by this substitution.

The presence of methyl radicals in the system would indicate the possibility of forming ethane by

$$CH_3 + CH_3 = C_2H_6 \qquad (26)$$

or

$$CH_3 + C_4H_{10} = C_2H_6 + C_3H_7 \; . \qquad (27)$$

If these mechanisms are the only ones involved, no radioactivity would be expected in the ethane when isobutane-2-C^{14} was irradiated. The greater activity yield of ethane in isobutane-1-C^{14} may indicate that these mechanisms are the predominate method of ethane formation.

If ethane can be formed from isobutane by

$$C_4H_{10} \xrightarrow{\gamma} C_2H_5 + C_2H_4 + H \tag{28}$$

$$C_2H_5 + C_4H_{10} = C_2H_6 + C_4H_9 \tag{29}$$

activity should be noted in the ethane using either isotope. However, the amount using the isobutane-2-C^{14} should be three times the amount from isobutane-1-C^{14}. The yields are exactly the reverse. It may be that both mechanisms for ethane formation are possible, with the radical mechanism predominating.

Another possibility not previously considered is the ion-molecule reaction. This type of reaction, generally leading to rearranged products, may very well explain the activity obtained in the ethane fraction using isobutane-2-C^{14}. These reactions may also explain the formation of ethylene and acetylene. The temperature independence of the ethylene yield lends additional weight to this possibility.

D. Propyne, Propylene and Propane

Table 6 lists the activity yield ratios of propane and propylene formation for the two labeled compounds. In all cases the activity yield from isobutane-2-C^{14} was about 1.5 times the activity yield using isobutane-1-C^{14}. On the basis of this value, mechanisms for formation of propane and propylene are postulated below.

$$C_4H_{10} \xrightarrow{\gamma} C_3H_7 + CH_3 \qquad (30)$$

$$C_4H_{10} \xrightarrow{\gamma} C_3H_6 + CH_4 \qquad (31)$$

$$C_3H_7 + C_4H_{10} = C_3H_8 + C_4H_9 \qquad (32)$$

$$C_3H_7 = C_3H_6 + H \qquad (33)$$

Table 6. Activity yield ratios for propane and propylene

Compound	Temperature	G_a yields 2-C^{14}	 1-C^{14}	Ratio
Propane	20°	3.61	2.51	1.44
	-20°,-16°	2.91	1.82	1.60
Propylene	20°	1.39	0.88	1.58
	-20°,-16°	0.72	0.50	1.44

For the above mechanisms, the specific activity ratio, f, for isobutane-2-C^{14} to propane or propylene is one; f equals 1.5 for the specific activity ratio of isobutane-1-C^{14} to propane or propylene. The ratio of the f values is then 1.5.

No propyne was noted in these studies.

E. C_4 Radiation Products

Isobutene G_a values were calculated to be 1.87 and 0.79 for the gaseous and liquid state irradiations, respectively when isobutane-2-C^{14} was used. Radioactive impurities of isobutene in isobutane-1-C^{14} made it impossible to obtain better results than 2.0 ± 0.6 and 1.0 ± 0.5 for the gaseous and liquid state irradiations, respectively.

The large dependence of the yield on temperature and state make it appear that a radical type mechanism rather than a molecular process is responsible for the major portion of the isobutene. Thus

$$C_4H_{10} \xrightarrow{\gamma} C_4H_9 + H \qquad (20)$$

$$C_4H_9 = C_4H_8 + H \qquad (34)$$

appear to be more probable than

$$C_4H_{10} \xrightarrow{\gamma} C_4H_8 + H_2 \, . \qquad (22)$$

This observation is also noted in the data on hydrogen production. A qualitative comparison of the data obtained for the two labeled compounds can be made. It appears that the amount of isobutene is primarily independent of isotope position. Therefore, it may be estimated that the ratio of the specific activity ratios is one, and that $G(i\text{-}C_4H_8)$ is identical with $G_a(i\text{-}C_4H_8)$.

A comparison of the liquid and gaseous state irradiations show that the isobutane yield is decreased by 1.87 - 0.79 = 1.12. Obviously, the yield of hydrogen produced by isobutene formation is decreased by a similar amount. A comparison of the $G(H_2)$ yields at -16°C and 20°C shows the difference to be 3.92 - 2.21 = 1.71, leaving 1.71 - 1.12 = 0.59 unaccounted. This difference may be attributed to the difference observed in propylene yield due to radical processes eliminating hydrogen atoms between -16°C and 20°C but may also be due in part to the production of higher molecular weight species having the general formula, C_nH_{2n}. Higher molecular weight products have been noted in another investigation (38), but were not studied in this investigation.

There was no evidence of butene-1 or butene-2 being formed, but a surprisingly large amount of n-butane was observed. The formation of n-butane obviously involved a rearrangement process, which can be explained readily by an ion-molecule mechanism, except for the fact that the n-butane formation was temperature sensitive, whereas ion-molecule reactions are insensitive to temperature effects.

It appears that the n-butane activity yields are not dependent on isotope position. Thus a reaction such as

$$R_1R_2 + R_3R_4 = R_1R_3 + R_2R_4 \tag{35}$$

where the R_i's represent radical species such as H, CH_3, C_2H_5, C_3H_7 and C_4H_9 can be considered only when both R_1R_2 and R_3R_4 are isobutane molecules. If only one of these species were isobutane then the activity yield would be sensitive to the position of the carbon-14 atom. The data is not conclusive enough to present a mechanism for n-butane formation.

F. C_5 Radiation Products

Normal pentane was not observed as a product of the irradiation of isobutane. This was to be expected since methyl radical substitution for hydrogen in isobutane should yield only isopentane and neopentane.

On a statistical basis, the substitution reaction

$$CH_3 + C_4H_{10} = C_5H_{12} + H \tag{36}$$

should favor the formation of isopentane over neopentane by a factor of nine; there is the possibility of substituting a methyl group for any of nine primary hydrogens, but only one tertiary hydrogen. In addition, the steric effects of the methyl groups around the tertiary carbon atom should hinder the substitution of the tertiary hydrogen. It is impossible to reconcile a mechanism similar to reaction 36 with the data obtained in this investigation. The data for isobutane-1-C^{14} showed the activity yield of neopentane to be 1.34/0.37 = 3.62 as great as the isopentane activity yield at 20°C, and 0.75/0.33 = 2.27 as great as it at -16°C.

Mass spectra observations (39) showed that the tertiary hydrogen of isobutane was removed 55 times more rapidly than the primary hydrogen. This would favor neopentane formation over isopentane formation if the reaction occurred principally by a radical mechanism such as

$$C_4H_9 + CH_3 = C_5H_{12} \tag{37}$$

or

$$C_4H_9 + C_4H_{10} = C_5H_{12} + C_3H_7. \tag{38}$$

A comparison of the stabilities of the C_4H_9 radicals would also predict neopentane to be the principal C_5 radiation product. The tertiary radical has a much greater stability than the primary radical, and should have a greater probability of reacting with a methyl radical.

It would be expected, on the basis of reaction 37 or 38, that the activity yield of neopentane should be 1.33 times greater for isobutane-1-C^{14} than for isobutane-2-C^{14}; the specific activity ratio, f, by the above mechanisms should be one for neopentane using isobutane-2-C^{14} and 0.75

using isobutane-1-C^{14}. A comparison of the activity yield of neopentane from isobutane-1-C^{14} to that from isobutane-2-C^{14} gives 1.34/0.92 = 1.46 as the ratio at 20°C and 0.75/0.45 = 1.67 as the ratio in the liquid. The difference between experimental and predicted values for the liquid irradiation is beyond the experimental error of the detection method. No explanation is offered to account for this difference. The specific activity ratio in neopentane, using isobutane-2-C^{14} is one; therefore, G(neo-C_5H_{12}) is also 0.92 at 20°C, and 0.45 at 20°C.

A study of the formation of unsaturated C_5 products was not included in this investigation.

Many of the products investigated have been assumed to be formed by thermal free radicals. It is very probable that the radiolysis involved radicals for which the energy distribution was not a Maxwell-Boltzmann distribution for the temperature of the irradiation, but corresponded to a somewhat higher temperature. However, these reactions have been classified here as thermal, rather than hot radical reactions.

Reactions such as

$$C_2H_5^+ + e \xrightarrow{\gamma} C_2H_4 + H \qquad (39)$$

which has been proposed for ethylene formation by electron bombardment of methane (40), may very well account for some of the products observed in the irradiation of isobutane, although these reactions are not as probable as the mechanisms proposed.

VI. SUMMARY AND CONCLUSIONS

A study of the effect of temperature on the hydrogen and methane yields for the cobalt-60 gamma radiolysis of isobutane was made. It was found that these products were formed by both temperature dependent and temperature independent processes. Thermal radical reactions were postulated to account for the temperature dependent portion of the yield. Mechanisms involving direct elimination of hydrogen or methane molecules were proposed to account for the temperature independent portion. Mass spectra studies on isobutane were compared with the temperature studies. It was shown that the mass spectra yields of ions, corresponding to the loss of radicals or molecules of methane and hydrogen from isobutane, were in agreement with the calculated yields of the radical and molecular processes from the radiolysis. Approximately 11% of the hydrogen and 36% of the methane were attributed to temperature independent processes.

The effect of the position of the carbon-14 atom in isobutane on the radioactivity yields of the low molecular weight radiation products was shown. The labeled compounds studied were isobutane-1-C^{14} and isobutane-2-C^{14}.

Radioactivity was not observed in the methane component when isobutane-2-C^{14} was irradiated. It was therefore concluded that the center carbon atom did not contribute to the formation of methane. When isobutane-1-C^{14} was irradiated, the methane yield based on radioactivity measurements was found to be about one-third of the yield based on thermal conductivity measurements. A mechanism, in which a methyl radical or molecule was eliminated from the isobutane, was postulated to account for this ratio.

The hydrogen and methane yields observed for isobutane in this investigation were compared with the published yields for other saturated hydrocarbons. The statistical nature of the radiation processes producing hydrogen and methane was shown. It was found that the yield of methane was a function of the ratio of the number of methyl to carbon bonds to the total number of carbon to carbon bonds in the molecule.

The yield of radioactive ethane, produced by the radiolysis of isobutane-1-C^{14} in the liquid and gas phase irradiations, was found to be approximately three times greater than the ethane yield for isobutane-2-C^{14}. The ethylene yield, however, was unaffected by a change in position of the carbon-14 atom. Two different mechanisms were proposed to account for the radioactive ethane yield. The acetylene yield was also determined.

The activity yields of propane and propylene from the irradiation of isobutane-2-C^{14} were observed to be about 1.5 times greater than the corresponding yields when isobutane-1-C^{14} was irradiated. Mechanisms similar to those explaining the methane yield were postulated on the basis of this value.

Propyne was not observed.

The yield of n-butane was much greater than expected. No attempt was made to postulate a mechanism for n-butane formation.

The isobutene yield was determined for the gas and liquid phase irradiations of isobutane. The difference in yield in going from the liquid to the gas phase did not account for the entire difference in hydrogen yield between the two phases. The large difference in the isobutene yield, observed by going from 20°C to -20°C, implied that a large proportion of the isobutene was formed by a thermal radical, temperature dependent process.

The isopentane and neopentane yields were determined. The neopentane yield was considerably greater than the isopentane yield; this was not expected on the basis of a random statistical process. A comparison of the stabilities of the primary and tertiary isobutyl radicals showed that tertiary radical formation was favored. Mechanisms for the formation of the pentanes were proposed involving these radicals, rather than mechanisms involving attack of the isobutane molecule by methyl radicals. In addition, the activity yields of neopentane from the two labeled compounds were compared and explained.

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VIII. ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. A. F. Voigt for his valuable guidance during the course of the investigation.

The author also wishes to thank Mr. R. G. Clark and Mr. W. A. Stensland for the design of the gas chromatograph used in this investigation, and for their suggestions concerning the chromatographic and counting systems. The author is grateful to Mr. C. E. Lang for many informative discussions.

Special appreciation is extended to Dr. J. C. Picken and his staff at the Veterinary Medicine Research Institute for their invaluable cooperation and assistance during the many irradiations that were conducted.