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THE INFLUENCE OF OXYGEN ON THE REACTIONS OF RECOIL CARBON ATOMS WITH SATURATED HYDROCARBONS AND GENERALIZED DESCRIPTIONS OF PRODUCT YIELDS FROM THE REACTIONS OF ENERGETIC CARBON ATOMS WITH SATURATED HYDROCARBONS IN OXYGEN-SCAVENGED SYSTEMS.

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THE INFLUENCE OF OXYGEN ON THE REACTIONS OF RECOIL CARBON ATOMS WITH SATURATED HYDROCARBONS

and

GENERALIZED DESCRIPTIONS OF PRODUCT YIELDS FROM THE REACTIONS OF ENERGETIC CARBON ATOMS WITH SATURATED HYDROCARBONS IN OXYGEN-SCAVENGED SYSTEMS

by

Peter Lieberman

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May 12 '67
date

Robert A. Odum
Chairman of Examining Committee

May 12 '67
date

Alfred P. Wolf
Visiting Examiner
Brookhaven National Laboratory

5-5-67
date

Richard H. Wiley
Executive Officer

Clyde R. Dillard

Herbert Meislich

Robert A. Odum

M. H. J. Wijnen

Supervisory Committee

The City University of New York

Dedicated to

My Parents

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INTRODUCTION

A. General Considerations on Chemical Effects of Nuclear Transformations

Chemical effects of nuclear transformations is one branch of a larger discipline sometimes called "hot atom" chemistry. In fine this latter domain is the reactions of atoms with high translational energy. Such atoms with excess kinetic energy compared to ambient may be generated in many ways, by shock waves, by photolysis reactions, and in molecular and atomic beams as well as by nuclear transformation. Strictly speaking, the chemical effects under consideration do not stem from the nuclear transformation directly, but rather from the high energies imparted to the atoms released by the transformations.

Upon bombardment or irradiation many elements undergo nuclear reactions which result in the emission of some particle or photon from the nucleus. Since momentum must be conserved in this process the nucleus will necessarily recoil. Nuclear reactions take place at very high energies, typically millions and billions of electron volts, and the transformed nucleus receives a powerful impulse. Since the energy being imparted to the recoiling nucleus is orders of magnitude greater than the energies of chemical bonds (the latter are seldom more than 5 eV), bonds to the atom (if any) rupture as it recoils into the surroundings with high initial translational energy. Now upon interaction with its surroundings, the energetic atom loses energy by elastic and inelastic collisions.

When energy of the atoms becomes comparable with that of

chemical bonds, at energies below perhaps 15 eV, reactive encounters may lead to stable, isolable products. Experiments are designed so that after the excess energy is substantially dissipated the atom will be intimate with a substrate with which it may interact chemically.

The nuclear transformation is chosen so that the recoil nuclide produced is unstable. Products incorporating the hot atom may then be assayed radiochemically.

These reactions are different in some important aspects from normal chemical reactions. In a classical chemical reaction, energy is added, for example as heat, to some collection of reactant molecules whose energies are distributed according to the Boltzmann relation. When some fraction of the molecules acquires sufficient energy to overcome the potential energy barrier to reaction, products are formed subject to the limitations on available energy. These reactions taking place at or just above the minimum or threshold energy are called threshold reactions. In threshold reactions the vast majority of collisions between reactants take place below the threshold energy. Since there is a sufficient number of unreactive collisions that statistical principles apply, a kinetic analysis may be used to describe the rates of reaction.

In the case of hot reactions (reactions of hot atoms), reaction energy is brought into the system by only one reactant. Energy loss by the hot atoms is rapid, typically half the excess energy per collision, estimated by classical mechanics. This means that the hot atoms will be in a given energy region for only a few collisions. Considering that hot reactions do take place with appreciable yields,

reaction probabilities in the region of excess kinetic energy are orders of magnitude greater than for conventional reactions and are of the order of one tenth. Moreover, if there are more reaction paths open to the atoms at higher energies, then the products and product distributions from hot reactions in general will differ from the products and product distributions from reactions of the same atoms after they have lost sufficient energy to be close to thermal equilibrium with their surroundings. Conventional kinetic treatment under these conditions is impossible.[1] However, specialized kinetic theory of hot atom reactions,[1, 1a, 1b] treatments in terms of gross cross sections for production of a given product,[1c] and completely theoretical approaches[2a, 2b] may prove fruitful. Also, chemical reaction mechanisms developed to describe threshold reactions may not be expected to describe hot reactions adequately.

The hot atoms in these systems may of course react over a wide range of energies above and down to thermal energies. Reaction probabilities for the production of the various products will depend on energy of the incident atom. One approach to the complete description of a hot reaction system would be a set of quantitative relationships for reaction between a hot atom and substrate molecule to produce each given product giving reaction probability as a function of kinetic energy of the atom from threshold to maximum energy at which production still takes place. But hot atom chemistry is a relatively new field, and the complexities and problems being manifold, the first such quantitative relationship has just recently appeared.[2a, 2b]

Exemplary of the considerable problems and complexities are the consequences of the birth of hot atoms from nuclear transformations at such high energies. The energies are high enough to produce ionization and excitation; one must consider electronic and ionic states of the recoil atom at the time it enters an encounter that results in final products. Moreover, some recoil atoms may combine with additional atoms, forming energetic intermediates which, in turn, give rise to the final products.

Production of hot atoms by nuclear transformation in general necessitates subjecting the entire system of interest to ionizing radiation. Consequently the radiation chemistry of the reactants and products must be considered in any analysis of the results. Moreover, chemical products not incorporating the hot atom will be created. These will arise from molecules fragmented by collision with the energetic atoms and moieties released in the eventual recombination of the atoms. However, since only the recoil atom is radioactive, side products will not be detectable in the assays. Properly speaking, the yields described should be called radiochemical yields, since contributions not containing the unstable nuclide are not determined in the assays. The use of the tracer technique allows the experiments to be done at extremely low conversion, since radioactivity allows measurement of quantities far below those detectable by any other physical methods. Consequently the radiation damage and possible secondary products from radiolysis of or attack on the primary ones are minimized.

An introduction to the chemistry of recoil carbon is provided by the excellent review articles of Wolf,[3,3a] Wolfgang,[4] and MacKay

and Wolfgang,[5] while the "Chemical Effects of Nuclear Transformations" series published by the International Atomic Energy Agency is an excellent source for progress in the entire hot atom field.

B. Statement of Research

This investigation, like most scientific research, is comprised of an examination of previous theories and an extension into new domains. The theories examined, evaluated, and extended involve (1) efforts to relate the yields of products to the structure of the substrate molecules, (2) inferred reaction paths and mechanisms by which the products are formed, (3) the role of added oxygen, and (4) the influences of radiation in recoil carbon atoms systems. In addition, much of Section I is devoted to a thoroughgoing critical review of work on these systems.

Two series of experiments were performed in which reactions of recoil carbon atoms with saturated hydrocarbons were studied. In each, the yields of the products ethylene, acetylene, and carbon monoxide were measured. The first series involved determination of the yields from two similar systems. One system was normal butane with from 0% to 90% added oxygen. Yields were measured at 14 different oxygen concentrations ranging from 0% to 90%. The other system was isobutane measured at 15 different concentrations over the same range.

These studies are a natural extension of earlier investigations on methane, ethane, and propane, all with added oxygen. However, data from the earlier studies are sparse in the middle oxygen concentration region and no measurements were made above 50% oxygen. In the present study, investigations in the middle and upper oxygen

concentration regions and the study of the butanes constitute new areas of research. The results of the investigation of the two butane systems have given information which relates to the last three items in the first paragraph.

Information relating yields of products to structure came from the second series of experiments in which product yields were determined at a constant percentage of oxygen from 14 different substrates in the gas phase: methane, ethane, propane, n-butane, n-pentane, isobutane, neopentane, 2,3-dimethylbutane, cyclopentane, n-hexane, n-heptane, isopentane, isohexane, and 2,2-dimethylbutane. The measurements on the last five compounds were done for the first time in this investigation; the yields from the others had been measured previously. The extensive remeasurements made in the course of this work demonstrated that the values reported earlier are about 25% too low. Theories based on the low results have therefore been subjected to some revisions. The values for the yields from all the substrate compounds have been used in this study to formulate improved structure dependence theories and a new type of yield prediction based on first principles.

Finally, efforts to improve the analytic accuracy have been successful. Reliable comparisons involving differences of 1% yield or less may be made for the first time.

I. RECOIL CARBON ATOM SYSTEMS

A. Interest

The present work is an investigation into some of the aspects of the behavior of recoil carbon atoms. Carbon is of interest of course as the most fundamental reactant in organic chemistry. Only in recent years have reactions of the atomic element come under study. Its reactions in a completely unbonded state will be entirely different from those of any allotrope of the bulk element. Reactions of atomic carbon may give information of value about partially bonded carbon intermediates which occur commonly in conventional organic reactions.

An investigation of the reactions of recoil carbon will benefit from the wealth of accumulated information about the chemistry of carbon compounds. Any general principles of hot atom chemistry educible from hot carbon reactions may find application in systems of hot atoms of other elements.

From a physical-chemical point of view, the study of these atom-molecule interactions is interesting because it gives information on some of the fundamental parameters governing chemical reaction. Also, because conventional kinetic theory cannot be used, hot atom experiments afford a valuable means of obtaining kinetic information in the high energy ranges. The hot atom approach to the study of chemical reactions is analogous in a sense to the biological investigation of large organisms with a microscope. The current prospects are very promising.

B. Production of Recoil Carbon Atoms

Within the method of nuclear transformation there are many nuclear reactions which will give rise to radioactive recoil carbon atoms. Table 1 lists some nuclear processes producing such hot

TABLE 1

SOME NUCLEAR PROCESSES USED TO GENERATE RECOIL CARBON ATOMS

Nuclear Reaction	Apparatus Necessary	Energy of Incident Particle (MeV)	Cross Section (mb)	Reference
$^{12}C(n, 2n)^{11}C$	Cyclotron	20.2 23.5 26.2 & 37.9 29.7 & 36.3 33.5	0 (Threshold) 5 10 15 17.6 (max)	6 , 7
$^{12}C(p, pn)^{11}C$	Cyclotron, proton Synchrotron, or linear Accelerator	1,000- 3,000	~27	8a , 8b , 9
$^{12}C(\gamma, n)^{11}C$	electron Synchrotron	18.7 20.2 & 22.4 20.8 & 21.9 21.4	0 (Threshold) 5 10 14 (max)	10
$^{14}N(p, \alpha)^{14}C$	Cyclotron Van de Graaf	4.4 6.7	0 (Threshold) 95	11
$^{14}N(n, p)^{14}C$	Reactor	thermal	1.8×10^3	12
$^{16}O(p, pn\alpha)^{11}C$	proton Synchrotron	420 - 980 5,700	~8 - 10 12	13 , 14

carbon, along with pertinent nuclear cross sections. The choice of isotope and nuclear process for a given investigation depends on the reactors and/or accelerators available, the chemistry of the system under investigation, the desire for minimum radiation damage to the system, and the half-life and activity yield needed for analysis. Data on these parameters are tabulated for the systems of interest in Table 2. Where the reactions of recoil carbon with carbon-containing substrates is under study, the substrate can also serve as the source of carbon for the nuclear transformation, as it did in the present work.

Addition of nitrogen or nitrogen-containing compounds to the system as was done for example by Ache and Wolf,[18] would have been necessary in order to use either the $^{14}N(p, \alpha)^{11}C$ or the $^{14}N(n, p)^{14}C$ process. The chemistry of the resulting system is then more complicated, additional products like HCN appearing.[19] No electron accelerator of energy high enough to reach the $^{12}C(\gamma, n)^{11}C$ process is currently at Brookhaven National Laboratory, where this research was performed. However, both the BNL 60-inch cyclotron and the 3-GeV proton synchrotron, the Cosmotron, were used to work the $^{12}C(n, 2n)^{11}C$ and the $^{12}C(p, pn)^{11}C$ reactions, respectively. (Fast neutrons needed for the former process are generated by bombarding a lithium target with deuterons accelerated in the machine: $^{6}Li(d, n)$; $Q = +3.38$ MeV.[22])

The $^{12}C(n, 2n)^{11}C$ process was first applied to a carbon recoil study in organic systems by Suryanarayana and Wolf.[17] Stöcklin et al.[20] showed the chemical consequences of the $^{12}C(p, pn)^{11}C$ reaction to be identical to those of the $^{12}C(n, 2n)^{11}C$ reaction despite differences in

TABLE 2

PARAMETERS OF NUCLEAR REACTIONS

APPLIED TO RECOIL CARBON PRODUCTION

Nuclear Reaction	Energy of Recoil Atom (MeV)	Activity Attainable (dpm/mg of) target atom at t_o)	Typical Radiation Dose to System (r)	Reference
$^{12}C\,(n,2n)^{11}C$	0.13 (avg)	$10^3 - 10^4$	$10^5 - 10^6$	3, 15
$^{12}C\,(p,pn)^{11}C$	~1.8 (mean)	$10^3 - 10^4$	$10^4 - 10^5$	3
$^{12}C\,(\gamma,n)^{11}C$	~0.5 (mean)	$10^6 - 10^9$	$10^3 - 10^6$	3, 16
$^{14}N\,(p,\alpha)^{11}C$	~2.1 (max)	$10^3 - 10^7$	$10^5 - 10^9$	3
$^{14}N\,(n,p)^{14}C$	0.045	$10^0 - 10^4$	$10^5 - 10^9$	3, 17
$^{16}O\,(p,pn\alpha)^{11}C$	——	$10^3 - 10^4$	$10^4 - 10^5$	3

recoil energies (see section I C), reaction vessels, and other conditions.

^{11}C has a half-life of 20.5 minutes.[21] This is very short compared with isotopes more commonly used as radioachemical tracers. It decays according to

$$^{11}_{6}C \longrightarrow {}^{11}_{5}B + \beta^{0}_{1} + 1.98 \text{ MeV} \quad .$$

As a consequence of this rapid decay, analysis of recoil products must be carried out speedily, a few hours being the time limit on useful activity. Degradative experiments to locate the labeled atom in the molecule are impossible except in special cases.

The number of counts observed in an assay of a particular reaction product depends, of course, on many additional factors like the yield of the product, duration of residence in the counter, efficiency of the counter, background, sample size, and so forth.

There is little radiation damage to the system for the nuclear reactions used. Possible effects on these and similar systems are discussed in section IV.

C. Recoil and Cooling Processes

The Q value for the ejection of a neutron from the ^{12}C nucleus is −18.7 MeV.[22] To remove a neutron, an incident photon must have energy greater than −Q. The spectrum of recoil energy imparted to the product nucleus is described by Wexler[23] for various processes. As may be seen from Table 2, the energies imparted to the carbon atom are orders of magnitude greater than the ~15 eV energy of the restraining chemical bonds. As the nuclear particle or particles are

emitted, momentum must be conserved, and the nucleus recoils, rupturing all chemical bonds to the atom.

For atoms like carbon recoiling in the MeV energy range, the first consequence of the recoil event will be ionization of the atom. The high-energy atoms quickly lose all electrons with Bohr-orbital velocities comparable to the translational velocity of the atom. The recoil atom now begins its encounters with atoms of the surrounding medium, and its excess energy is degraded by several different mechanisms. In the very high energy region, energy loss is by electronic collisions resulting in ionization and excitation of the molecule struck. When the velocity of the atom diminishes to electron orbital velocities, the primary energy loss occurs via electron exchange collisions. In this energy range the recoiling carbon atom picks up electrons in succession, its charge declining towards neutral as its velocity becomes small compared to electron orbital velocities, i.e., in the kilovolt range. At energies below about 15 keV, Rutherford scattering becomes important. Hard-sphere scattering becomes the major means of energy loss around 5 keV. It is only in the lowest energy region, towards the end of its track, that the carbon atom collides as an atom with other atoms and molecules. Consequently, providing only that the magnitude is great, the particular value of the energy at which the carbon atom recoils will not influence the charge state of the carbon atom when it reaches the reaction energy range.

The last-described collisions are slow enough that the nucleus of the ato or atoms struck responds during the impact. In this energy range the atom loses energy by elastic collisions (in which kinetic energy is

conserved) and inelastic collisions (in which some of the translational energy is converted into rotational, vibrational, and/or electronic energy of the struck molecule). It is generally agreed[3-5] that chemical reactions by the hot atom can take place only when it is in the lowest of the above-described energy ranges. If the carbon atom escapes reaction while having excess kinetic energy it will, of course, continue cooling towards thermal equilibrium with its surroundings. It may then react without excess translational energy (vide infra). Products from reactions of the high-speed atoms are generally referred to as "hot products," while "thermal products" denotes those arising from the reactions of atoms in or near thermal equilibrium with their surroundings.

The picture presented of the degradation of excess translational and electronic energy in matter results from such diverse studies as charge transfer and electron capture and loss in atom and ion beams, ranges of charged particles in various media, and dislocations of atoms in crystal lattices upon irradiation. It is a synthesis of several successful theoretical treatments and is founded on much experimental evidence.[23-41]

D. State of the Carbon Atom Upon Reaction

The carbon atoms at the time they give rise to the final products have a history of high energy. It is reasonable to suppose that this will have a bearing on their state when they enter a reactive chemical encounter. The questions which need to be considered are the state of the carbon atom with respect to electronic excitation, ionization, and translational energy when it reacts. Experimental evidence on these questions unfortunately is very slight.

1. Charge State

The charge state of the carbon atom is the best understood of the three questions in this section. As described in section I C, theoretical considerations allow the prediction that the equilibrium charge for the carbon atom in the energy range in which it enters chemical combination is zero. The charge distribution of the recoil atoms will be determined by the energetic history of the carbon atoms with respect to charge transfer processes. Cross sections for these processes as a function of energy show that recoil carbon atoms which have descended from high energies to about a hundred electron volts should be neutral.[28,37-40] A complete description of average charge from 0 to +6 as a function of kinetic energy for recoil carbon is given by Wolke and Sodd.[35] Electron loss cross sections for carbon atoms moving through various gases support the theoretical expectation that there should be negligible reionization of carbon atoms which have reached neutrality.[41]

There is a resonance phenomenon governing electronic transitions resulting from atomic collisions.[36] The prediction based on the application of this principle is that the only carbon species at translational energies where reactions take place will be neutral. Wolfgang and co-workers have made a calculation of the charge state of the carbon in mixtures of ethylene and oxygen based on the resonance principle.[42] They find that the carbon will be neutral upon reentry and assert that the charge-state question is settled. However, this conclusion may be unjustified. Wexler[43] has pointed out that the resonance rule does not take account of the processes of excited ions. Moreover, charge exchange processes have been found to be

predominantly stepwise, proceding mostly via transfer of a single electron at a time. Since no one has demonstrated that the exchange processes are actually completed during passage of the carbon ions through the energy range where exchange is most probable, the possibility remains open that the carbon ions reach the lower energy regions.[43]

To date, there has been no convincing experiment giving direct evidence on the charge state of recoil carbon atoms in the reactive energy range.

2. Electronic State

Treatment according to the resonance principle also indicates that highly excited electronic states do not play an important role in carbon atom reactions,[42] but this is subject to the same uncertainties governing the application of the resonance rule described in the preceding section. Carbon has two low-lying excited states, the $C_I(^1D)$ at 1.3 eV and the $C_I(^1S)$ at 2.7 eV.[44] Both of these are thought to be long-lived[45] singlet states. The ground state is a triplet, $C_I(^3P)$.[44] Only these three states are expected to be significant contributors to the reaction scheme of atomic carbon. Marshall et al.,[42] Nicholas et al.,[47] and Dubrin et al.[46] have rationalized product yields from ethylene plus recoil carbon under various conditions using the assumption that carbon reacts in these three states. The evidence is indirect, however, and certainly not conclusive.

The role of excitation state in carbon atom reactions is further considered in section I F.

3. Translational Energy

The greatest among the uncertainties about the state of hot carbon atoms at the time of reaction is the translational energy. To date,

there is not one experimental datum on this most fundamental parameter. It may not be until the solutions are found to manifold problems plaguing atomic and molecular beam experiments that the first such data are seen. Meanwhile estimates have been made based on inferred reaction paths taken and on products formed by carbon atoms thought to be reacting in their hot range. The consensus seems to be that this range centers upon several electron volts and is very likely to be between 1 and 10 electron volts. It should be noted here, however, that recent results indicate a qualitative similarity between reactions of hot carbon and those of carbon which has lost most of its excess translational energy. There are some indications that the high reactivity of carbon atoms may be due at least as much to high inherent reactivity of the carbon atom as to excess translational energy.[42, 48]

Experiments have been conducted with carbon arcs which generate thermal carbon atoms as well as fragments consisting of two or more carbon atoms.[49-58a] Products indicate that few reactions with saturated hydrocarbons[55] and olefins[49-51, 53] are qualitatively similar to those in highly moderated recoil systems.[59] The carbon arc work is described and discussed in section IF.

E. Criteria for Hot Reaction

Because of the fact that carbon atoms may react while in the hot or thermal regions and that product distributions will not be identical in the two cases, working procedures are needed to distinguish the product yields of the thermal carbons from those of the energetic ones.

Several criteria have been used to distinguish the reactions of atoms with high translational energy from those which have undergone

many collisions and come close to or into thermal equilibrium with the surroundings. Traditionally distinctions between hot and thermal reactions have been made by observing the dependency of product yields upon (1) addition of moderators, (2) changes in temperature, (3) addition of scavengers, and (4) changes of phase of the system. Of course, there are many products from the reactions of carbon atoms with simple hydrocarbons, and the question must be asked for each product individually. Moreover, the possibility must be entertained that some portion of a given product arises from hot reaction and the remainder from thermal reaction. This possibility is especially germane to recoil carbon in the light of the qualitative similarity of products from hot and thermal species.

1. Moderators

Moderators are inert materials, the noble gases for example, whose function is to lower the average energy of recoil atoms entering reactive encounters with the substrate.

If the largest fraction of a reaction mixture is an unreactive substance, then recoil atoms will make the majority of the moderating (slowing) collisions with that substance. Thus in systems containing increasing proportions of moderator, reactions of thermal atoms will be the increasing contributor to the products.

According to classical mechanics, momentum transfer in an elastic collision between two bodies may be greatest when the masses of the bodies are equal. Experimental evidence confirms the prediction that neon should be a better moderator for carbon than either krypton or xenon.[47] In practice, more than 90% moderator must be used before limiting of yield trends becomes apparent,[47] and results have been

reported from systems as high as 99.7%[60] and even 99.9%[47] in moderator.

The moderator techniques do have limitations, of course. When the percentage of hydrocarbon in the system is very low the small amount of carbon available for the nuclear transformation results in correspondingly low activity production. Also cross sections for the nuclear activation of the rare gas by the bombardment must be low or the nuclide produced must have a very short half-life. (However these difficulties are obviated if a heavy ion accelerator is used to produce the hot carbon.) Another complication arises from the fact that energy transfer in the irradiated medium will be changed as the composition is altered. The distribution of any excited states playing a role in the reactions may change. Yields of products arising from collisional deactivation of excited intermediates may be affected. In the reactions of carbon atoms with ethylene in presence of 90% and 95% neon, the noble gas seems to function predominantly as a moderator.[42]

2. Temperature Dependency

From the fundamental definition of hot atom processes, the efficiency of a hot atom reaction is independent of the temperature of the substrate. This is because the energy for the reaction is supplied in excess by the translational energy of the hot atom. Temperature differences of hundreds of degrees of the substrate are swamped by the translational energy of hot atoms. For example using the relationship that

$$\text{Kinetic Energy} = \frac{3}{2}\,kT \quad ,$$

a 3-eV carbon atom will have a temperature equivalent above 23,000°K. Consequently, products whose yields are temperature dependent must

be coming from thermal processes, and hot product yields will be temperature independent. However, it is a mistake to conclude that the converse is necessarily true, i.e., that a product yield which shows temperature independence must be from a hot atom reaction. A product yield may stay constant over a wide range of substrate temperatures if the energy for the reaction is present in excess even at the lowest temperature studied. This may be the case if, over the temperature range used, the energy of activation for the reaction is very low or nil which, in turn, may be the case if the intrinsic reactivity of one of the reactants is very high. Since this may be true for carbon,[42,61] as was indicated in section IID3, both hot and thermal reactions of carbon atoms may be temperature independent. In other words, for carbon atoms, thermal reactions at room temperature may not be threshold processes.

On the other hand, in practice a temperature dependent radiochemical yield of some product may result from an initial hot encounter proceding via some long-lived, carbon atom-containing intermediate which comes into the thermal range before giving rise to more than one stable product. Very little study has been made in this direction as yet.

3. Scavengers

A scavenger is a material with high reactivity towards thermal radicals. Added in low concentrations to a system containing radicals, it will suppress or eliminate radical reactions, especially radical induced chain reactions.

Scavengers may function by different paths. Scavenger molecules may combine with radicals, producing a species of much greater stability.

Conjugated aromatic molecules may exhibit this behavior if the adduct with the radical allows great delocalization of the unpaired electron. Other scavengers like 1,3,5 trinitrobenzene or triphenyl methane act by donating a hydrogen atom to the radical, the scavenger-minus-hydrogen moiety that remains being much more stable than the radical removed. Sometimes radicals themselves, for example 1,1-diphenyl-2-picrylhydrazyl (DPPH), are used as scavengers. In this case the radical used as scavenger must be able to add to other radicals but unable to create radicals from molecules ("initiate") or to dimerize. Oxygen is another scavenger which functions in this manner.

For scavenger action the reaction rate of the radical with the scavenger must be much greater than with the other material present. Then scavenger concentrations may be kept very low. This is necessary if the scavenger is to have no gross effect on the chemical system, i.e., for the scavenger not to become a participant in the main reaction.

Since their introduction to the hot atom field by Schwarz et al.,[62] scavenger techniques have been widely used.

In recoil atom systems, scavengers have played two roles. First, they act to prevent the destruction of radiochemical products by suppressing the concentration of radiolytically produced radicals in the systems.[20,61] Second, they have been used in some systems to help distinguish hot products from thermal products.

The reasoning behind the use of scavengers in the second case is as follows. It is assumed as a gross first approximation that hot atoms, because of their great energy, react with equal probability with scavenger and substrate. Since the scavengers are present at

levels of a few percent or less, the contribution to the products from reactions between hot atoms and scavenger molecules will be only a few percent of the total yield. In the thermal energy range, however, the recoil atoms will react more rapidly with the scavenger than with the substrate. Then the small percentages of added scavenger will eliminate or sharply suppress the thermal yields without affecting the hot yields. A comparison of radiochemical yields from scavenged systems with those from unscavenged ones should allow identification of the reactions leading to hot and thermal products.

Wolfgang has argued that a specific exception to this criterion exists for the carbon atom.[63] Very highly moderated systems of hydrocarbon and recoil carbon in the presence of scavengers give essentially the same products as unmoderated scavenged systems.[47] This is considered another indication that carbon atoms at room temperature are above threshold energy for reaction with hydrocarbons. Thermal carbon atoms therefore have the qualitative similarity to hot carbon atoms that they have high probabilities for reaction with hydrocarbons yielding a variety of products. If very low-temperature systems are employed, threshold processes for carbon atoms may be reached, but of course as the system temperature drops, the research field is reduced to the condensed phases.

It should not be concluded from the above that thermal and hot product distributions will be essentially identical, nor are they found to be.[42,46,47,60] Energy added to the reaction complex as excess kinetic energy of the hot carbon alters the product spectrum. Additional higher energy reaction paths, including bond scissions and rearrangements, will certainly be available in the case of the hot carbon

that were not energetically feasible for the thermal species. This is discussed in detail in the section on carbon atom reactions.

Oxygen is now the most widely used scavenger in gas phase recoil carbon research. Semenov[64] has given a complete description of the mechanisms by which oxygen scavenging proceeds. Certain additional limitations attendant on its use must be kept in mind. First, there is evidence that its efficiency for reaction with triplet species is much less than that with radicals.[65] Its reactivity with excited singlet species would be expected to be lower still, considering the multiplicities. Second, the use of oxygen as scavenger when products from oxygenated substrates are under study makes interpretation of the results more difficult. Thus, in a study of the reactions of atomic carbon with π-bonded inorganic molecules, including oxygen, ethylene was used as the scavenger.[66]

The first use of scavengers in ^{11}C recoil systems was reported by Suryanarayana and Wolf,[17] who added 1,3,5-trinitrobenzene and DPPH to the substrate, benzene. Oxygen was subsequently introduced into recoil carbon work in a study of the reactions of recoil ^{14}C in anhydrous ammonia.[67] Carbon monoxide and carbon dioxide had been observed from the interactions of carbon atoms with oxygen-containing organic and inorganic compounds in solid and liquid phases by Yankwich et al.[68] The reaction of recoil carbon with free oxygen in the gas phase was described by Pandow et al.,[69] who showed carbon monoxide to be the major product in yields approaching 100%. An appraisal of the energy of possible reactions makes evident the basis for this yield.

$$C_{(g)} + O_2 \rightarrow CO_2 \; ; \qquad \Delta H = -266 \text{ kcal}$$

$$C_{(g)} + O_2 \rightarrow CO + O \; ; \quad \Delta H = -139 \text{ kcal}$$

Carbon dioxide formed in a concerted reaction would have an internal energy of 266 kilocalories (without considering the additional translational energy of the carbon atom). Comparing this with 127 kilocalories, the bond dissociation energy of the OC=O bond, it is evident that carbon dioxide is unlikely to arise in the gas phase except possibly from 3-body collisions.

Studies on the γ-radiolysis of saturated hydrocarbons[70,71] have shown that small quantities of unsaturates are generated which rapidly react with hydrogen atoms produced in the system. This behavior is consistent with, for example, the findings that hydrogen atoms add to ethylene 422 times faster than they abstract hydrogen atoms from n-butane.[72] This gives rise to a self-scavenging effect in hydrocarbons subjected to radiation. For unscavenged recoil carbon systems it will diminish apparent yields of unsaturated products from saturated substrates. Consequently oxygen has been added to the substrate in most such gas phase studies. Thus, MacKay and Wolfgang[61] added 2% oxygen to a variety of saturated hydrocarbons, Stöcklin and Wolf used 0.58% and 14% oxygen[73] and 4.5% oxygen[1c] in various studies, and Stöcklin et al.[20] used 0.12% oxygen as well as trying 2.0% acetylene and 1.2% ethylene scavengers in methane. When olefins are the substrates, they will act as self-scavengers, and losses of unsaturated yields should be minimized. This expectation is borne out in butenes[60] and in ethylene, in which the drop in yields of allene, acetylene, and methylacetylene is inappreciable upon addition of ~4% oxygen.

Studies have been made to ascertain the role played by oxygen in saturated hydrocarbon systems at various concentrations. The necessity of differentiating between concentration ranges in which the

oxygen is acting as scavenger and those in which it is in competition with the substrate for the carbon atoms of all energies was pointed out early.[73] Detailed descriptions of the dependence of major product yields on amount of added oxygen have appeared[1c,20] but discussion of these is postponed until the section on reactions of carbon atoms.

4. Phase

One of the criteria originally advanced for the differentiation of hot reactions was phase independence. The idea was that the high energy of the hot atoms was sufficient to overcome the constraints of the medium on condensed-state substrate molecules. If the hot atom dissipates the last of its excess energy in a small volume, a local high-temperature, gaseous reaction zone will be created momentarily in which the recoil atom enters its final chemical combination. Thus products from hot reactions in condensed phases should be the same as in the gas phase. The difficulty that vitiates the generality of this approach is that the conditions described may correspond more closely to a small cage system than an extent of free gas. Cage effects like the reaction of the carbon atom or reaction intermediates with radicals produced locally by the deposited energy are likely to result. Moreover, if the lifetimes of any intermediates are comparable to or longer than that of the gaseous reaction zone, then constraints of the medium will have an effect. Also if the intermediate survives the gaseous reaction zone, its de-excitation will be promoted by more frequent collisions in the condensed phase.

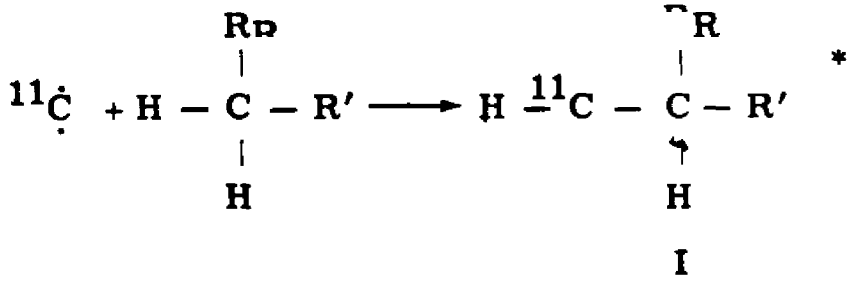
F. The Reactions of Carbon Atoms

Dodson and Miller[74] first suggested the presently accepted thinking on the pathway of hot atom reactions. In explaining experimental

observations on a system of hot chlorine atoms in a liquid hydrocarbon system, they proposed that the recoil atoms form chemical complexes with the hydrocarbon which then decompose via several paths to various products. This chemical approach to the understanding of hot atom reactions has supplanted the earlier purely physical approaches. Considerable headway has been made in the hot atom chemistry of carbon-atom systems in particular, based on the idea of a reaction complex or intermediate. In contrast with chlorine or other monovalent species, carbon-atom substrate-molecule complexes may be expected to undergo rearrangements and reactions with additional substrate molecules as well as various decompositions to yield the final products.

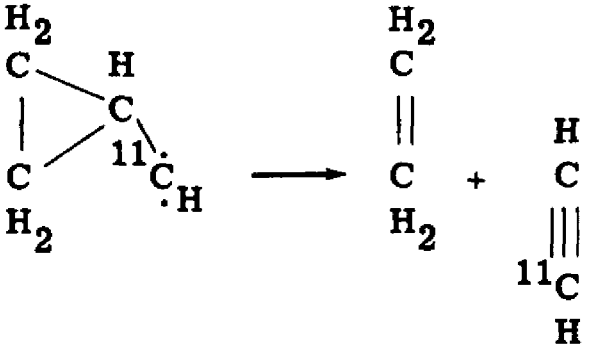
A wide variety of experiments and techniques has been brought to bear in the effort to elucidate the reaction scheme of carbon atoms. At present, knowledge of the most fundamental parameters (e.g., energy of the carbon atoms, lifetimes of the intermediates) is qualitative only. Qualitative and comparative arguments have advanced understanding of the behavior of carbon atoms substantially. This progress is now described.

A large body of evidence supports the theory that carbon atoms react with hydrocarbons by inserting into carbon-hydrogen bonds and carbon-carbon double bonds but not carbon-carbon single bonds. Insertion type events had been postulated as a reaction mechanism in recoil carbon systems by Wolf et al. as early as 1956.[75] MacKay and Wolfgang[61] advanced the insertion of carbon atoms into alkyl carbon-hydrogen bonds in their explanation of the high yields of acetylene from the reaction of carbon atoms with many hydrocarbons. The acetylene arose, they argued, by insertion forming an excited intermediate, I,



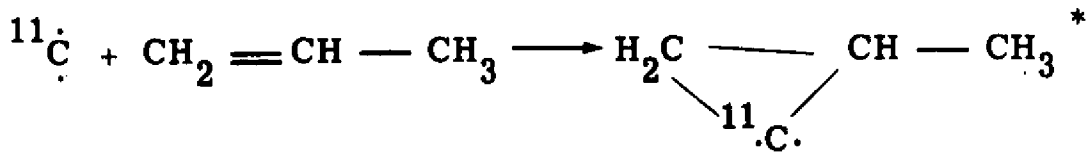
I

which can then decompose to ^{11}C-acetylene and to other labelled products. Acetylene yields were about 30% from methane, ethane, and propane under the conditions of the experiment. The very large yield of acetylene from cyclopropane, 65.5% – about double that from the other hydrocarbons studied – was presented as further evidence of the proposed mechanism. Only the carbene intermediate formed by C–H bond insertion in cyclopropane can decompose directly to products via electronic rearrangement with little motion of the atomic nuclei.



Small yields of isobutene (2.4%) and 1-butene (3.0%) from propane were observed, and it was suggested that these might arise from deactivation of the intermediate before decomposition could occur.

MacKay et al.[76] postulated the insertion of carbon atoms into carbon-carbon double bonds via a preliminary cyclic addition complex, II, for example from propylene



II

This insertion complex can rearrange to several different products, methylallene, butyne-1, 1,3-butadiene, for example. A further study of the reactions of carbon with ethylene substantiated the finding and added indications that carbon was more reactive towards ethylenic than towards saturated hydrocarbons.[48] Decisive evidence came with the degradation of the allene produced from the reaction of carbon with ethylene. The ratio of center to terminal ^{11}C labeling in allene was 1.8 in the gas phase demonstrating that (1) carbon does insert into C=C bonds, and (2) C=C insertion is preferred to C–H insertion. In 95% neon moderator the ratio increased to 3.2, showing that thermal carbon atoms are only moderately more selective than hot carbon atoms, and lending additional support to the suggested similarity of their reactions.[77]

The idea that methylene, CH_2, participates in the reactions in hot-carbon systems was originally suggested by Wolf et al.[75] Support for this postulate came from the observation of yields of cyclopropane from ethylene substrate,[48] and of ethane from methane,[20] and the finding that yields of C_{n+1} (n = number of carbon atoms in the substrate) saturated products from saturated substrates increase in condensed phases.[73] Furthermore, the yields of the butanes from propane approach the statistical distribution (3 n-butane: 1 isobutane) which might be expected from the reaction of energetic methylene. Dubrin

et al. have estimated that 6% of the carbon atoms react to form CH_2 based on their finding of 6% combined yield of cyclopropane and propylene from ethylene substrate.[46] This fraction increases to 9% in 4:1 hydrogen-ethylene mixtures.[78]

Stöcklin and Wolf[73] demonstrated that the intermediates formed between carbon atoms and both ethane and propane live long enough to be able to lose energy by collision in condensed phases. This was evidenced by two complementary trends: an increase in yields of products with one carbon more than the substrate and of higher boiling compounds, and a decrease in the yields of products resulting from fragmentation of the complex (acetylene and ethylene) in the condensed phases compared to the gas phase.

A powerful double tracer technique involving the use of deuterated substrates stimulated much new research when it was introduced to the field. New chromatographic techniques[79] made possible the separations of deuterated, partially deuterated, and non-deuterated light olefins. The separated fractions could be radioassayed individually. Thus allene produced by carbon recoils in a 1:1 ethylene:perdeuteroethylene substrate mixture was found to be more than 85% C_3H_4 and C_3D_4 (the remainder being isotopically mixed), demonstrating that the bulk of the allene arose from the interaction of a carbon recoil with only one substrate molecule.[80] The same technique applied to the study of the formation of acetylene from ethylene or ethane[81] showed about the same proportion of the acetylene produced to be isotopically mixed so that acetylene, too, is produced primarily from a single substrate molecule. Furthermore, the isotopic composition of the acetylene from the substrates CH_3CD_3 and CH_2CD_2 again averaged

about 85% unmixed, supporting the contention that acetylene proceeds not only from a single substrate molecule but also primarily from interaction at just one carbon atom within the substrate molecule. However, elementary statistical considerations show that if 15% of a given product is mixed, as much as 30% of it was formed by non-specific processes.

The mode of reaction of carbon atoms with π-bonded inorganic molecules was investigated in a study of products from the substrates O_2, CO, CO_2, SO_2, N_2, N_2O, NO, and NO_2.[66] The π-bond insertion of carbon atoms has already been described for ethylene. The authors here use bonding orbital overlap considerations and analogy with the ethylene case to support their postulated mechanism of an end-on attack in the compounds investigated. However, the analogy is an inexact one, since (1) energy redistribution to the C—H bonds may occur in ethylene, and (2) the chemical bond
in oxygen is different from the C=C bond in ethylene. Also, end-on attack seems unlikely by virtue of geometric considerations for a reactant with the high reaction probability attributed to carbon atoms. Some success was found in correlating products and yield trends with reaction enthalpies.[66] Thus the enthalpy of reaction of carbon atoms with nitrogen producing the cyanide radical is 50 or 75 kcal/mole (depending on the electronic state of the carbon atom) endoergic, which correlates well with the fact that this product of hot carbon atoms is not observed from thermal carbons. From nitrous oxide, however, the production of ·CN is exoergic, and appreciable yields of it are observed from both the hot and thermal carbon atom systems. The nearly 100% yields of carbon monoxide from oxygen gas remain

undiminished in presence of 99% moderator, again consistent with the high exoergicity of this reaction. The reactions of carbon with nitric oxide and nitrogen dioxide are also described.[66]

Stöcklin et al.[20] reported on carbon atom reactions in methane-oxygen systems. A dependence of product distribution on dose was observed in the pure hydrocarbon. The yields 13.9% CH_4, 17.7% C_2H_2, 12.4% C_2H_4, 23.9% C_2H_6, and 11.2% C_3H_8 at 4.8×10^{-4} eV/molecule became 6.9%, 14.0%, 6.6%, 29.4%, and 20.2%, respectively, at 8.3×10^{-4} eV/molecule. The following reaction scheme was proposed to account for the formation of ^{11}C-propane in neat methane.

$$^{11}C^{*} + CH_4 \longrightarrow \longrightarrow \longrightarrow {}^{11}CH_2{=}CH_2$$

$$CH_4 \xrightarrow{\wedge\wedge\wedge} CH_3\cdot + H\cdot$$

$$H\cdot + {}^{11}CH_2{=}CH_2 \longrightarrow {}^{11}CH_3{-}CH_2\cdot$$

$$CH_3\cdot + {}^{11}CH_3{-}CH_2\cdot \longrightarrow {}^{11}CH_3{-}CH_2{-}CH_3$$

The sharp reduction of ethane yields in the presence of scavenger concentrations of oxygen, ethylene, or acetylene and the consistent enhancement of acetylene and ethylene yields led the authors to conclude that reduction of primary unsaturated products by hydrogen was likely occurring in the unscavenged systems. It was further concluded that part of the ethane arose in the unscavenged system from the insertion of $^{11}CH_2$ into substrate molecules. The authors also studied the yields of carbon monoxide, ethylene, and acetylene from methane as a function of added oxygen up to 50%. Their results may

be seen in Figure 1. The rapid rise in the acetylene and ethylene yields below $\frac{1}{2}$% oxygen were explained as the result of scavenging by the oxygen of radiolytic fragments which otherwise destroy the primary products. Subsequent declines in these yields and the concomitant increase in the carbon monoxide yield then resulted from the reactions of oxygen with the hot carbon atoms and other precursors of the observed products. The oxygen thus played two roles in the system: first, as a general radical scavenger suppressing secondary reactions of radiolytic species, and second, in the higher concentration ranges as a competitor with the substrate for the hot carbon atoms and other precursors. When ethylene was used as the scavenger, a total 6.2% of the possible methylene reaction products ethane ($^{11}CH_2 + CH_4$) and cyclopropane ($^{11}CH_2 + H_2C{=}CH_2$) were observed.

Stöcklin and Wolf[82] noted a proportionality between the yields of acetylene from various scavenged (4.5 volume percent oxygen), gaseous alkanes and the fraction of the carbon present in the molecule as methyl groups (Figure 2). The acetylene yields were not found to be proportional to the fraction of hydrogen present in the molecule as primary C–H. The suggestion was offered that methyl groups have a high cross section for the formation of acetylene.

The authors postulated that methyne (CH) participates in the reactions in hot carbon systems. They suggested this species to be the precursor of ethylene from hydrocarbon substrates. The observations were (1) absence of a deuterium isotope effect in the production of ethylene, (2) proportionality between ethylene production and relative number of primary C–H bonds from various scavenged

^{11}C PRODUCT YIELDS FROM METHANE/OXYGEN SYSTEM

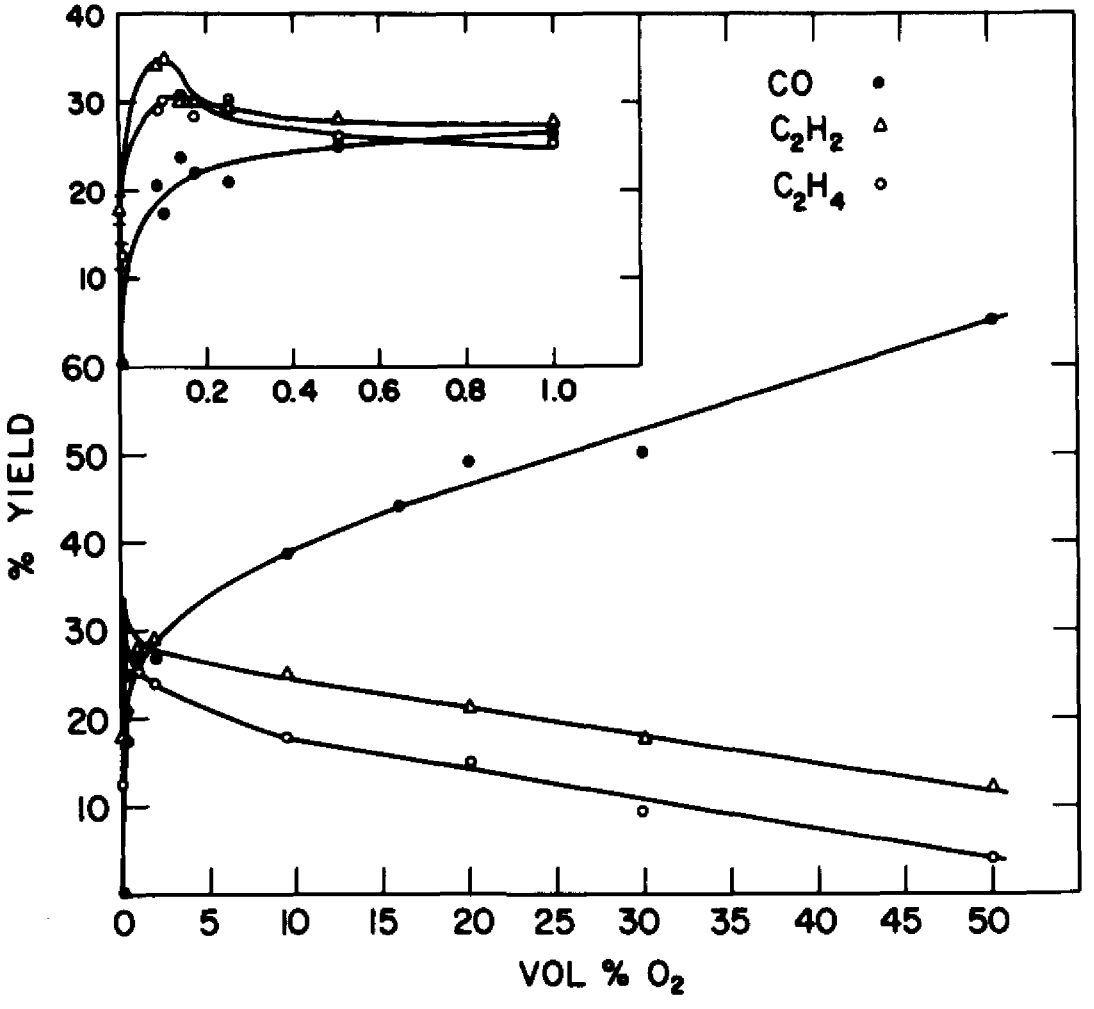


FIG. 1

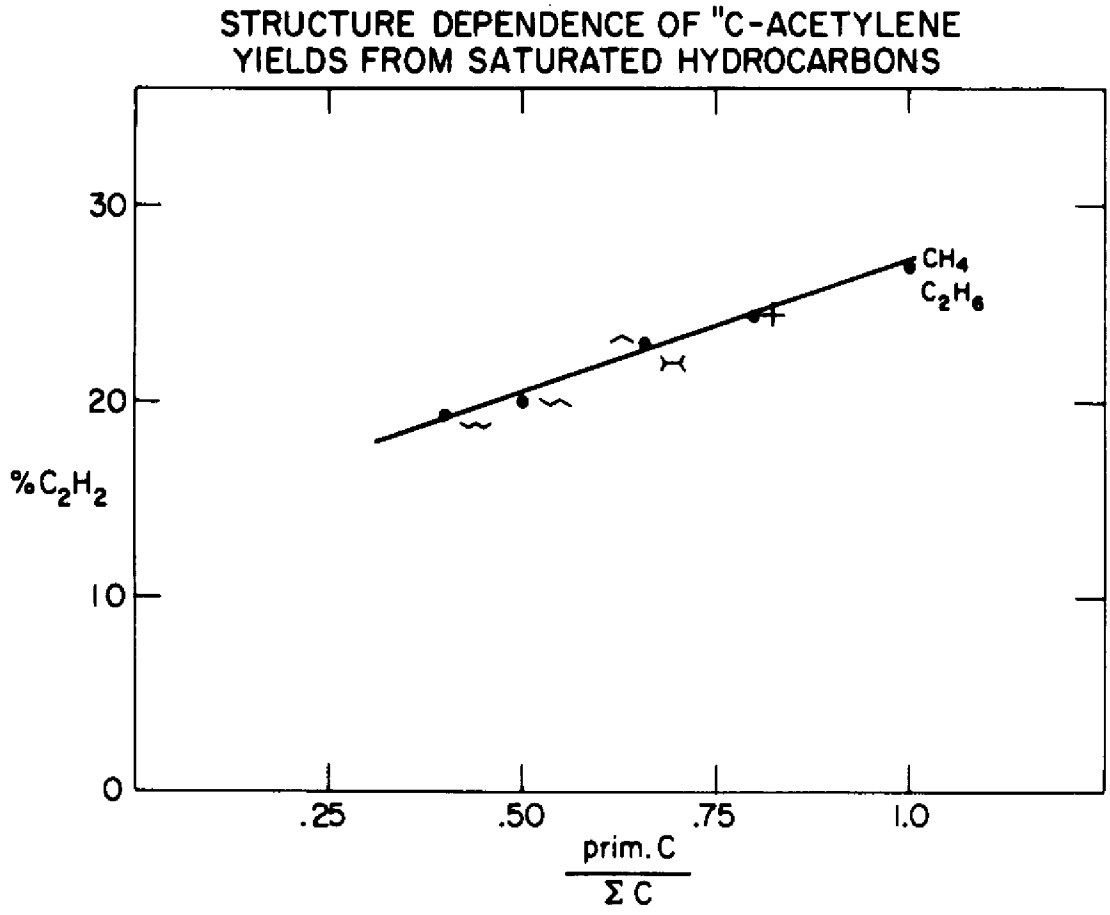

STRUCTURE DEPENDENCE OF "C-ACETYLENE
YIELDS FROM SATURATED HYDROCARBONS
30
20
10
0
% C_2H_2
CH_4
C_2H_6
.25
.50
.75
1.0
prim. C
Σ C

FIG. 2

(4.5 volume percent oxygen), gaseous alkanes (Figure 3), and (3) comparatively quite small yields of ethylene (~1% or less) from alicyclic substrates. An insertion into a primary CH bond by methyne

$$^{11}:\dot{C}H^{*} + CH_3R \longrightarrow H_2{}^{11}\dot{C} - CH_2R^{*}$$

followed by collapse of the excited intermediate

$$H_2{}^{11}\dot{C} - CH_2R^{*} \longrightarrow H_2{}^{11}C{=}CH_2 + R\cdot$$

was postulated. The mechanism suggested was reasonable being the simplest direct route to the products consistent with the observations. Absence of an insertion isotope effect was attributed to very high energy of the methyne moiety. An analogous path involving methyne insertion into certain secondary C—H bonds was postulated as the source of the smaller yields of propylene. Dubrin et al. have argued that the ethylene and propylene may arise as carbon atom insertion products.[80] An unequivocal identification of the precursor(s) of these products is still awaited.

Evidence for the formation and reaction of methyne was adduced in a study of recoil carbon reactions in ethylene-hydrogen mixtures.[78] The indications were that yields of products attributable to methyne reaction (i.e., pentene-1) amount to only a few percent, rising slowly to a maximum of ~7% in mixtures close to 100% hydrogen. If this is the actual extent of methyne participation, the large yields of ethylene from the saturated hydrocarbons (up to 25.5% from methane) can certainly not stem from methyne reaction. However, the greater availability of hydrogen atoms in saturated hydrocarbons (more hydrogens

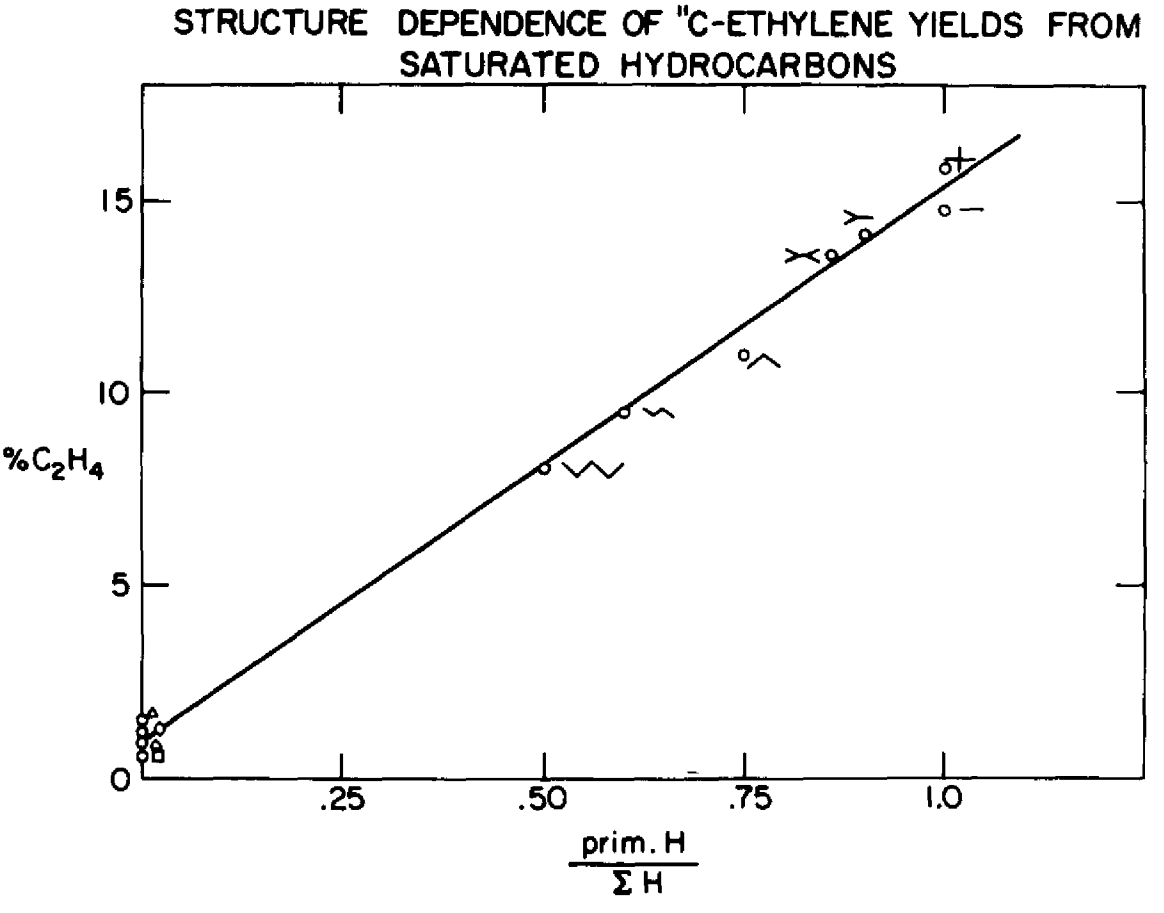

STRUCTURE DEPENDENCE OF "C-ETHYLENE YIELDS FROM SATURATED HYDROCARBONS
15
10
5
0
%C2H4
.25
.50
.75
1.0
prim. H / Σ H

FIG. 3

per molecule, lower bond dissociation energy for the hydrogens) must be remembered in this connection.

An apparent proportional relationship similar to those for ethylene and acetylene production was found later for carbon monoxide. Yields appeared to be inversely proportional to the number of hydrogen atoms in the alkane molecule from scavenged (4.5 volume percent), gaseous alkanes, methane to C_4 (Figure 4).[1c]

In the same study a general explanation was undertaken of the behavior of yields of the major products, carbon monoxide, ethylene, and acetylene from the substrate systems of methane, ethane, and propane, all with added oxygen. The dependence of these yields on the amount of added oxygen may be seen in Figures 5-7. The explanation of the methane system which differs somewhat from the other two has already been given. For the ethane and propane systems, the following explanation was offered. In the region below ~1% oxygen, rapid scavenging of the thermal carbon atoms and other possible thermal intermediates is taking place. This is shown by the rapid increase in the carbon monoxide yield and the rapid decline in ethylene and acetylene yields, reflecting elimination of the portions of their yields arising from thermal processes. Further corroboration for this explanation is the complete elimination of the few-percent yields of saturated thermal products, methane and ethane, below 1% added oxygen. The rapid thermal scavenging reaction reaches saturation with complete scavenging of the thermal carbon and intermediates around 2% oxygen. The demarkation is masked by the onset of competition by the oxygen with the substrate for the hot carbons, resulting in a continued slow increase of carbon monoxide yield and decreases of ethylene and

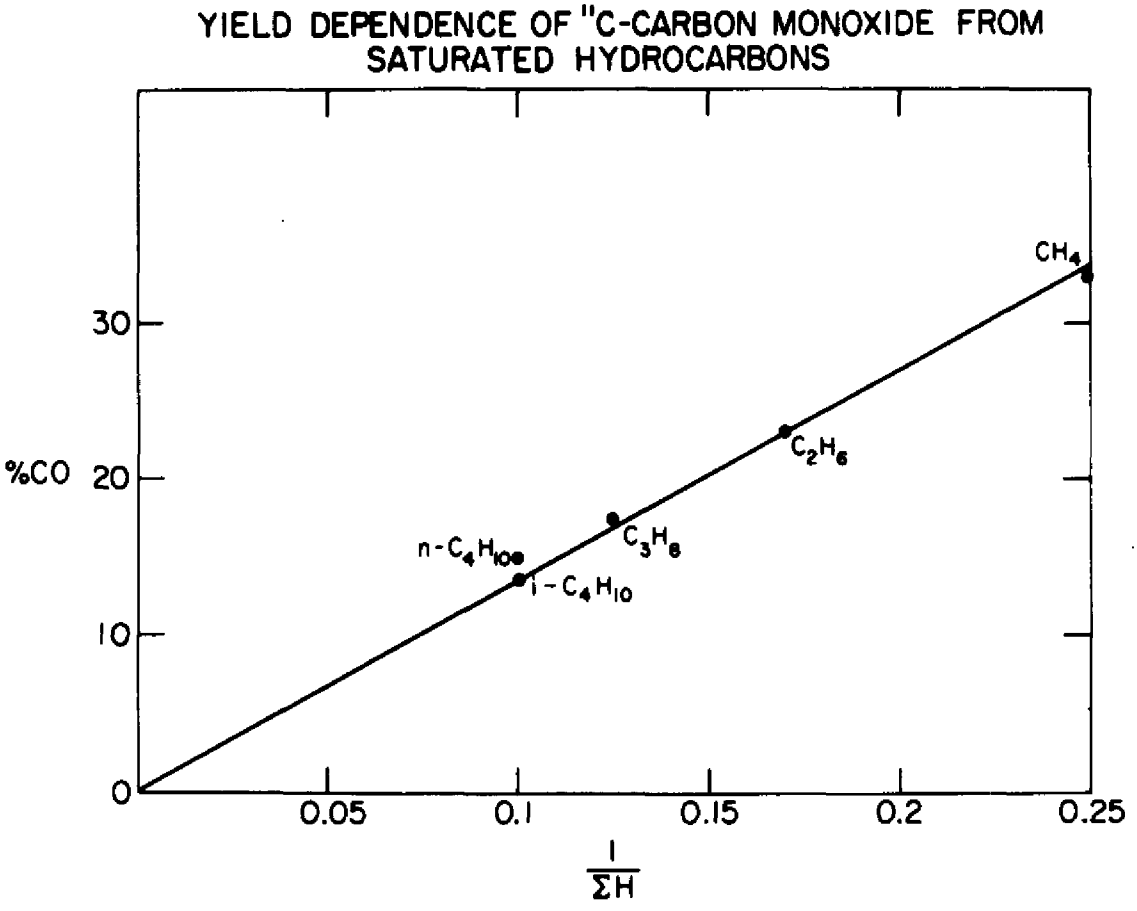

YIELD DEPENDENCE OF "C-CARBON MONOXIDE FROM SATURATED HYDROCARBONS
%CO
30
20
10
0
0.05
0.1
0.15
0.2
0.25
1/ΣH
CH4
C2H6
C3H8
n-C4H10
i-C4H10

FIG. 4

YIELDS OF ^{14}C-CARBON MONOXIDE FROM THREE SATURATED HYDROCARBON/OXYGEN SYSTEMS

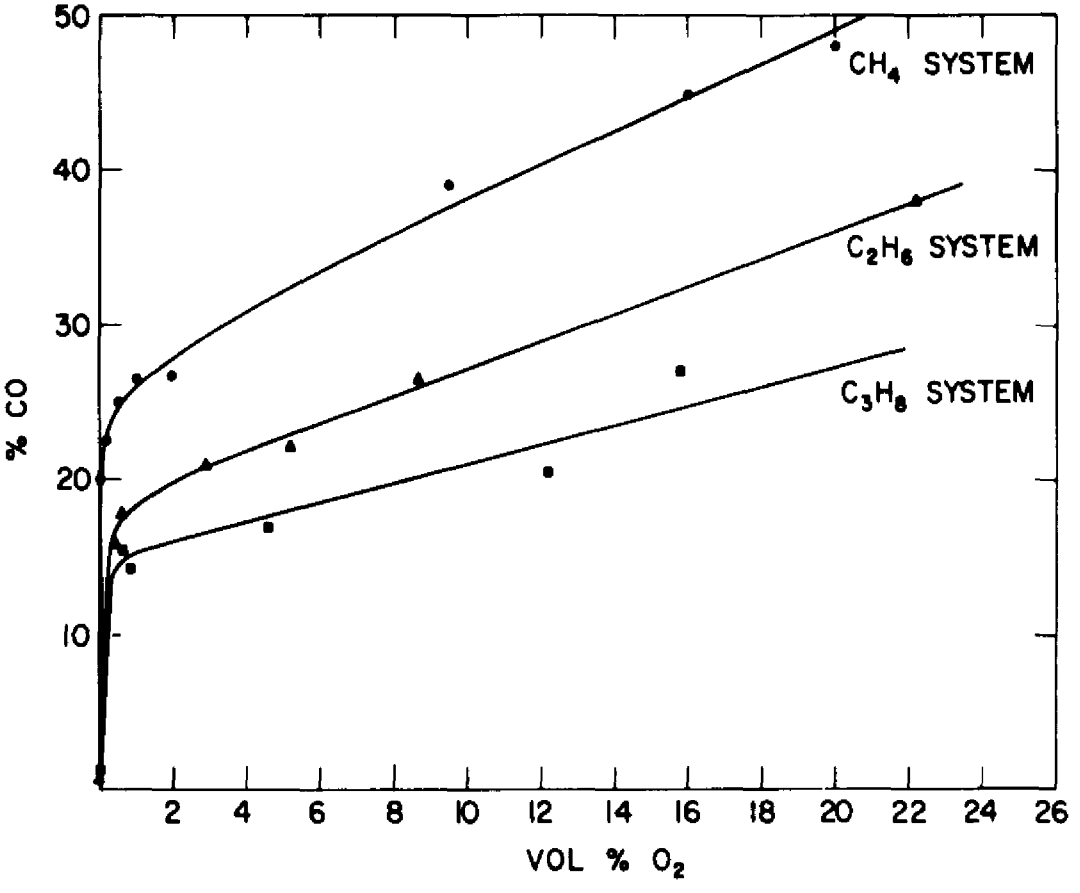


FIG. 5

YIELDS OF ^{14}C-ETHYLENE FROM THREE SATURATED HYDROCARBON/OXYGEN SYSTEMS

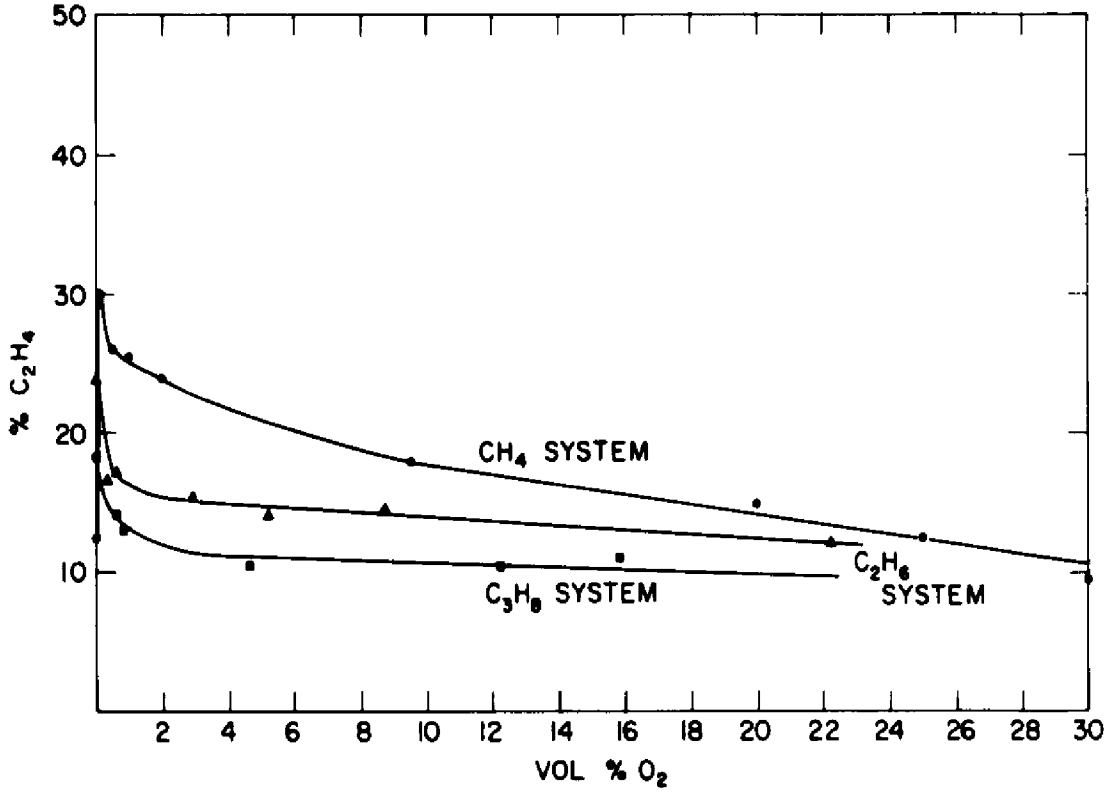


FIG. 6

YIELDS OF ^{14}C-ACETYLENE FROM THREE SATURATED HYDROCARBON/OXYGEN SYSTEMS

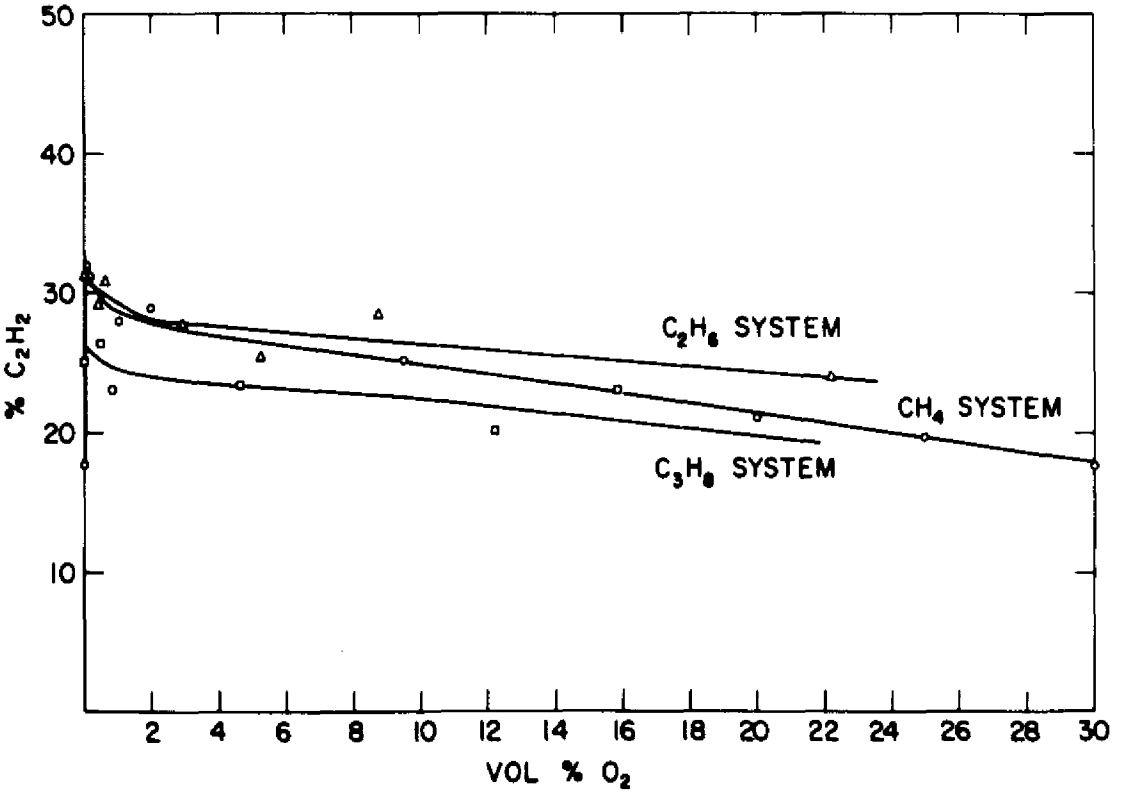


FIG. 7

acetylene yields. The consistency of this explanation with results of the present study is discussed in section IV.

Ache and Wolf[83] found a high degree of isotopic mixing (17.4%[83a]) in the acetylene from 1,1 ($^2H_2$) cyclopropane. This is inconsistent with the one-step concerted collapse of the carbon-cyclopropane complex, the mechanism put forward by MacKay et al.[76] and demonstrates that if the reaction proceeds as proposed, the intermediate in this system persists at least long enough to undergo hydrogen migration. The 12-18% (of the total acetylene produced) of monodeuteroacetylene formed from such compounds as $CH_3CD_2CH_3$ and $CD_3CH_2CD_3$,[83] like the ~15% mixed acetylene from the ethane and ethylene systems,[81] indicates that the generally accepted C—H bond insertion route for acetylene formation cannot be the complete explanation. (The $5\frac{1}{2}$% yield of acetylene from benzene is further evidence of the operation of other mechanisms.[84])

Yields of isotopically mixed acetylene were consistently greater from partially deuterated substrates than from 1:1, perdeutero:perproto substrate mixtures, a fact which is consistent with a primarily intramolecular mode for acetylene production.

One of the directions taken by investigators has been an attempt to establish cross sections for formation of given products or for reaction with given bonds or groups as a function of known parameters of the substrate or system. Ingenious experiments and calculations have been made to this end. Thus in one study by Ache and Wolf[18] a ratio for the production of acetylene from CH_3- to that from $-CH_2-$ was obtained by the use of the specifically deuterated propanes. Here are the acetylene yields (expressed as percentage of the total acetylene

formed) from one of the compounds studied: from 2,2 ($^2H_2$) propane, 69.9% was C_2H_2, 11.5% as C_2HD, and 18.6% as C_2D_2. If the yield of perdeutero acetylene is divided by 1, the number of methylene groups in the substrate, and the yield of perprotoacetylene is correspondingly divided by 2, the quotients are in the ratio of 1.88. This number agrees well with those computed from other partially deuterated substrates, the average of which is 1.9. The constancy of this value computed from the various partially deuterated compounds and its agreement with a value calculated from straight chain alkane data led the authors to the inference that the primary acetylene-producing interaction of the hot carbon atom is with an entire group – either methyl or methylene – within the molecule rather than with particular C–H or C–D bonds. However, it must be noted that the reverse conclusion was initially drawn from similar data[83] and that the confirmatory argument based on straight chain alkanes is vitiated by data presented herein (see sections III and IV).

Some other values reported are the ratio ≅2 of the cross section for production of carbon monoxide from hot carbon to that for the production of acetylene from hot carbon (in systems of hydrocarbon, oxygen, nitrogen),[19,83] and the ratio of the cross section ≅4 for the reaction with oxygen versus with a primary C–H bond (in oxygen-hydrocarbon mixtures).[1c] The allene degradation work cited[77] also gives information on the preference ratio between C–H bonds and C=C bonds. However, it is impossible to distinguish terminal labelled product from C–H insertion from that arising from rearrangement of the postulated cyclic C=C insertion intermediate. Consequently the numbers obtained are actually only limiting values. In general the

derivations of these reaction cross section ratios involve some substantial approximations and assumptions which leave the validity of the results open to some doubt.

In a thoroughgoing examination of the reactions of carbon with ethylene[42, 46] a reaction scheme based on the insertion of carbon atoms into C=C and C–H bonds was adequate to account for a large variety of yield observations, including the source of minor products. Propylene formed from ethane was found to be nearly all terminal-carbon-labelled, consistent with the general belief that carbon atoms do not insert into carbon-carbon single bonds.[42] The expectation that molecules with more degrees of internal freedom would be better deactivators found support in this study. Inert-gas atoms were less efficient than ethylene molecules in deactivating the collision complex between a carbon atom and an ethylene molecule. Less of the simple insertion product, allene, and more of the electron rearrangement product, methyl acetylene, were found as concentration of inert gas increased.

A hypothesis based on assumed conservation of spin was presented that given electronic state species were the precursors of different products.[42, 46] Evidence was adduced to support this view. Allene and methylacetylene were said to arise from singlet carbon while the acetylene and five-carbon products were suggested to be coming from triplet carbon atoms. If acetylene and the C_5 products do come from the same triplet carbon-ethylene complex then trends in their yields should be complementary. Such behavior is indeed observed. Condensed phase and added moderator each increased the C_5 product yields and diminished the acetylene yields. These trends are

reasonable if, in the condensed state, the complex is stabilized by rapid energy loss, while in excess inert gas, the important effect is moderation of the excess energy of the free carbon atoms, so that the complexes formed are of lower initial energy. The effect of 4% added oxygen on product yields is also consistent with the proposed electronic state scheme. Oxygen is postulated to be of considerably lower reactivity towards singlet species as opposed to triplets. The added oxygen in these systems diminishes the yield of C_5 products but not that of allene or methylacetylene. The acetylene yield would not be expected to decrease since this compound arises from a complex which decomposes before it is deactivated collisionally and therefore before it can be scavenged by the oxygen. The formation of allene mostly as C_3H_4 and C_3D_4 from C_2H_4 and C_2D_4, respectively, indicates that carbon-hydrogen-bond rupture is not necessary to form the product.

Further support for the C–H bond insertion mechanism in the ethylene-carbon atom system was the detection of a 1.5% yield of vinyl cyclopropane,[46] a product to be expected from the addition of a vinyl carbene across the double bond of a second ethylene molecule.

Recently the state of hot atom chemists' understanding of the chemistry of carbon atoms and especially the role of the spin states therein has come into some doubt. This is the result of a large body of recent work by P. S. Skell and co-workers on thermal carbon atoms produced in carbon arcs. The atoms are deposited on paraffin hydrocarbon surfaces at -196°C after evaporation from the electric arc in a vacuum. Substrates are condensed onto the surface during or after carbon deposition. A considerable volume of work is consistent

with the reaction scheme evolved. Except for some C_3 species, ^3P, ^1S, and ^1D carbons are the only states of the atom to reach the wall (the others having lifetimes short compared with the time of flight from the arc to the wall). The excited species decay according to

$$^1S \longrightarrow {}^1D \; ; \; \tau_{\frac{1}{2}} = 2 \text{ sec}$$

$$^1D \longrightarrow {}^3P \; ; \; \tau_{\frac{1}{2}} = 15 \text{ sec}$$

inferred from the dependence of yields on the time elapsed between deposition of the carbon and reaction with the substrate.

The ^3P carbon reacts entirely by the consecutive insertions into the double bonds of two olefin substrate molecules, the first insertion being stereospecific, the second not. The products of these reactions are spiropentane and its derivatives.[51] Both the ^3P carbon and the cyclopropylidine intermediate formed by its addition to a C=C bond are selective reagents: relative rates for their reaction with various olefins vary as much as 32:1.[53] The ^1D and ^1S may also react by successive insertions to form spiropentanes from olefins, both insertions being stereospecific. The ^1S has the additional reaction mode of insertion into double bonds to form allene analogs[51]

$$C\ (^1S) + \diagup C{=}C \diagdown \longrightarrow \diagup C{=}C{=}C \diagdown$$

Of the three atomic species, only the ^1S is capable of insertion into C–H bonds. The ^1D and ^3P forms show no reactivity towards saturated hydrocarbons.[55] Moreover, even the ^1S carbons are unreactive towards the compounds neopentane and cyclohexane at temperatures at which they react with lower-melting saturates. The three types of primary products from the ^1S insertions into C–H bonds in alkanes are (1) cyclopropane derivatives resulting from an initial

insertion of the carbon followed by a second internal insertion into a C–H bond of the β-carbon, (2) olefins (C_{n+1}, where the substrate is C_n) resulting from hydrogen migration in the carbene intermediates, (3) saturated hydrocarbons (also C_{n+1}) arising via hydrogen abstraction from the medium by the intermediate.[58] Most significantly, acetylene has never been detected as a product from the reaction of arc-generated carbon atoms with any hydrocarbon substrate.

Notwithstanding that these results are from condensed phases (thermal decomposition in the arc seems to preclude gas phase experiments), the contrast with the recoil carbon work is obvious. A slight common ground between arc and recoil carbon results lies in Wolfgang's observation of several percent yields of possible spiropentanes from 2-butenes and, in one case, to reduce acetylene yields to about 1% in condensed phase under the most extreme moderation conditions.[60]

The obvious possibility must still be entertained that a complex involving the matrix is acting as the carbon atom donor in the condensed phase arc experiments. Indeed, the ^1S reactions in which C–H insertion does occur are observed by evaporating the substrate onto the previously deposited carbon. Wolfgang has suggested that reliable results from arc evaporated carbon may be contingent on working at ultrahigh vacuum,[59] since modification or complexing of reactive species on surfaces is known to occur otherwise.[85] Also, if the thermal carbon atom does not possess the very high reactivity postulated, then the very low temperatures at which the arc carbon reactions were studied may account for the differing results. A firm basis for a rapprochement of the two bodies of data is still needed.

Since it had been demonstrated that carbon atom-substrate molecule adducts exist long enough to be stabilized by collision, the possible influence of bond energy on the production of fragmentation products was of some interest. The effect on acetylene production in systems of alkyl halides and propane was investigated by Ache and Wolf.[18] In an elegant piece of research using the double tracer technique, acetylene production from the methylene group in CH_3-CH_2-X ($X = CF_3-$, CH_3-, F–, Cl–, Br–, I–) molecules was compared with the strength of the CH_2-X bond. This bond must be broken to form acetylene from the methylene group in the reaction scheme by which acetylene proceeds from the carbon atom insertion into C–H bonds. Therefore, the strength of the bond to be broken might be expected to influence the acetylene production. Indeed, the fraction of acetylene produced from the methylene group was found to stand in inverse proportion to the C–X bond dissociation energy.

The influence of bond energy on hot yields was first observed in hot tritium systems for the production of HT from a variety of hydrocarbons.[86] That bond energy should also play a role in carbon atom systems was by no means obvious, since the carbon systems are much more complex – having, for example, many more possible modes of reaction for a given intermediate.

A number of studies of the reactions of carbon atoms in liquid hydrocarbons by Voigt and co-workers have appeared.[84,87,88,89] This work is related to gas phase studies, but important distinctions must also be borne in mind. Solvent cage effects are instrumental in the explanations of observed yield trends.[89] In the most comprehensive of these studies, Clark and Voigt[89] report some interesting findings.

Most notably they present formulas giving as a function of structure of the substrate (1) the combined percentage yield of ethane and ethylene and (2) the fraction of the total C_2 product yield in the form of these two compounds. For the first of these, for example, the relationship is $\%(C_2H_6 + C_2H_4) = Ax + By + Cz$, where x, y, and z are the fractional amounts of hydrogen in the $-CH_3$, $-CH_2$, and $-CH$ groups of the particular substrate molecule. The coefficients A, B, and C are empirically derived from the actual ethane plus ethylene yields from liquid ethane, cyclohexane, and benzene, respectively. Values calculated from the relationship for 15 hydrocarbons agree reasonably well with the experimental yields from the substrates. The substantive result of the structural study is that the amount of hydrogen available at the site of the carbon atom insertion determines the degree of unsaturation of the C_2 product which may be formed. It was also observed that variation of yields with dose is slow below about 5×10^{-2} eV/molecule (with virtual independence when scavenger was present). Indications were found that a small part of the ethylene and ethane yields arose from the radiation induced reduction of acetylene. This was consistent with a seeming slight increase of ethane yields at higher doses. Another significant observation was that part of the ethane and ethylene yields were sensitive to added scavenger while none of the acetylene was. The relationship of these findings to results from the present study is discussed in section IV. Despite the apparent success of the structural formulas some care must be exercised in accepting the conclusions of the study. This is because application of the formulations depends on the assumption that the percentage of carbon atoms converted to methyne will be constant in all liquid hydrocarbons.

Other interesting work which has been done with hot carbon atoms includes the investigation of the reactions with the substrate cyclopentadiene[90] and numerous investigations of nitrogen-containing systems.

G. Analytical Techniques

For the short-lived ^{11}C nuclide only rapid analytical procedures are useful. It is not surprising therefore that radio-gas chromatography, i.e., on-stream radio assay of products separated by gas chromatography, is the general method in use. The idea of combining these two powerful techniques originated with Kokes et al.[91] Evans and Willard were the first to apply the combination to the analysis of products from recoil systems.[92] The method has been steadily refined and enlarged until today there may be found nearly every form of radioactivity sensor on chromatographs used in recoil studies. Some of the noteworthy advances have been the continued improvements in counter design,[93-95] and automation to supplement the endurance of the researcher.[96] Radio-gas chromatography has been the subject of a review by Cacace.[97]

One aspect of the domain which should be mentioned is economy of time and money. The short half-life of ^{11}C combined with the dearness of accelerator time makes every minute of analysis time precious. In ^{11}C work there is no leisurely repeated or long-term counting of activities. The researcher is usually forced to gain the maximum usable information from each experiment. A natural and inevitable consequence of this situation is that analytic results are on quite a different accuracy scale from, for example, ordinary gravimetric analyses. This is evident from readings of most reports of results on recoil ^{11}C systems.

II. EXPERIMENTAL

A. General Technique

The routine procedure for experiments was as follows. The irradiation vessel was filled on a vacuum line with the substrate, usually a mixture of hydrocarbon and oxygen. The sample was then irradiated with nuclear particles from a cyclotron or proton synchrotron. Analysis was by radio-gas chromatography, a technique in which the effluent of the gas chromatograph is passed through a flow-type radiation counter. Aliquots of the unseparated sample mixture were passed directly through the counter to determine the total volatile activity produced in a given irradiation. The activity detected as a given product in the chromatographic separation was then normalized and is expressed as a percentage of the total induced volatile activity.

B. Materials

The hydrocarbons employed were Phillips Petroleum Company research grade. Assays provided with the materials gave purities to be between 99.88 and 100.00 mole percent. The average purity

was 99.95%. All hydrocarbons except methane were repeatedly recrystallized under vacuum before use. The oxygen was Matheson Company prepurified grade and was used without additional purification.

C. Preparation of Samples

Samples were prepared on a vacuum line. The following technique was used for the samples of the butanes plus oxygen and for most of the samples of other hydrocarbons plus 4.5% oxygen. Irradiation vessels were attached to a section of the line along with a bulb of the hydrocarbon gas, a bulb of oxygen (or oxygen-hydrocarbon as described below), and a small condensation bulb. After re-establishment of a suitable vacuum ($\sim 10^{-4}$ torr) the desired pressure of oxygen was admitted to the irradiation vessel. For samples with a high percentage of oxygen a Töpler pump was sometimes used to raise the pressure. The irradiation vessel was then shut and the line pumped down again. Hydrocarbon gas was then admitted to the line and condensed into the small vessel using liquid nitrogen. After closing off the hydrocarbon source bulb, the hydrocarbon was gradually warmed. When the hydrocarbon pressure exceeded that of the oxygen in the irradiation vessel, the latter was opened and the expansion continued to ambient atmospheric pressure as read on a mercury manometer. Since hydrocarbon was flowing into the irradiation vessel continuously, there

was no opportunity for the oxygen to diffuse out.

Samples with a low percentage oxygen ($\frac{1}{2}$% to 2%) were prepared by first making up a nine-to-one hydrocarbon-to-oxygen mixture. By using a pressure of this mixture ten times the desired pressure of oxygen, manometer registering and reading errors were minimized. For low percentage oxygen runs the line was flushed repeatedly with each material prior to its admission to the irradiation vessel. For neat hydrocarbon runs both the line and the irradiation vessel were flushed.

Eight of the hydrocarbons in the 4.5% oxygen series have vapor pressures below one atmosphere at room temperature. Five of these – normal, iso-, and cyclopentane, 2,3 dimethylbutane, and 2,2 dimethylbutane – were run at reduced total pressures (between 190 and 574 torr), since sufficient activity for analysis could be obtained from the smaller samples. Sample preparation was as described above except that total pressures of the samples were less than one atmosphere. At the lower vapor pressures of the heavier hydrocarbons, the amount of material obtainable in the gas phase at room temperature was insufficient. Consequently samples of these materials (n-hexane, n-heptane, and 2 methylpentane, all with 4.5% oxygen) were irradiated at temperatures around 100°C. The technique is described in section II F.

D. Irradiations

Irradiations were performed by the Brookhaven National Laboratory sixty-inch cyclotron and the Brookhaven National Laboratory Cosmotron.

For cyclotron runs a water-cooled lithium hydride target (Figure 8) was placed against the beam port and the irradiation vessel

LEGEND FOR FIGURE 8

A Aluminum Retainer Plate

B Aluminum Middle Plate with Trough for Lithium Hydride

C Brass Cooling Back

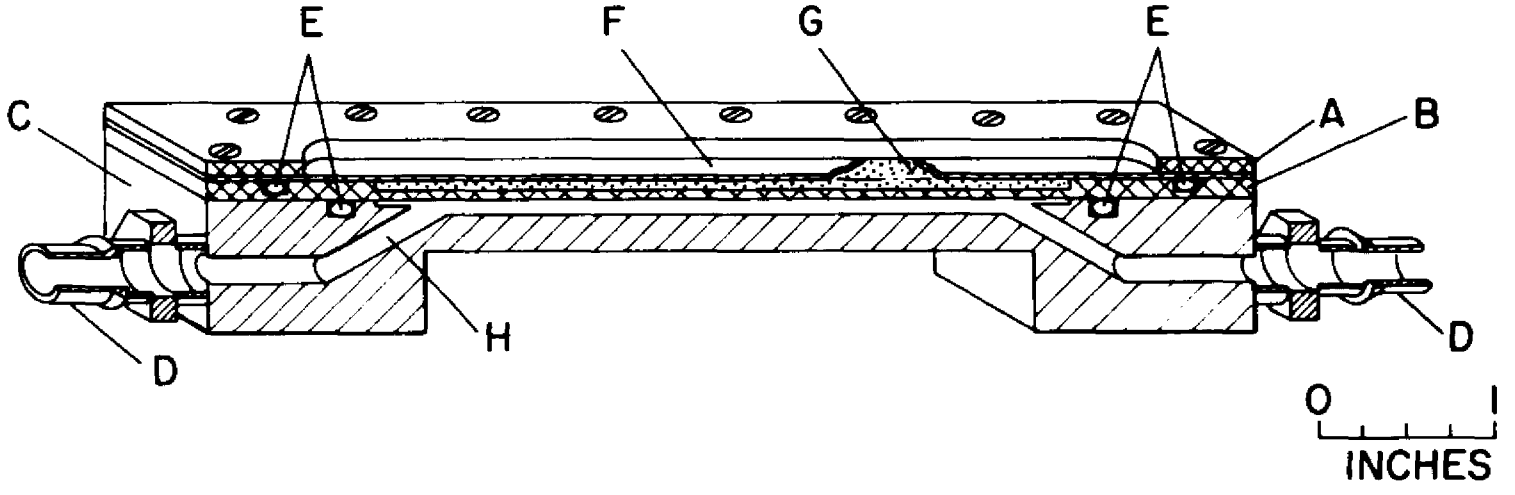
D High Pressure Quick-Disconnect Fittings for Water Coolant

E O-Ring Seals

F Aluminum Foil, 2 mil

G Lithium Hydride in Trough

H Channel for Water Coolant



LITHIUM HYDRIDE CYCLOTRON TARGET

FIG. 8

behind and against the target. $20\frac{1}{2}$ MeV deuterons from the machine impinging on the target produce fast neutrons by the $^{7}Li(d,n)$ reaction. Standard bombardments were 40 μA hr of deuterons (current 60 μA, irradiation 40 minutes).

At the Cosmotron, samples were bombarded for 40 minute periods at rates between 2.5 and 4.6 sec/pulse. The energies of the protons were between 1 and 3 GeV for different bombardments. Cross section of the $^{12}C(p,pn)^{11}C$ process is rather insensitive to proton energy in this region. The maximum available intensity of the Cosmotron was always used – about 10^{11} to 10^{12} protons/pulse in the external beam. Integrated external flux ranged from 1.06×10^{13} to 7.08×10^{13} protons.

Cyclotron irradiations produced of the order of 10^{4} and Cosmotron irradiations of the order of 10^{5} disintegrations per minute per cc of sample gas at N. T. P. at the end of the irradiation. Where hydrocarbon-oxygen substrate mixtures were as high as 90% oxygen, only the proton-induced process gave activities adequate for accurate analysis. This is due to the additional ^{11}C production from the oxygen by the $^{16}O(p,pn\alpha)^{11}C$ process, which has a cross section about 0.4 times as great as the ^{12}C process at the energies used.[13]

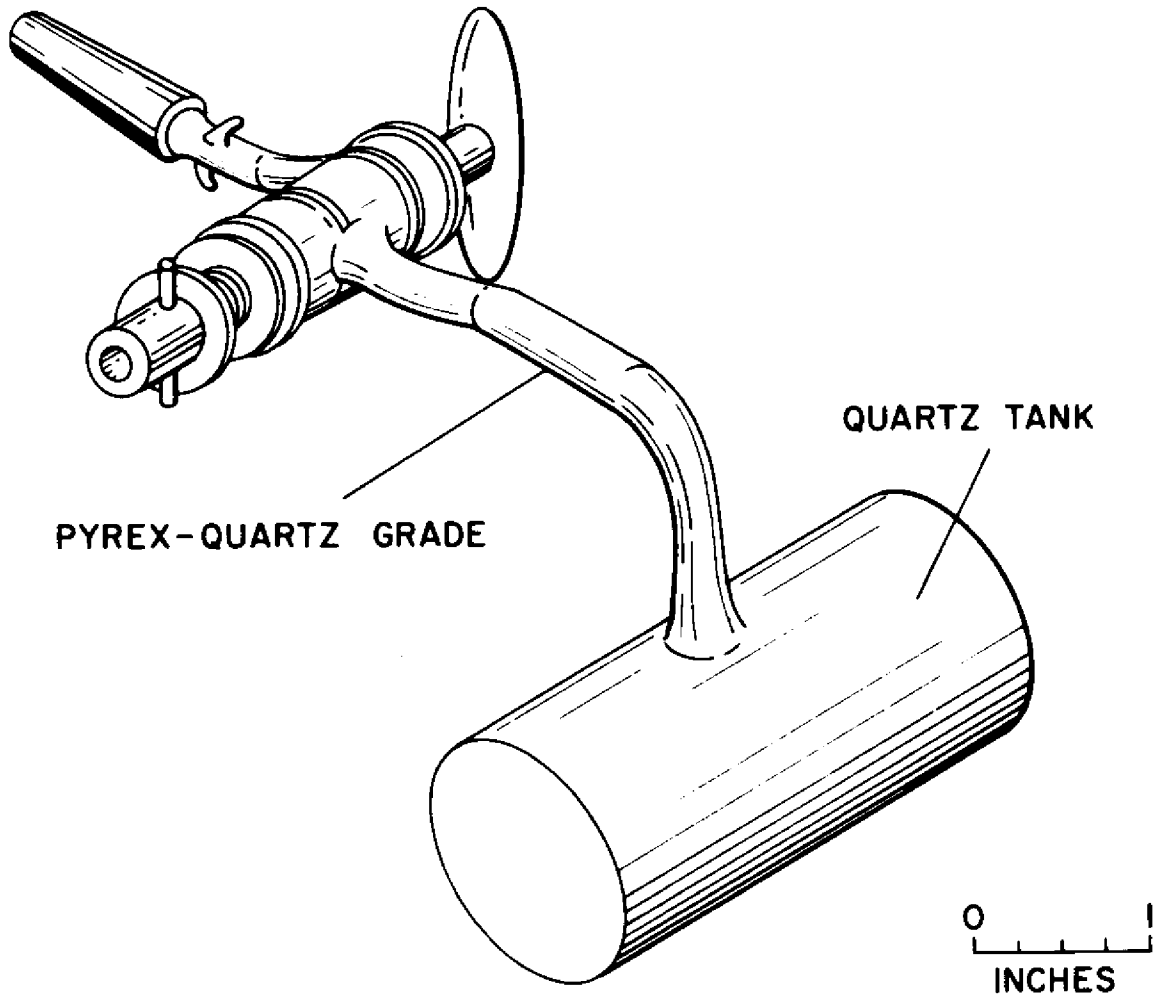
Under the worst experimental conditions encountered, which existed in only a handful of measurements, between 100 and 200 counts registered above a background of about 40 counts. The average, however, was several thousand counts, most counts in the range from the upper hundreds to the middle thousands.

Cosmotron tanks were aligned with the proton beam using Polaroid films placed in front of and behind the tank holder. Proton bursts

at 1/100th normal operating intensity exposed the film. The location of the tank with respect to the beam could be judged from the position of the beam spot with respect to a tank reference mark made on the front film in advance. The alignment of the tanks in the beam was revealed by the shadow of the tank walls and tank holder on the rear film. Successive pictures were taken and adjustments made until the position and alignment were deemed satisfactory. The tank holder rested on a jack mounted on a machine table. The combination table-jack provided all adjustments necessary for positioning and alignment without the need for direct manipulation of the holder.

E. Dosimetry

Measurements were made at the cyclotron of the radiation dose accompanying a bombardment. A standard cyclotron irradiation vessel (Figure 9) was filled with an improved Fricke dosimeter solution described by Weiss et al.[98] The tank was positioned as usual in the cyclotron beam and given one-third the usual bombardment. At this dose, the response of the dosimeter is still linear.[99] Absorption of the solution at 305 mμ was measured with a Beckman model DU-2 spectrophotometer immediately before and promptly after the irradiation, giving $\lambda = 0.054$ and $\lambda = 2.24$, respectively. A second experiment was made in which the irradiated solution was diluted one to ten before taking the absorption, to bring the reading onto a sensitive range of the spectrophotometer. Allowing for the dilution, values for λ before and after irradiation were 0.43 and 2.64, respectively. The dose in rads was calculated directly from the absorption readings,[100] giving the values 6.13×10^4 r and 6.19×10^4 r, equal to 3.83×10^{18}



CYCLOTRON IRRADIATION VESSEL

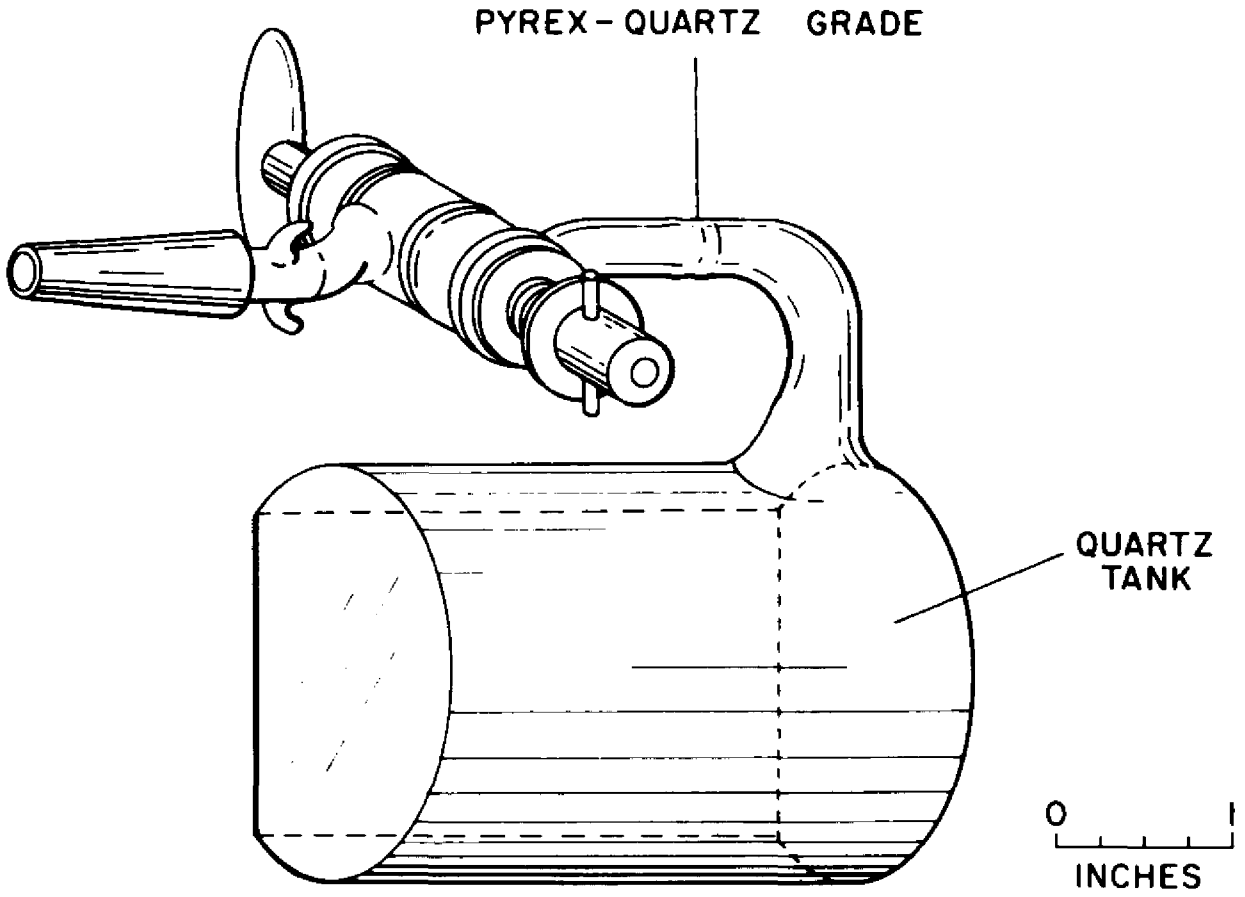
FIG. 9

eV/g and 3.86×10^{18} eV/g, respectively. The absorbed dose per molecule will depend on the number of molecules per gram of the substrate. Here are some values: for 100% butane, 1.11×10^{-3} eV/molecule; for 100% oxygen, 6.13×10^{-4} eV/molecule; values for mixtures of intermediate composition may be interpolated. For a 95.5% heptane-4.5% oxygen mixture, 1.86×10^{-3} eV/molecule; for a methane-oxygen mixture of the same proportions, 3.21×10^{-4} eV/molecule.

F. Irradiation Vessels

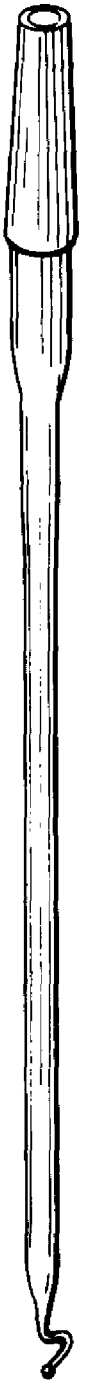
Vessels for the irradiations were designed to suit requirements of the sample and bombardment. Most irradiations at the cyclotron were performed with cylindrical vessels (Figure 9). Vessels designed to bring more of the sample closer to the lithium target were tried (Figure 10) but the design modification failed to improve the specific activity. The bodies of the cyclotron vessels were made of quartz to minimize radiation to personnel after bombardments. (Pyrex becomes very active because of the creation of ^{24}Na.)

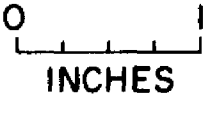
For the irradiation of higher-molecular-weight hydrocarbons, a technique was devised to get sufficient material into the vapor phase to produce workable activities. Thin-walled ampoules were made by closing one end of a 5 mm o.d. tube and immersing it to a depth of about 10 cm in hydrofluoric acid solution until about 1/3 of the wall thickness had dissolved. The unetched end was joined to a 10/30 male ground joint (Figure 11), and the closed end pulled into a hook-type break tip with a width no greater than the diameter of the tube. The piece was then weighed on an analytical balance. After attaching the tube to the vacuum line, hydrocarbon was condensed into the tube at ice temperature and the ampoule quickly sealed off with a needle flame, with



REDESIGNED CYCLOTRON IRRADIATION VESSEL

FIG. 10

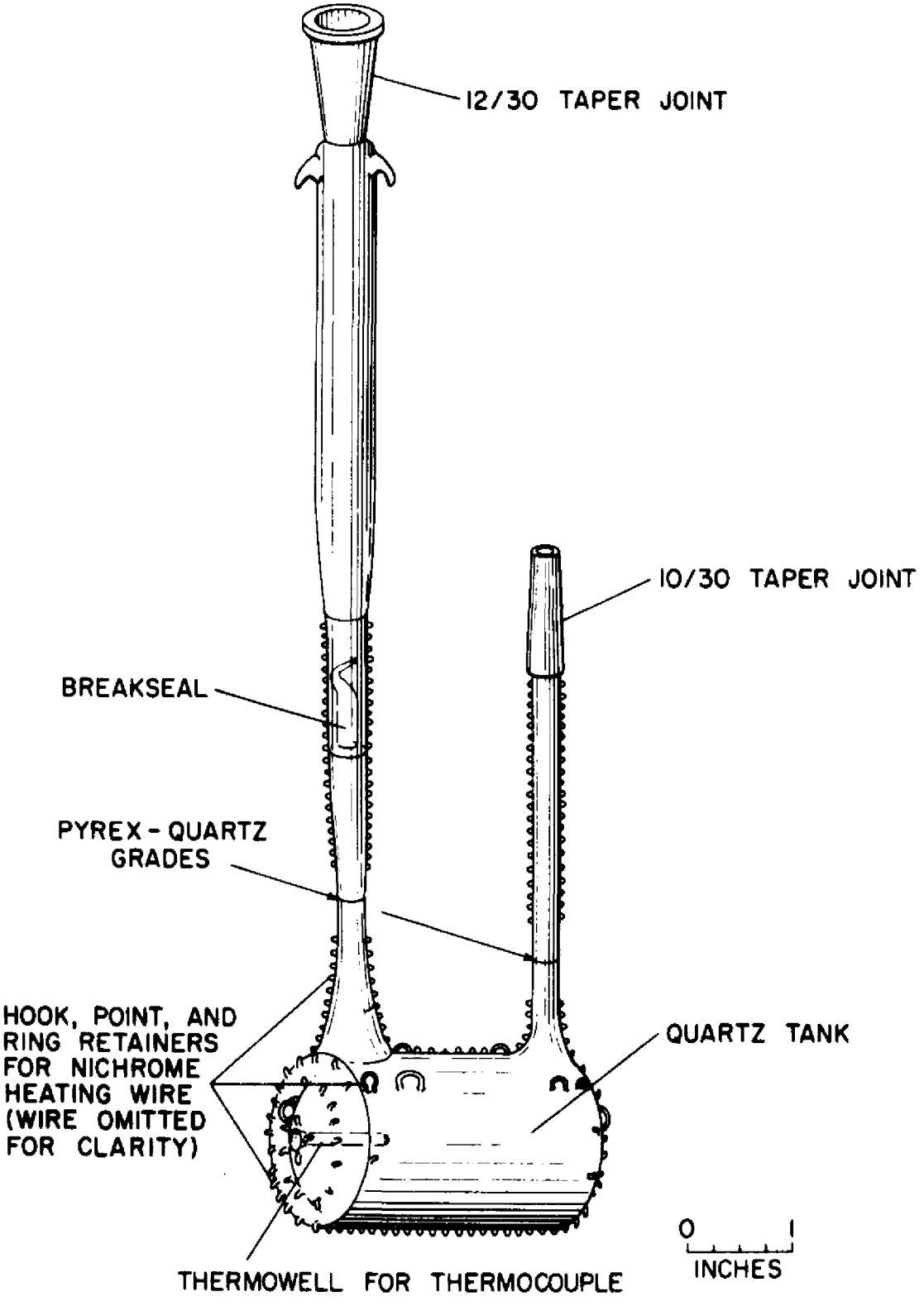




THIN - WALLED AMPOULE
FIG. 11

the sample kept chilled. By allowing the ampoule to drop under its own weight during sealing, connection to the upper tube could be reduced to a fine thread. The thread was then broken with no loss of glass and the two pieces cleaned and weighed. Weight of the hydrocarbon in the ampoule was then known by difference. Weighing the ampoule without the joint piece gave by difference the mass of the Pyrex which, with the density, yielded the volume of the Pyrex in the ampoule. The total volume of the ampoule was next determined by displacement of water in a 10 ml. graduated cylinder. The volumes of the ampoule and the Pyrex were used later to correct for the internal volume of the irradiation vessel and the free volume within the vessel after breaking the ampoule.

Now the ampoule was gently lowered into an irradiation vessel of special design (Figure 12). The glass was drawn to a narrow neck just below the 12/30 male joint. The internal volume of the vessel was measured by gas expansion. Now, making allowances for the volume above the constriction and the free volume increase upon breaking the ampoule, the room-temperature pressure of oxygen needed in the vessel was calculated so that after sealing at the constriction, breaking the ampoule and heating to 100°C, gas in the ampoule would be 4.5% oxygen. The oxygen was added and the sealing accomplished quickly, the point just below the constriction being covered with a wet asbestos strip during the heating. The cell was then wound with Nichrome wire on all surfaces. In position at the cyclotron, the cell was heated to 100°C (measured with a thermocouple in the thermowell) by passing alternating current through the Nichrome wire, and kept at this temperature throughout the irradiation. After bombardment, samples were removed via the breakseal.



HEATED CYCLOTRON IRRADIATION VESSEL

FIG. 12

Irradiation vessels for the Cosmotron runs (Figure 13) were fabricated of 2S aluminum. Since the proton beam is practically unattenuated by passage through the vessel, several vessels could be irradiated simultaneously. A vessel holder served to maintain alignment with the beam. A specially designed vessel incorporating its own jump target for 1 GeV protons was made for use in the internal beam of the machine (Figure 14). (A jump target is a block of metal to intercept the circulating proton beam. The thickness is calculated to deflect or "jump" the beam so that its next circulation carries it through the target.) The target also carries a foil which serves the purpose of the Polaroid film in the external beam irradiations.

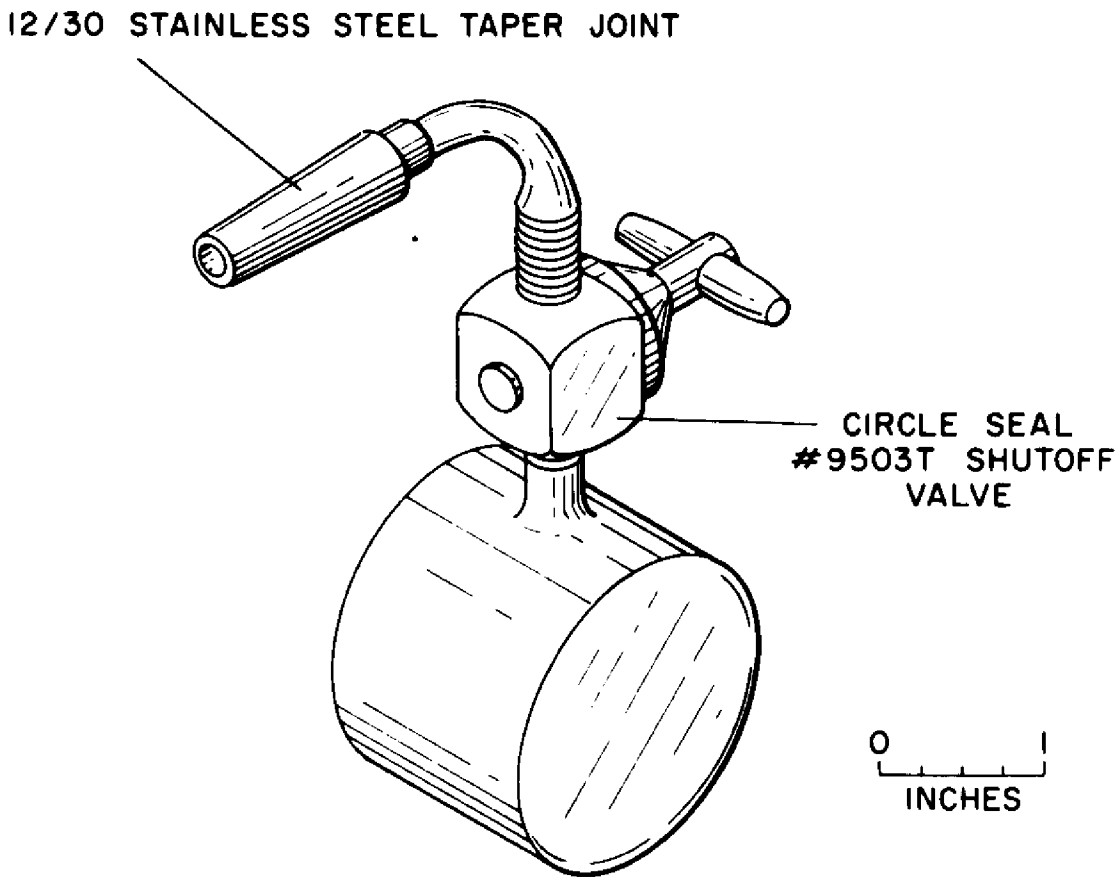
Since this target was designed for insertion into the Cosmotron internal vacuum on a fixed-position ram, valuable time could be saved by the elimination of repeated alignments. Ends of this irradiation vessel were cupped rather than flat to withstand the external vacuum.

All irradiation vessels and their valves were leak tested with helium before being put into service.

G. Analyses

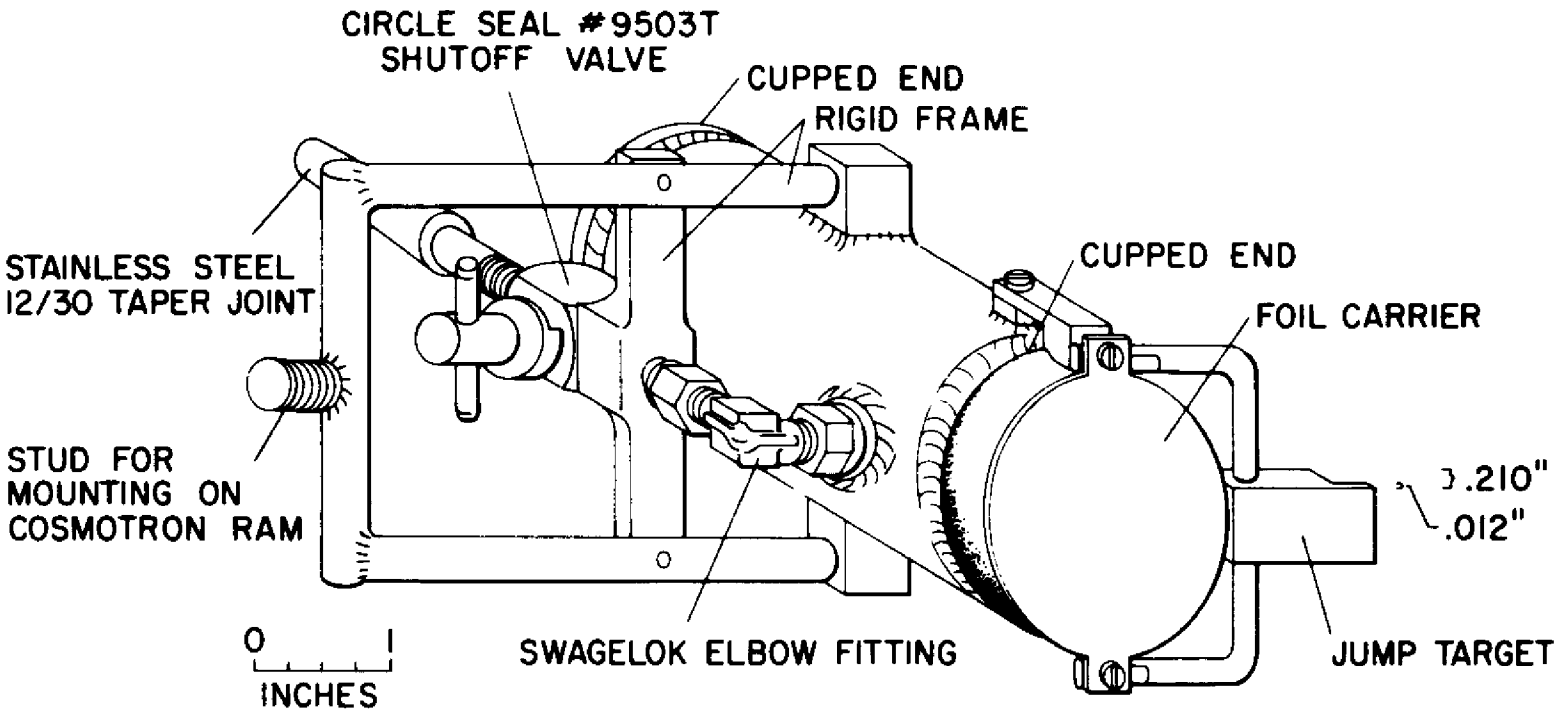
As soon after irradiation as possible the target vessel was attached to the vacuum line and the sample pumped with a Töpler pump into five aliquot U-traps of known volume (Figure 15) which had previously been filled to several torr pressure with a carrier gas. The carrier gas was a mixture of approximately equal parts of the substances to be analyzed for – usually carbon monoxide, ethylene, and acetylene, and sometimes methane and propylene in addition.

The aliquots were analyzed at room temperature with gas-liquid chromatographic columns of silicone and carbon. The silicone column



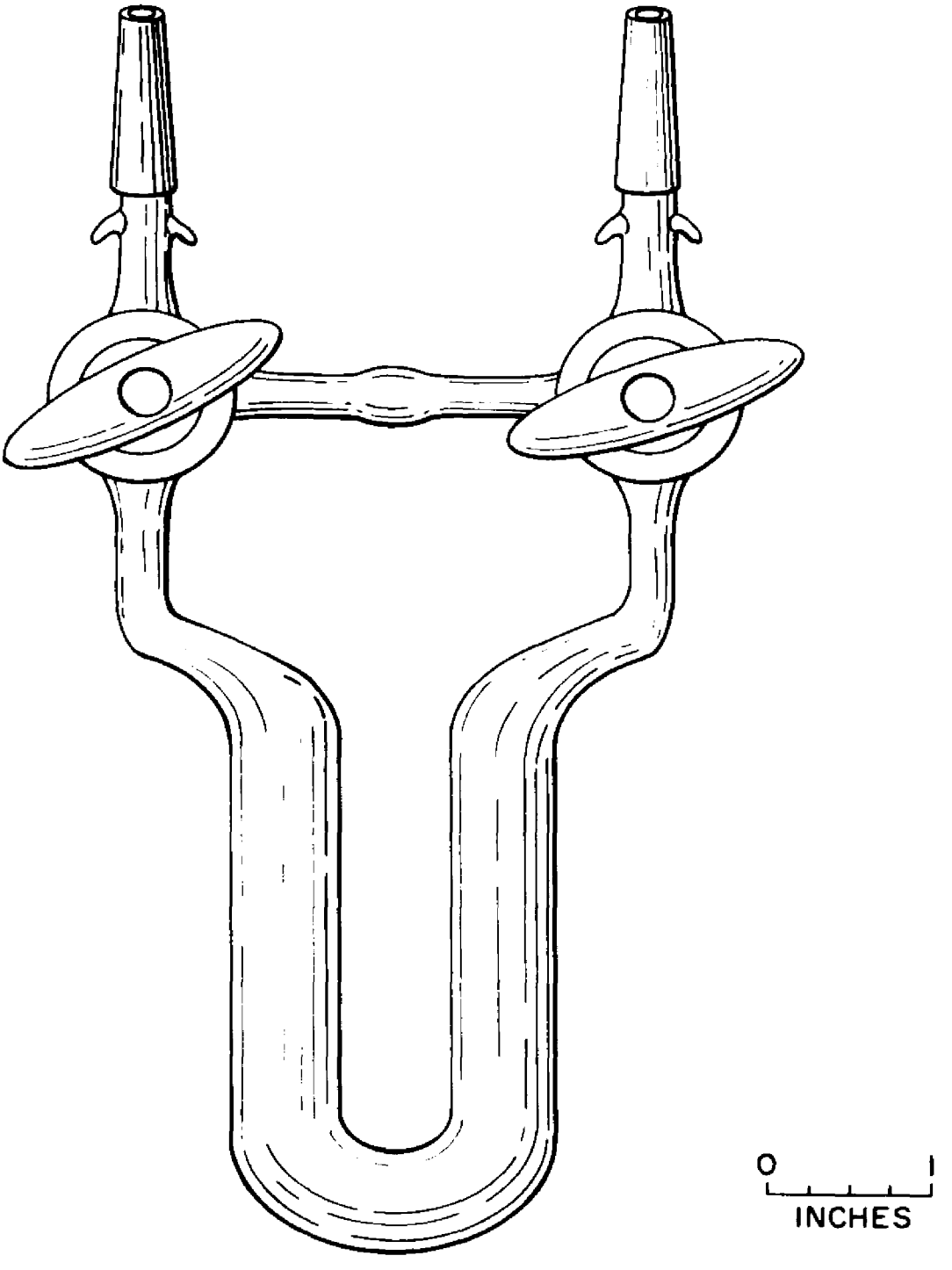
COSMOTRON IRRADIATION VESSEL
FOR EXTERNAL BEAM

FIG. 13



COSMOTRON IRRADIATION VESSEL
FOR INTERNAL BEAM

FIG. 14



ALIQUOT U-TRAP

FIG. 15

(445¼ cm × 5 mm i.d., 2½% Dow Corning Silicone 550 on activated alumina, Burrell Corp.) separated carbon monoxide, ethylene, ethane, acetylene, and propylene. The carbon column (197½ cm × 5 mm i.d., Activated Carbon, 40-60 mesh, Columbia Carbon Corp.) was used to separate carbon monoxide from methane. As the peaks emerged from the column they passed through first a thermal-conductivity detector and then a 4π sandwich-type flow counter. High voltage was provided by an Atomic Instrument Co. model 1091 supply, modified. The scaler was a Hewlett-Packard model 5532A electronic counter. Output from the scaler combined with output from a Hewlett-Packard model HO3 571B digital clock was fed to a printer (a Hewlett-Packard model H24 562A digital recorder) which every ten seconds printed out time elapsed since the end of the bombardment and the counts accumulated over the ten-second period. The flow rate through the counter was measured with a soap bubble flowmeter and stopwatch, during the passage of the peak through the counter, and recorded manually on the printed tape.

After the chromatographic analysis the remaining aliquots were flushed through the system bypassing the columns and directly through the thermal conductivity cell, counter, and flowmeter. These "bypasses" measured the total induced ^{11}C volatile activity and allow activities in each compound to be expressed as percentage of the total. Previous measurements have indicated that 95-100% of the total induced activity is recovered in the gas phase from gas phase saturated substrates.[19,20,73] Switching between columns and from column to bypass was accomplished using a gas manifold system.

H. The Counters

The proportional counter was of a type previously described[93] (Figure 16). In early experiments activity tailed badly as it passed through the counter. This was traced to the design of the Teflon insert first used (Figure 17). Since part of the Mylar sheet which serves as the window was supported on one side (by the Teflon) but not on the other, any slight increase in pressure would flex the Mylar into the counting chambers creating slit pockets between the Teflon and the Mylar. Entrapment of activity in these pockets was responsible for the observed tailing. This problem was solved by redesigning the insert (Figure 18). One case of erroneously high results was traced to slight wrinkles in the Mylar sheet. Subsequently the Mylar was stretched taut on an embroidery hoop during vacuum evaporation of the gold films on the Mylar and during assembly of the counter. In a very few experiments, a cylindrical proportional counter was used for comparison purposes.

J. Calculations

Yield percentages were calculated by totaling the counts over the passage of a given peak; correcting for background, radioactive decay, flow rate through the counter, and sample size; and dividing the resultant counts by the similarly adjusted average bypass counts.

The raw data appear printed on a paper tape. Figure 19 is a sample section of the data tape produced during the passage of two activity peaks through the counter. The section shown records the passage of ^{11}C-carbon monoxide and ^{11}C-ethylene in run 139/L. The substrate was 95.5% isopentane and 4.5% oxygen at room temperature. On the tape the six left-hand columns are the time, the two left-most columns being the hours, the next two the minutes, and the next two

LEGEND FOR FIGURE 16

A Teflon Insert

B Mylar Foils, $\frac{1}{4}$ mil with Evaporated Gold Film

C Center Wires

D Counting Chamber Blocks, Chromium-Plated Brass

E Counting Gas (P-10) Inlets

F Counting Gas Outlets

G Sample Gas Inlet, Burrell-Type Connectors

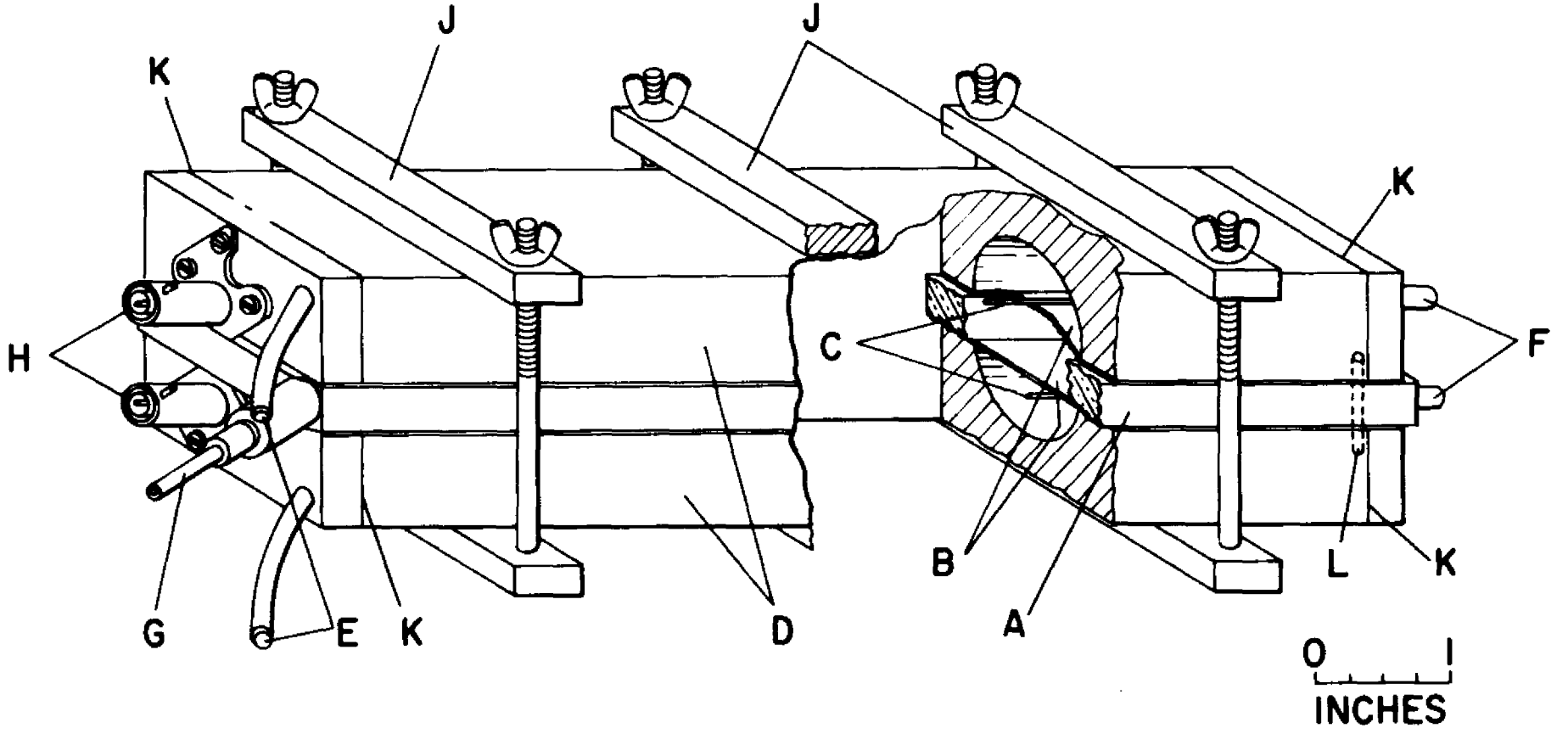
H Electrical Connectors for High Voltage and Signal

J Clamps

K Silver Solder Joints

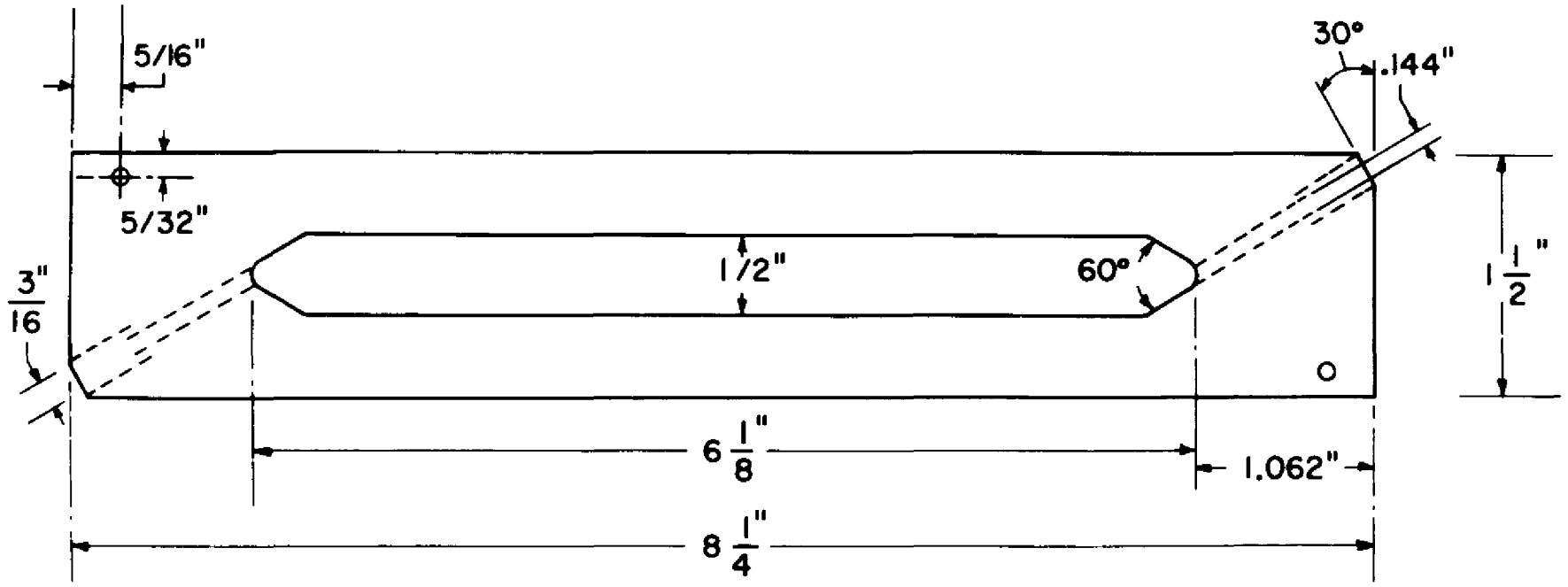
L Alignment Pin

Not Shown: Sample Gas Outlet-Located Diametrically Opposite Inlet



SANDWICH FLOW COUNTER

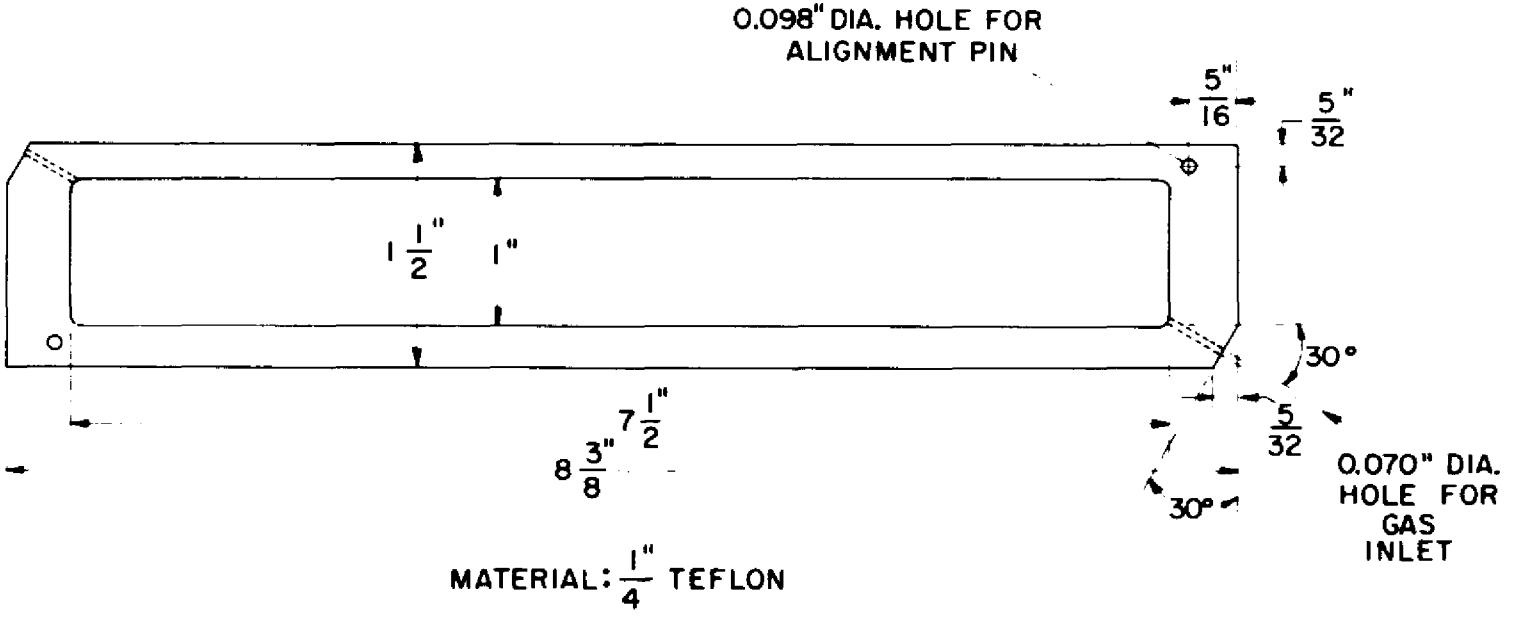
FIG. 16



MATERIAL : $\frac{3}{4}$" TEFLON

TEFLON INSERT FOR FLOW COUNTER

FIG. 17



REDESIGNED INSERT FOR GAS FLOW COUNTER

FIG. 18

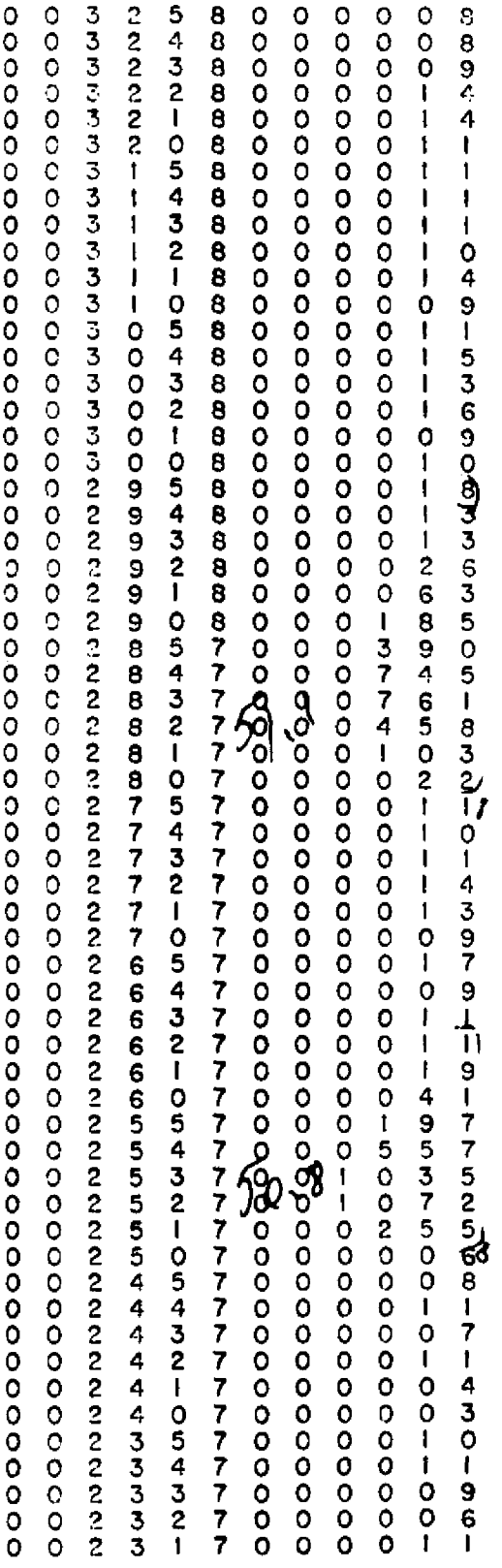


FIGURE 19

SECTION OF DATA TAPE FROM RUN 139/L

the seconds. The remaining six columns represent the number of counts from hundreds of thousands to units.

A sample calculation is as follows. The ^{11}C-carbon monoxide peak is seen starting with the printout at 25 minutes 17 seconds. The limit of the peak is judged to be 26 minutes 27 seconds. The background averaged over 100 seconds prior to emergence of the peak is 8 counts per 10 second period. A typical treatment of these data is shown in Table 3. The sum of the counts in the peak (3187, column 1) is corrected for background by subtraction of (8 counts/10 sec) × (80 sec) = 64 counts, giving net counts due to radioactive carbon monoxide, column 2. The approximate time of the highest count rate is entered in column three. Decay correction factors for ^{11}C were calculated at the BNL computer center yielding a table of values of e^{-kt} every ten seconds from t = 0 to t = 2 hours and 50 seconds. For 25 minutes and 30 seconds, $N/N_o = e^{-kt} = 0.4204_5$, and this divided into 3123 gives 7428 as the number of counts at t_o. The number 50.8, handwritten on the data tape and appearing in column 5 represents the number of seconds required for passage of 80 ml. of gas through the system, measured by the soap bubble flowmeter during passage of the activity peak through the counter. For purposes of comparison of separate runs the number of counts is now adjusted to a standard arbitrary flow rate of 41.6 sec/100 ml by multiplying by 41.6/(50.8)(1.25). The result, 4866, appears in column 6. Next the sample size is calculated by multiplying the volume of the aliquot trap used for this analysis (29.97 ml) by the pressure in the trap ($250\frac{1}{2}$/760 atm). The result, 9.878 ml atm, is divided into the result in column 6 to give 492.6, the number of counts at t_o per ml atm at standard flow.

TABLE 3

SAMPLE CALCULATION OF RESULTS

Total Counts	Counts minus background	Time of maximum Count rate (min : sec)	Counts at t_o	flow rate during passage of peak (sec /80 ml)	t_o counts at standard flow	t_o counts per cc^o atmosphere at std flow	% of total induced volatile activity	Compound
3187	3123	25 : 30	7428	50.8	4866	492.6	18.3	CO

The same treatment of the data for each bypass aliquot gives the three values, 2726, 2640, and 2691 (same units). The average of these numbers, 2686, representing the total induced volatile activity, is used to divide 492.6, representing activity as carbon monoxide, to give the result, 18.3% of the total induced volatile activity.

K. Recovery

The fraction of the total induced activity recovered in the gas phase was measured. Polyethylene foils were affixed to the front and rear of some of the tanks irradiated at the Cosmotron. After the irradiation these foils were counted in a well counter of the sodium iodide crystal type, and the observed disintegrations per minute per milligram carbon were corrected for activity losses.[101] The result was compared with that from a sample of the irradiated gas static-counted in an internal counter. The average recovery in 26 measurements on systems of the butanes and neopentane, each with oxygen, was 83% (average deviation: 5%). This agrees well with the measurement of Ache and Wolf, who obtained 80% recovery in the gas phase from ethane at 1 atmosphere after the $^{12}C(p, pn)^{11}C$ reaction.[19] For the present study, a correction was made for ^{11}C production in the oxygen-containing samples using 0.44 as the ratio of production from ^{16}O to production from ^{12}C (see Table 1).[13] There was no evidence of a trend in the gas phase recovery related to the percentage of oxygen present in the sample over the entire range studied.

L. Error Analysis

Errors in a given datum in these experiments may arise either in the course of the analytical measurement or from uncertainties

about actual composition of the sample. This section is accordingly divided into sections on errors associated with sample composition and errors stemming from the analytical measurements performed.

Owing to the differences in volatility of different substrates, various techniques were used in the preparation of different samples. As a consequence of the differences in procedure no standard errors can be established for the sample preparation step. For another reason, standard errors may not be attached to the experimental measurements either. The error inherent in a radioactivity assay depends on the amount of activity being measured and the relative background. Larger errors are naturally associated with the measurement of the smaller quantities. This fact is responsible for a trend of increase in relative error for series with diminishing carbon content, for example, the series of butanes as one goes from 0% to 100% added oxygen and the series of hydrocarbon plus 4.5% added oxygen as one goes from seven carbons to one. Short of evaluating the error for every measurement individually, the best that can be done is to evaluate the varying errors at the extremes of the scale. It should be noted that a direct interpolation for errors at the intermediate points is not justified. A lower beam intensity during a particular irradiation, or the late counting of a sample, may diminish the number of counts from a given sample to less than that from another sample of lower carbon content.

1. Errors Stemming From Sample Composition Uncertainty

Rapid catalytic or inhibitory reactions by minute traces of organic impurities in the hydrocarbons are not to be expected in hot atom systems. Consequently, impurities at the levels of those in the

hydrocarbon (0.12% maximum) are not expected to contribute detectable errors.

Traces of oxygen in neat hydrocarbon samples are known to influence product distributions considerably, carbon monoxide appearing in considerable yield, and methane rapidly disappearing.[20] In the present work, whenever carbon monoxide from neat hydrocarbons was assayed, the yields indicated that insufficient oxygen was present to alter the yield distribution. Since small percentages of oxygen do strongly affect the yield pattern, giving rise to carbon monoxide, the 0.4% maximum impurities in the oxygen can certainly not give rise to detectable effects.

a. Heated cell samples. The gravimetric measurements made for the heated cell experiments introduced errors below the 0.1% level. The necessity of estimating the volume above the seal-off point for these cells introduced a larger error. Measurements of the volumes of the stubs left after sealing indicated a leeway of ±0.4 ml which, compared to the ~80 ml internal volume of the cell introduces a latitude of ±0.5% in the final composition of the hydrocarbon-oxygen mixture.

Strictly, curves of yield versus percent added oxygen for each of the compounds studied would be necessary for accurate assessment of errors in results introduced by sample composition uncertainty. However, in the absence of the graphs a reasonable approximation is to use the curves obtained for the butanes to convert the composition uncertainty to an error limit on the results.

For carbon monoxide yields the slopes of percent ^{11}CO versus percent added oxygen are very close to 2/3 over most of the range.

Thus a latitude in sample composition of ±0.5% added oxygen means that the ^{11}CO yield measurement can be no better than ±0.3% because of composition uncertainty. The rate of fall-off of the acetylene and ethylene yields over most of the range of the graph is between -0.1 and -0.2. Again taking the worst condition, a -0.2 slope means a ±0.1% latitude in the ethylene and acetylene yield figures.

b. Unheated samples. The mercury manometer used for pressure measurements in filling room-temperature samples could always be read to ±1 mm or better. Inexact coincidence in closing a valve at the moment total sample pressure reached one atmosphere during expansion of the hydrocarbon gases could have produced a ±5 mm maximum error including the reading error. The expansion for the samples run below one atmosphere total pressure was always slower, and the reading was on a physically more accessible part of the manometer. Estimated latitude for the hydrocarbon pressure of these samples is ±3 mm including the reading error. For the substrate run at the lowest pressure, 2,3-dimethylbutane, the total pressure was 190 torr. If instead of the desired $181\frac{1}{2}/190$, the hydrocarbon was actually $184\frac{1}{2}/193$ of the total sample, the composition will be 95.6% hydrocarbon, only 0.1% off. If, however, the oxygen pressure reading is high by 1 torr and simultaneously the maximum error on hydrocarbon pressure is made, the sample may be $7\frac{1}{2}/194$ or 3.9% oxygen and 96.1% hydrocarbon. This means the composition is known to ±0.6% for these samples. The greater error of ±5 torr hydrocarbon pressure for the one atmosphere samples gives the same latitude since the larger error is associated with a larger sample. Again using the slopes of the curves we find the error limits: carbon monoxide ±0.4%, ethylene and acetylene and ethylene ±0.1%.

In local regions of some of the curves of yield vs. percentage added oxygen, the slopes are quite steep, for example, ~5 for the ethylene from n-butane between 0% and 1% added oxygen. Samples for this oxygen-sensitive region were prepared using suitable dilution techniques so that composition latitudes are very low in this range: ±0.02% at 0.5% oxygen, for example.

2. External Error

A time-dependent error arises from uncertainty in the half-life of the ^{11}C nuclide. The value is known no better than ±0.1 minute. The resultant introduction of error is small, however, the uncertainty in the decay constant being 0.48%. After 60 minutes, which is longer than the longest time elapsed between first and last activity corrections in any run, a latitude of ±1% in N/N_0 will be introduced. This is the outside limit of error introduced, and the average should certainly be less than $\pm\frac{1}{2}$%, since a simple analysis normally takes about 30 minutes from initial injection to completion.

3. Errors Stemming From the Analytical Measurements

Collection of the data required the measurement of counts in a peak, background counts, flow rates, and time.

The electronic clock which measured time elapsed since the end of the irradiation was found accurate whenever checked by a stopwatch, an electric clock, or another electronic clock.

The electronic units which measured and recorded the counts were also checked intermittently and found accurate and linear under all test conditions. The influence of errors in background estimation varies strongly with the number of counts observed from the sample. This number depends in part on the amount of activity produced, which

in turn depends on beam intensity, carbon content of the sample, and so forth. In the runs with a very high percentage oxygen, as few as 135 counts net comprised the ethylene peak. Misestimation of the background by 5 counts/10 sec and misjudgment of the limits of the peak by 20 seconds would give a maximum error of 40 counts, equal to 30% of the result. This large maximum error applies only to some of the smallest values, corresponding to yields between 1% and 2%. Thirty percent error is an undoubted overestimate, as is evidenced by much better agreement between duplicate runs at and above 75% oxygen. For six pairs of measurements of yields below 5%, the average deviation was 5.7%.

A large contribution to the errors inherent in the measurement arises from the statistical fluctuations in the disintegration rate during counting of the radioactivity. Standard deviations cannot be calculated, because each measurement is done under unique conditions so other means must be used to estimate the error.

Poisson distributions, which describe most nuclear counting experiments, may be applied to this case. For such a distribution, $\sigma = \sqrt{m}$, where σ is the standard deviation and m is the value of the mean. For a single measurement this formula can give only an approximation to the standard deviation for a hypothetical set of such experiments. Thus for the 135-count ethylene peak mentioned above the error would be about $100 \times (\sqrt{135}/135) = \pm 8.6\%$ due to random fluctuations in the count rate. Here are some representative examples of these errors from n-butane runs: at $82\frac{1}{2}\%$ oxygen, carbon monoxide, ± 0.74%; ethylene, ±4.7%; acetylene, ±2.6%; at 40% oxygen, carbon monoxide, ±2.0%; ethylene, ±4.9%; acetylene, ±3.5%.

Two overlapping measurements of flow rate were made during the passage of activity through the counter. A second bubble was sent up the flowmeter shortly after the first had passed the initial calibration mark. Readings were always in agreement to ±0.3 seconds which indicated good accuracy and the absence of significant flow rate drift during the activity passage. With a typical observed value of 45 sec for the flow rate, the measurement contributes no more than ±0.7% error to the result.

While it is obviously impractical to assign error limits to each of the nearly 200 points plotted, it is hoped that the treatment given affords an evaluation of at least the range of error limits in the data. Where the data are plotted graphically (section III) crossbars show the range of values for each measurement, which affords an idea of the actual reproducibility attainable.

III. EXPERIMENTAL RESULTS

A. The Oxygen Scavenged Butanes and the Structural Studies

The results are presented in Tables 4, 5, and 6. Radiochemical product yields are reported – as is usual in these studies – as percentage of volatile induced activity. The values reported have been corrected as described in the following section. Measurements were made of the yields of labelled carbon monoxide, ethylene, and acetylene from two systems, n-butane/oxygen and isobutane/oxygen from neat hydrocarbon to 90% oxygen. The results listed in Tables 4 and 5 have been plotted in Figures 20-25. Yields of the same products from a variety of different alkanes, all with 4.5% oxygen, were measured, and the results are given in Table 6.

The flags on the points in Figures 20-25 denote the limits of experimental results. Each of the data reported is the average of 2 determinations except as follows: in the n-butane system, 3 determinations at 0% oxygen and 4 at 4.5%; in the isobutane system, 3 determinations at 0.5% oxygen, 13 at 4.5%, 4 at 10%, and 4 at $82\frac{1}{2}\%$; in addition, in the structural study, 5 determinations each for n-pentane and neopentane, 10 for propane, and 3 for ethane.

Table 4

RADIOCHEMICAL PRODUCT YIELDS IN PERCENTAGE TOTAL VOLATILE ACTIVITY FROM ISOBUTANE/OXYGEN SYSTEM

Product \ Volume Percent Oxygen	0	0,5	1	2	4,5	10	20	30	40	50	60	62,5	75	82,5	90
CO	3,3 [a]	13,4	15,7	16,0	18,1	23,3	28,8	34,9	42,4	48,4	54,0	57,2	62,0	71,6	82,6
C_2H_4	24,5	19,2	20,1	19,9	18,4	18,1	15,4	13,8	12,2	10,1	7,5	7,5	4,8	2,9	1,8
C_2H_2	28,4	28,7	29,7	28,7	28,0	28,4	25,5	23,9	23,6	20,0	17,0	16,2	11,7	8,6	5,1

(a) This yield is CH_4 containing some CO.

Table 5

RADIOCHEMICAL PRODUCT YIELDS IN PERCENTAGE TOTAL VOLATILE ACTIVITY FROM NORMAL BUTANE/OXYGEN SYSTEM

Product \ Volume Percent Oxygen	0	0,5	1	2	4,5	10	20	30	40	50	62,5	75	82,5	90
CO	4,6 [a]	13,4	14,1	16,4	18,8	21,8	27,1	34,6	40,7	46,2	57,2	65,8	74,2	79,0
C_2H_4	17,2	12,9	12,1	12,8	12,0	11,2	10,2	9,2	7,6	6,4	5,3	3,0	2,3	1,1
C_2H_2	27,4	28,3	28,4	26,8	26,5	24,8	23,4	22,4	19,9	17,8	15,9	12,2	8,3	5,2

(a) This yield is CH_4 containing some CO.

Table 6

RADIOCHEMICAL PRODUCT YIELDS IN PERCENTAGE TOTAL VOLATILE ACTIVITY FROM SELECTED SATURATED HYDROCARBONS WITH 4.5 VOLUME PERCENT OXYGEN

Substrate / Product	Methane	Ethane	Propane	n-Butane	n-Pentane	n-Hexane	n-Heptane	Isobutane	Isopentane	Isohexane	Neopentane	2,2-Dimethyl-butane	2,3-Dimenthyl butane	Cyclopentane
CO	29.4	21.5	19.3	18.8	18.0	16.2	16.9	18.1	15.5	14.4	21.2	21.6	14.6	14.2
C_2H_6	25.5	16.4	12.2	12.0	10.6	9.4	7.6	18.4	14.7	12.1	22.2	18.3	15.9	1.3
C_2H_2	31.2	30.3	23.8	26.5	25.4	25.7	21.3	28.0	26.6	24.5	32.3	30.8[a]	26.7	31.9

(a) Average of two determinations: 28.2 and 33.4

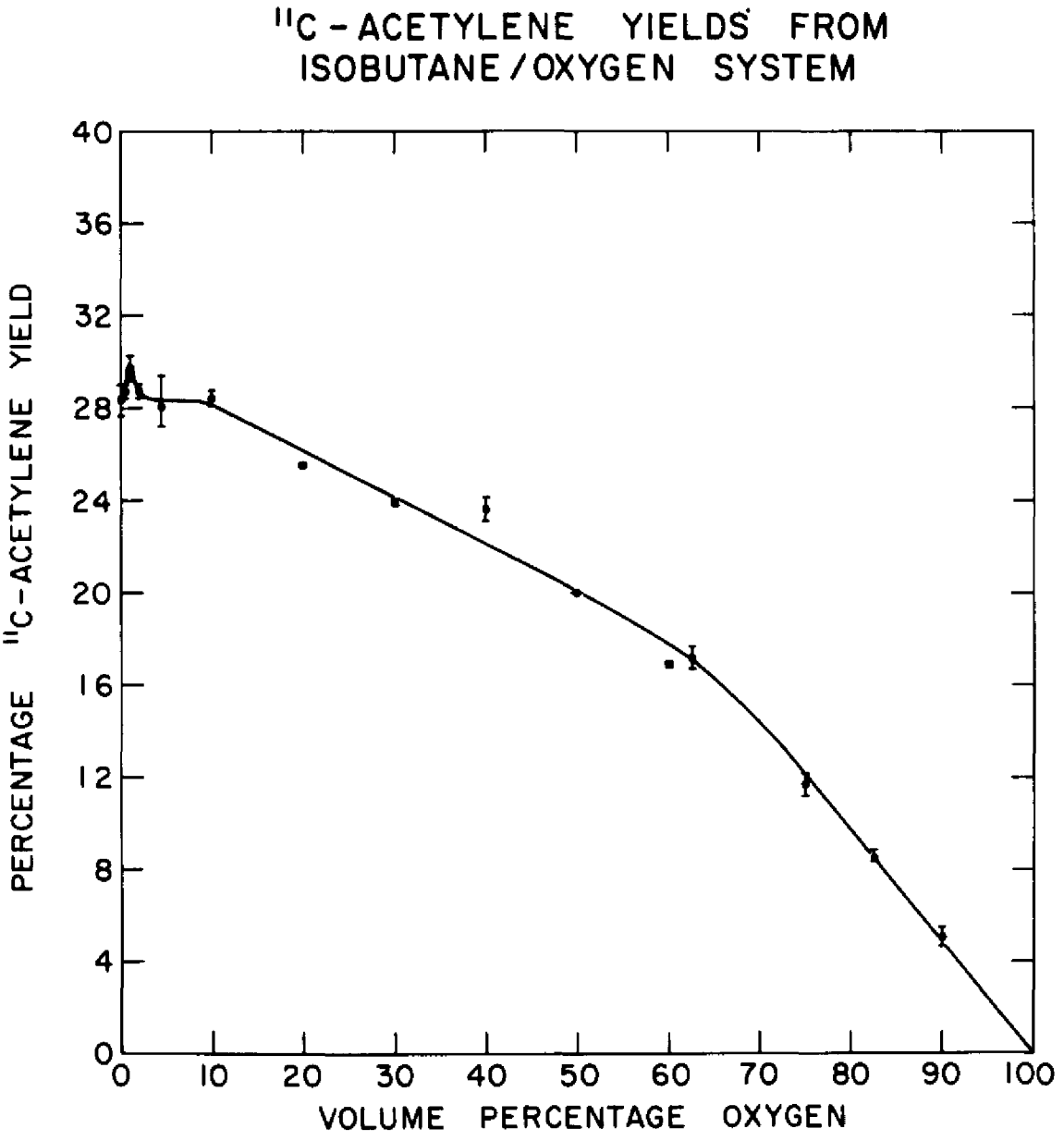

^{11}C - ACETYLENE YIELDS FROM
ISOBUTANE / OXYGEN SYSTEM
PERCENTAGE ^{11}C-ACETYLENE YIELD
0
4
8
12
16
20
24
28
32
36
40
0
10
20
30
40
50
60
70
80
90
100
VOLUME PERCENTAGE OXYGEN

Fig. 20

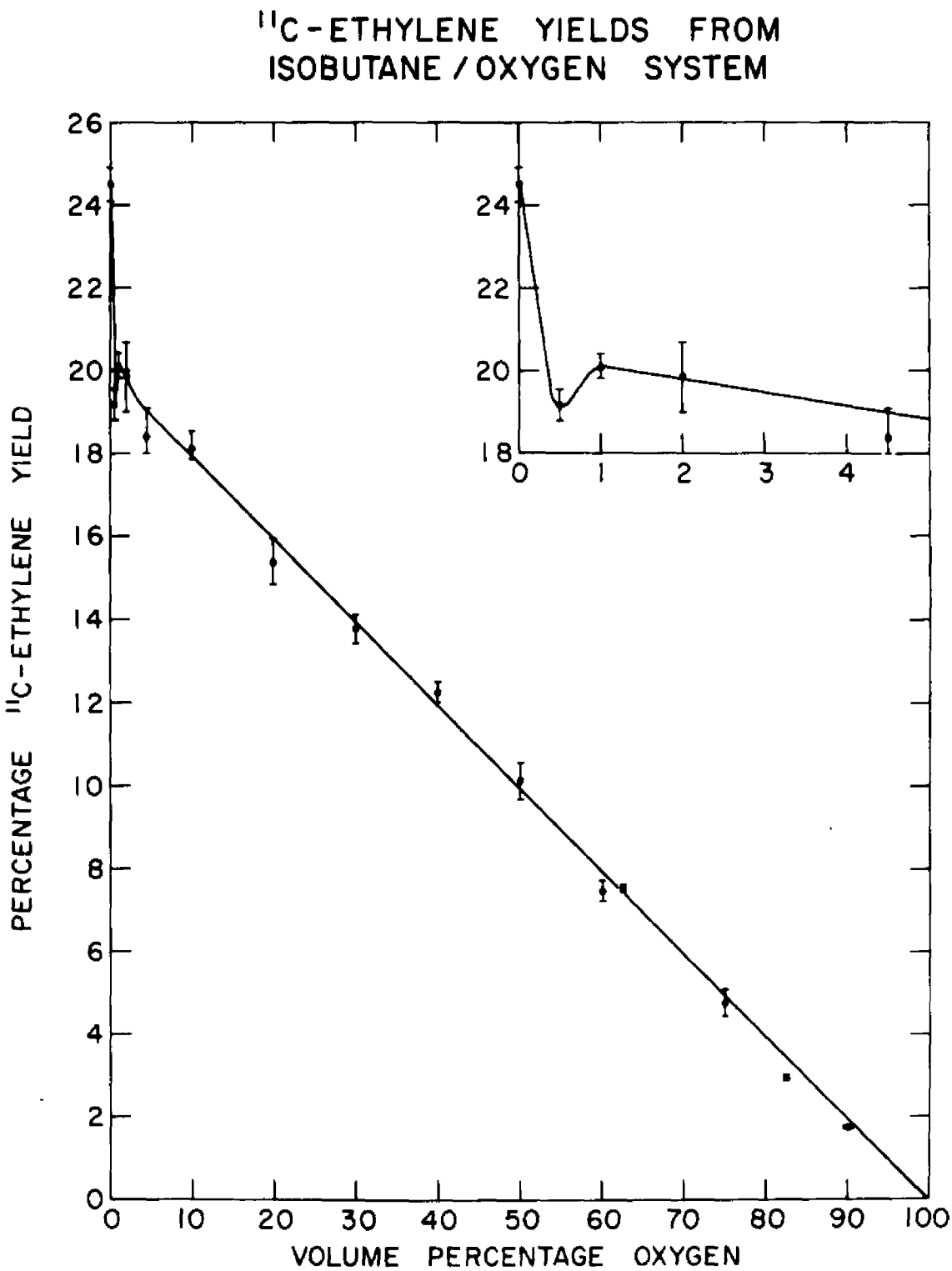

^{11}C-ETHYLENE YIELDS FROM
ISOBUTANE / OXYGEN SYSTEM
PERCENTAGE ^{11}C-ETHYLENE YIELD
VOLUME PERCENTAGE OXYGEN
0
2
4
6
8
10
12
14
16
18
20
22
24
26
0
10
20
30
40
50
60
70
80
90
100
18
20
22
24
0
1
2
3
4

Fig. 21

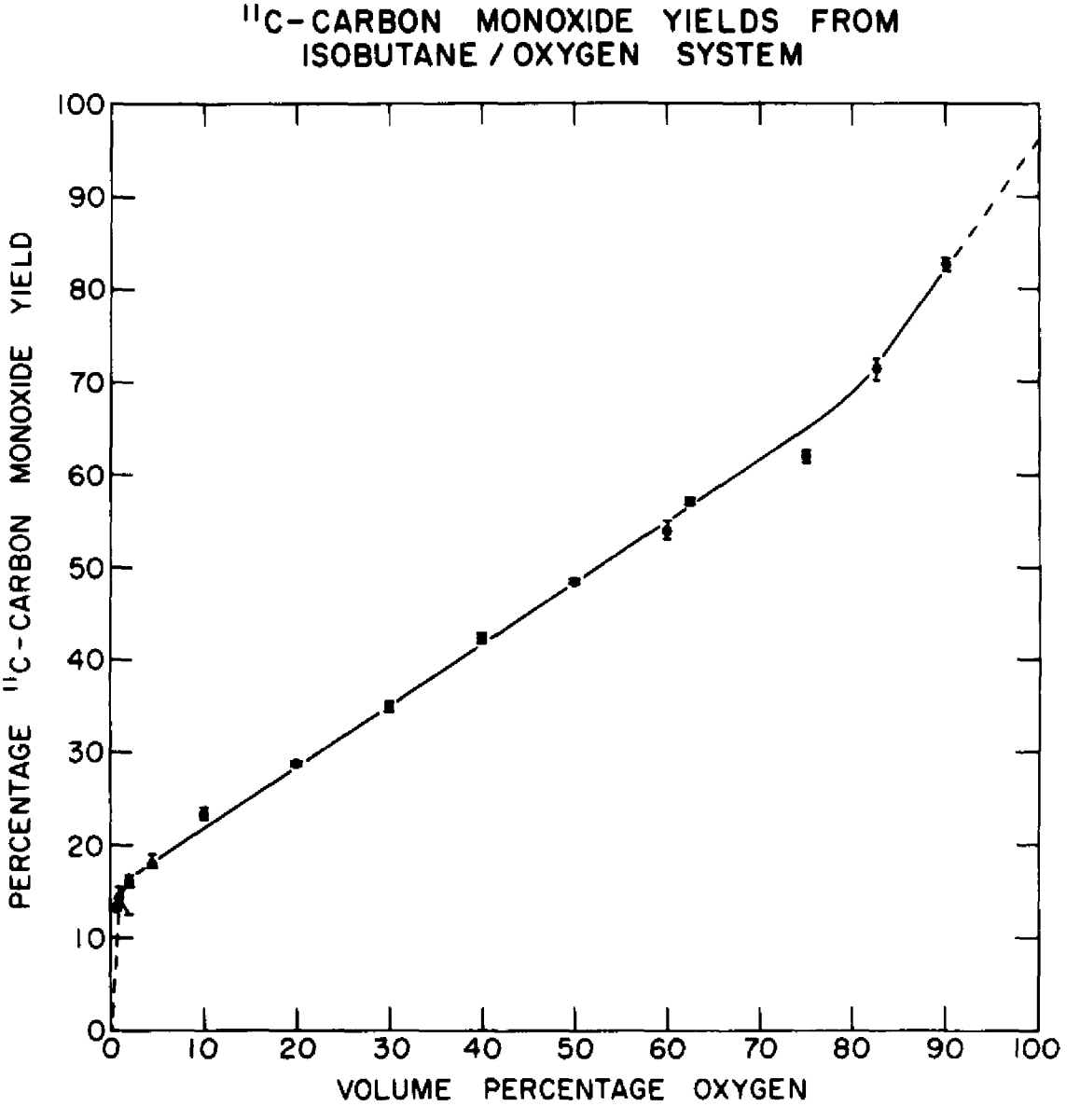

^{11}C-CARBON MONOXIDE YIELDS FROM
ISOBUTANE / OXYGEN SYSTEM
PERCENTAGE ^{11}C-CARBON MONOXIDE YIELD
VOLUME PERCENTAGE OXYGEN
0
10
20
30
40
50
60
70
80
90
100

Fig. 22

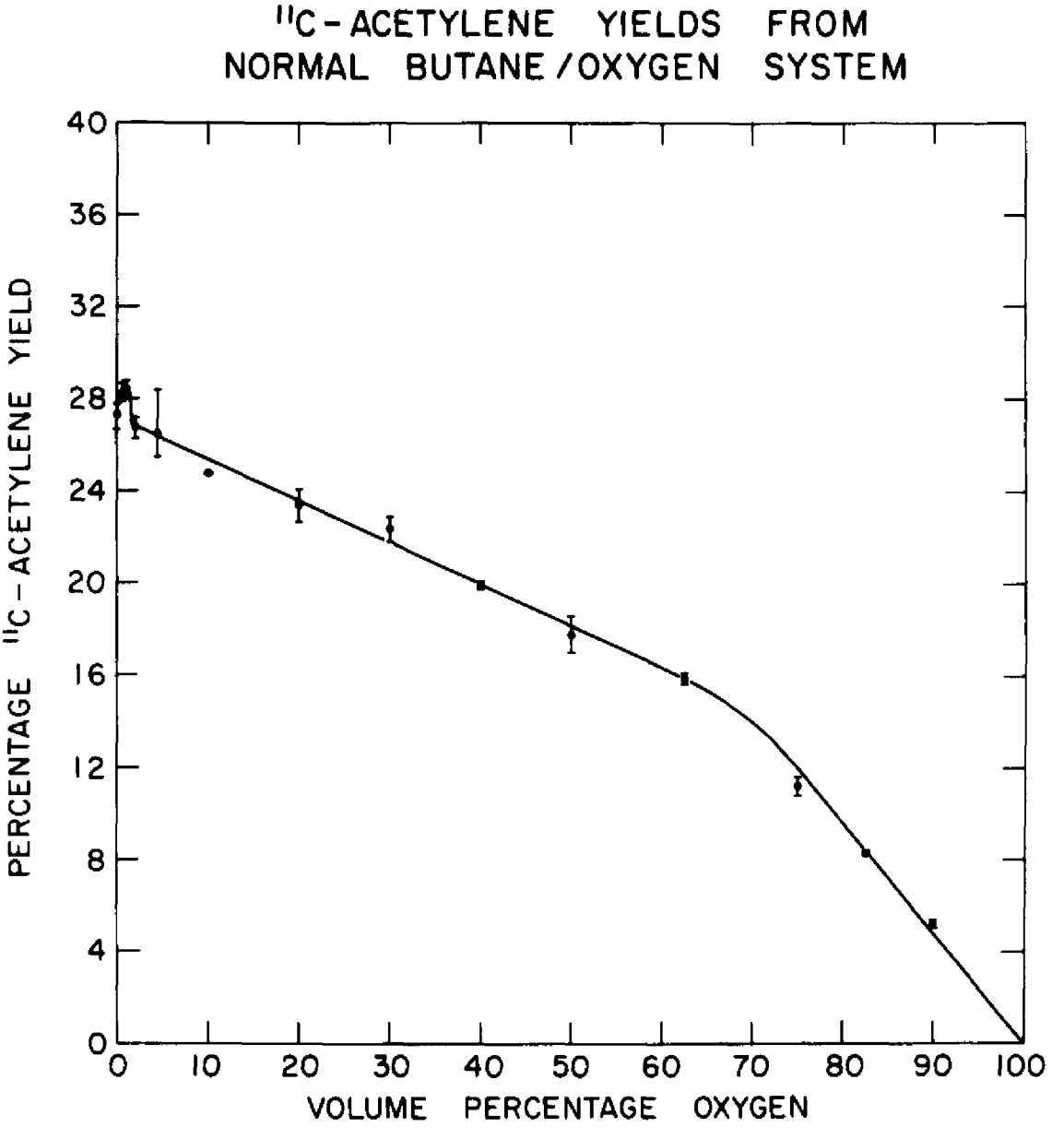

^{11}C - ACETYLENE YIELDS FROM
NORMAL BUTANE / OXYGEN SYSTEM
PERCENTAGE ^{11}C - ACETYLENE YIELD
0
4
8
12
16
20
24
28
32
36
40
0
10
20
30
40
50
60
70
80
90
100
VOLUME PERCENTAGE OXYGEN

Fig. 23

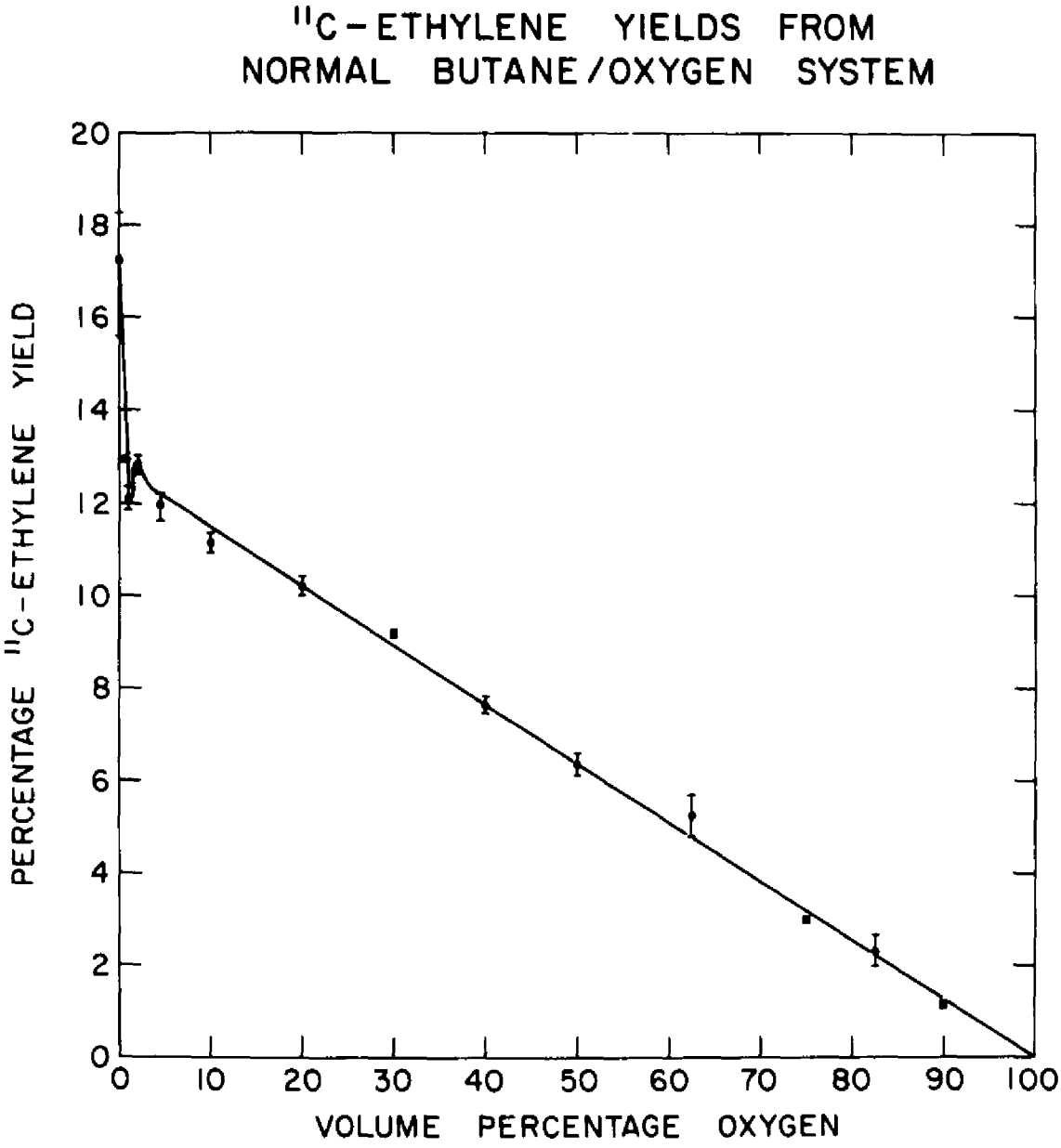

^{11}C – ETHYLENE YIELDS FROM
NORMAL BUTANE / OXYGEN SYSTEM
PERCENTAGE ^{11}C-ETHYLENE YIELD
0
2
4
6
8
10
12
14
16
18
20
0
10
20
30
40
50
60
70
80
90
100
VOLUME PERCENTAGE OXYGEN

Fig. 24

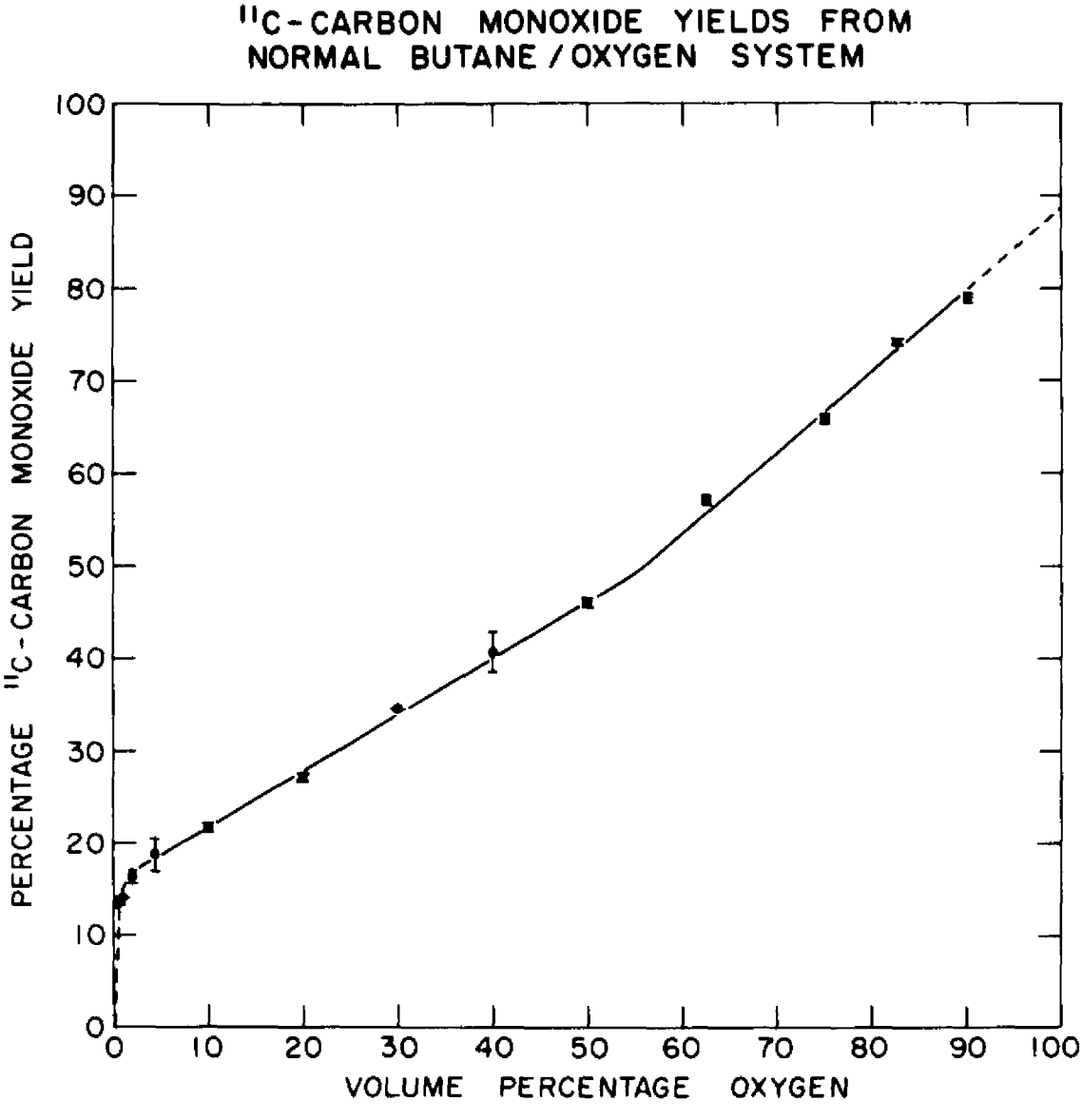

^{11}C-CARBON MONOXIDE YIELDS FROM
NORMAL BUTANE / OXYGEN SYSTEM
PERCENTAGE ^{11}C-CARBON MONOXIDE YIELD
VOLUME PERCENTAGE OXYGEN
0
10
20
30
40
50
60
70
80
90
100

Fig. 25

B. The Density Effect

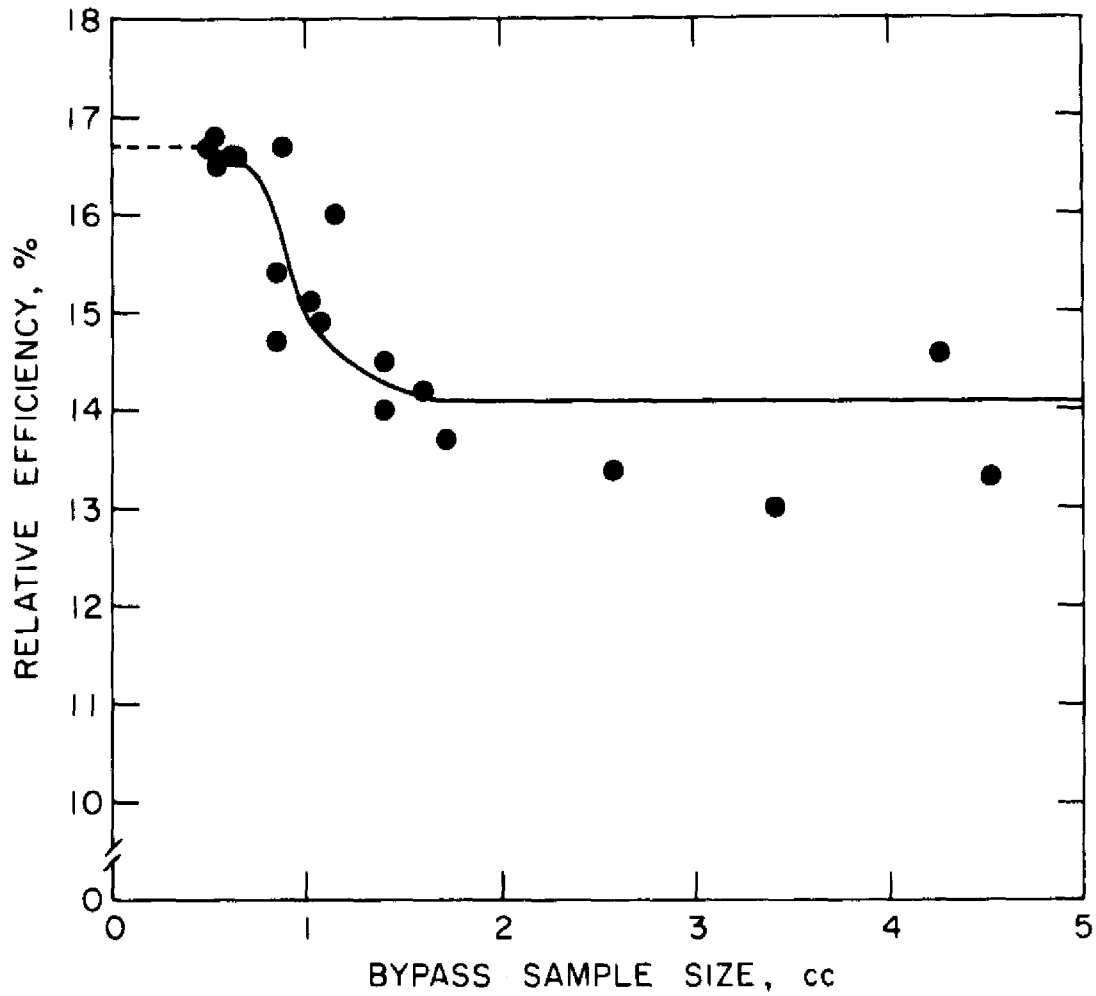
After redesign of the counter insert solved tailing problem in the analyses (section II H), reproducible results were obtained. Hydrocarbon-oxygen substrate systems previously examined by other workers in this laboratory[3, 15, 102] were run as a calibration and check. Reproducible results were obtained, but in fact the yields observed were approximately 40% higher than those from the previous studies. An independent check was made to determine which set of results was verifiable. After emergence from the chromatographic column and passage through the sandwich counter, the acetylene was condensed out of the gas stream in a cold trap at liquid nitrogen temperature. It was then transferred to a calibrated internal proportional counter and counted again. A sample of the irradiated gas mixture from which the acetylene had been separated was also counted for normalization. The results of several such checks seemed to be in good agreement with the higher numbers, and the investigation accordingly was continued. When the study was nearly complete, an error in the independent check experiments was discovered. Correction for the error gave a result which stood between the earlier low and the present higher values. Consequently data gathering was brought to a conclusion and the question of which findings were the correct ones was reopened. Experimentation finally revealed that the apparent efficiency of the counter in the bypass assay of the total induced volatile activity was a function of the direction in space of the gas flow through the counter. Upward passage of the gas gave higher apparent efficiency than downward, regardless of the orientation of the counter (i.e., regardless of

which end of the counter was at the top). Intermediate values were obtained when the gas flow was horizontal. The effect could not be observed for activity peaks which emerged from the chromatograph columns. It became evident that the effect was attributable to a gas density difference when large samples passed through the counter.

The bypass assay is done on roughly 10 cc of the original substrate gas containing the traces of radioactive materials produced in the irradiation. The ~30 cc trap is first pressurized to about one atmosphere in the helium stream of the chromatograph to minimize surge effects in the injection. After the flow conditions have restabilized, the sample is injected into the helium carrier stream just as a sample for column analysis would be. The injected sample travels to the counter through the chromatograph tubing, which has a narrow diameter in accordance with good chromatographic design. Consequently the bypass sample remains as a rather discrete slug of gas in transit to the counter. Consider what happens when the front of the sample reaches the counter. If the sample is (for example) 10 cc of neat butane mixed with 20 cc of helium from the pressurization, the density of the mixture is $5\frac{1}{2}$ times that of pure helium. If the counter is vertical with the gas flowing downward, the heavy mixture emerges into the top of the relatively large ($37\frac{1}{2}$ cc) internal cavity of the sandwich counter. Since the cavity is filled with helium, the heavy gas will drop very rapidly to the bottom, where it will be swept out of the sensitive volume by the continuous gas stream. As the dense gas falls, helium will be displaced upwards and take its place, so that the over-all flow rate through the counter remains constant before, during, and after passage of the heavy gas. Since equal volumes of gas

are being displaced in opposite directions, no effect on the over-all flow rate is observable externally on the bubble flowmeter. The net effect is thus that the heavy gas containing the radioactive constituents passes through the counter very rapidly, and the short residence time drastically reduces the counts observed from the bypass (and therefore the effective efficiency of the counter). If the gas stream is flowing upwards, the effect will be the reverse with the heavy gas collecting at the bottom of the cavity and remaining in it longer than would be expected from the over-all flow rate. The effect does not appear (or is below the threshold of detectability) for chromatographic peaks, since (1) the compounds being assayed are mostly of much lower molecular weight than the substrates, and (2) the peaks contain much less of the dense gas, typically 0.1-0.2 cc if carriers are used. The small amount of gas will become diluted with carrier as it emerges from the chromatograph column and become further mixed with the carrier in the counter cavity, and thus not behave as the bypass samples do. (Evidence of this behavior of small samples was actually observed, vide infra.)

A number of experiments have been made specifically to examine the density effect. All of the information gathered is consistent with the explanation offered. Figure 26 is a plot of relative efficiency of the counter used in this research on bypasses versus size of the sample (total cc of hydrocarbons) passed downward through the counter. The radioactive constituent in the samples was ^{11}C-acetylene prepared by irradiating neopentane. The acetylene was crudely separated from the neopentane and other products by fractional condensation and then purified chromatographically. The larger samples were doped with neopentane to bring the samples up to the desired size and to increase the sample density, in order to



VARIATION OF RELATIVE EFFICIENCY WITH BYPASS SAMPLE SIZE FOR SANDWICH FLOW COUNTER.

FIG. 26

approximate the conditions in regular bypasses. The plot is drawn in below 0.5 cc so that the limiting value as the sample size approaches zero is the true counter efficiency found by another method (vide infra). Samples of less than 0.5 cc could not readily be prepared with accuracy. This was due partly to the difficulty in obtaining acetylene of sufficiently high specific activity and partly to the problems in measuring and handling such small quantities of gas.

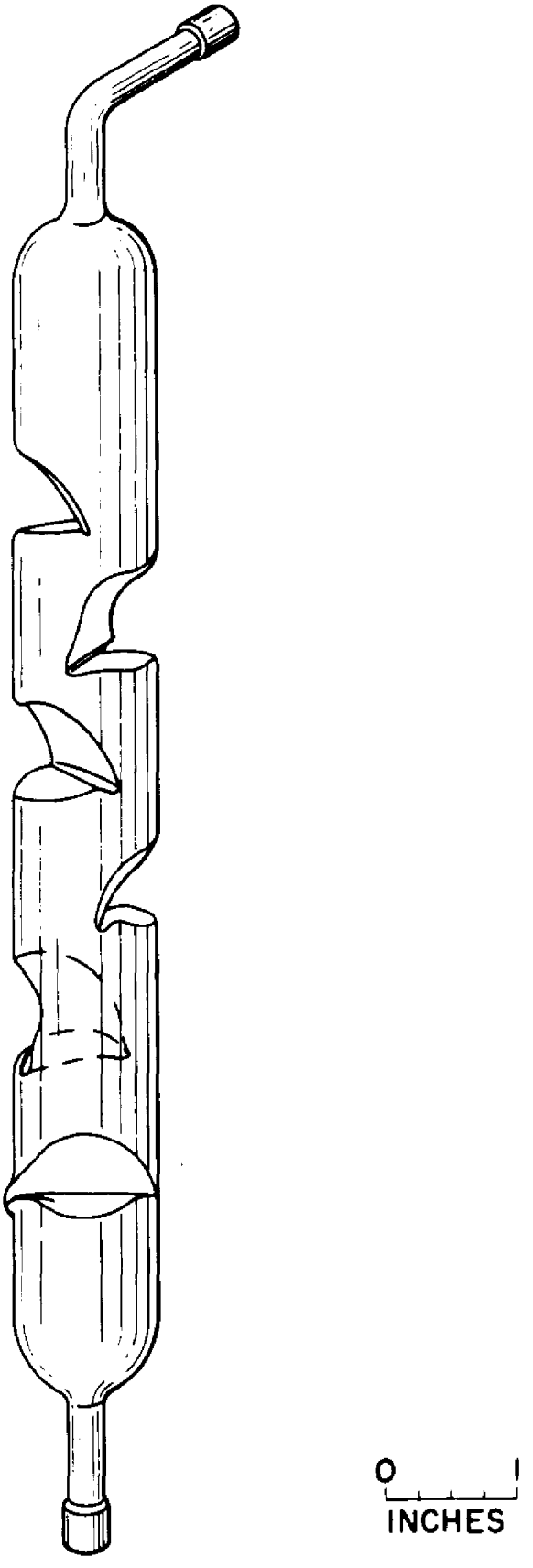
Above 2 cc the plot is drawn in as a straight line at 14.1%. This value corresponds to the average of 28 efficiency measurements (which showed very little spread) from ~10 cc bypass samples of various compositions. Experiments in which efficiency was measured for a few samples between 5 and 10 cc (not shown in Figure 26) gave acceptable agreement with the 14.1% value. The spread in the data seems to be attributable to ordinary statistical counting fluctuations. However, a clear transition in apparent efficiency is visible, dependent on sample size and in the direction consistent with the explanation offered. The apparent efficiency declines with larger samples of the heavy gas, appearing to reach a limiting value at about 2 cc. There is good reason to believe that a limiting value of 16.7% relative efficiency is being approached for the smallest samples run. This is indicated by the fact that for six samples between 0.43 and 0.64 cc the average relative efficiency for the three passed up the counter was exactly the same as for the three passed down it, 16.7%. Also 8 large bypass samples passed horizontally through the counter gave an average relative efficiency of 16.3%.

The results of using a gas mixer in the bypass line also support

the interpretation presented and indicate that the effect can be controlled. The mixer is shown in Figure 27. Bypass samples are passed up through it before entering the counter. The large volume combined with the indented baffles acts to dilute and mix the heavy gas with the helium, decreasing the density of the gas and destroying the sharp boundaries. This operation is confirmed by the data tape. The output shows the bypass activity peak to begin and end gradually. The time for passage of the sample is lengthened so that a bypass takes about 3 minues instead of the usual 1. This lengthening of the time required for a bypass is somewhat disadvantageous in ^{11}C work. However, a small baffled mixer combined with a horizontal counter should certainly give accurate analyses without sacrificing much time. It should be noted that a mixer similar to the one described, but without the baffles, as well as two other mixers in the form of gas traps, gave only a partial remedy of the false-efficiency problem.

Finally, the gas flow through the counter was redirected upward in the analytic setup used to obtain data in the present study. The data which emerged from several runs with this configuration reproduced the earlier low results.[3,15,102] It may be inferred that these results were derived under just the same circumstances, with upward gas flow through the counter.

For the present study, configuration of the analytic apparatus entailed downward gas flow through the counter. Since the setup was unaltered throughout the experiments in which the data were taken, the raw data obtained are subject to correction. Except for a few results taken after the density effect was discovered, the numerical values reported are all observed values corrected by multiplication with the



GAS MIXER

Fig. 27

factor 14.1/16.7 = 0.844. The corrected results stand in good agreement with the independent checks of acetylene yield previously described. The corrected results are also in good agreement with a number of values[102a] obtained from cylinrical flow counter experiments. The latter results depend on the calibrated absolute efficiency of the counter for tiny samples and do not involve bypasses at all.

Several measurements of the relative counter efficiency for bypasses with upward gas stream were made, giving an average value of 20.9%. If the earlier results of Stöcklin and Wolf[3, 15, 102] are corrected by the factor $20.9/16.7 = 1.25_2$, most of them come into excellent agreement with the present corrected results (average deviation 7.5% for 26 measurements) as may be seen from Table 7.

Radiochemical yields measured and calculated in seven different ways are shown in Table 8. The agreement is excellent, especially considering the usual levels of error in such data. In particular, the corrected data from the vertical gas flow experiments are in good agreement with the data from the horizontal gas flow experiments.

An additional reconsideration of the observations supports the validity of the application of a single correction factor to all the results. First, Figure 26 shows that the downward trend in efficiency has stopped for all samples above ~2 cc. All of the bypass samples in this study were larger than this. Second, density of the bypass sample obviously increases as one goes up the homologous substrate series from methane to heptane. The facts that corrected results from methane to pentane agree well with (1) the cylindrical counter data, (2) the corrected Stöcklin-Wolf data, and (3) the acetylene assays done as an independent check show that the density effect is not progressive over the range of the experiments done. Apparently the bypass densities are all above a threshold, just as the bypass sizes are.

TABLE 7

COMPARISON BETWEEN SETS OF CORRECTED RESULTS

	This Study			Stöcklin and Wolf[3, 15, 102]		
Product / Substrate	CO	C_2H_4	C_2H_2	CO	C_2H_4	C_2H_2
Methane	29.4	25.5	31.2	41.3	26.9	33.2
Ethane	21.5	16.4	30.3	28.8	18.5	34.4
Propane	19.3	12.2	23.8	21.9	13.8	29.0
n-Butane	18.8	12.0	26.5	18.8	11.8	24.9
Isobutane	18.1	18.4	28.0	17.0	17.6	26.5
n-Pentane	18.0	10.6	25.4	17.5	10.0	24.3
Neopentane	21.2	22.2	32.3	20.0	19.9	30.7
Cyclopentane	14.2	1.3	31.9	13.9	1.1	30.5
2,3-Dimethylbutane	14.6	15.9	26.7	16.5	17.0	28.5

The values in the table are yields in percentage of volatile induced activity.

Table 8

RADIOCHEMICAL PRODUCT YIELDS[a] FROM 95.5% ISOBUTANE, 4.5% OXYGEN SUBSTRATE DETERMINED BY VARIOUS MEANS

Product			Source
CO	C_2H_4	C_2H_2	
17.9	18.2	27.4	(b)
18.3	18.9	28.8	(c)
19.1	19.1	29.4	(d)
17.7	18.0	28.1	(e)
17.0	17.6	26.5	(f)
-	-	27.2	(g)
18.1	18.4	28.0	(h)

(a) In percentage of total induced volatile activity.

(b) Average of 5 determinations with downward gas flow through sandwich counter. Results were corrected by multiplying by 0.844.

(c) Average of 2 determinations from a cylindrical-type counter (without gas mixer) with horizontal gas flow.

(d) Average of 2 determinations with horizontal gas flow through sandwich counter.

(e) Average of 4 determinations with upward gas flow through sandwich counter. Results were corrected by multiplying by 1.252.

(f) Results of correcting Stöcklin-Wolf data by multiplying by 1.252.

(g) Average of 2 independent checks made by condensing acetylene out of chromatograph gas steam and assaying in internal static counter.

(h) Number average of all above results except (f).

IV. DISCUSSION

A. The Normal Butane/Oxygen System and the Isobutane/Oxygen System

1. Review

A short review of the observations made on saturated hydrocarbon/oxygen systems up to the present may be useful at this point. In a study of the methane system, Stöcklin, et al.[20] observed that yields of labelled carbon monoxide, ethylene, and acetylene rose steeply at low oxygen concentrations, reaching a local maximum in the cases of ethylene and acetylene (Figure 1). This behavior was attributed to "the elimination of radiolytically produced species which transform part of the 'primary' recoil products (e.g., stabilized C_2H_2 and C_2H_4) to other compounds thereby causing an initial rise in the yield of acetylene-^{11}C and ethylene-^{11}C." An expansion of this terse statement follows. Given quantities of labelled acetylene and ethylene are being formed as products of the reactions of recoil carbon atoms or fragments with the pure hydrocarbon substrate. Under the influence of the radiation which accompanies the bombardment, a considerable quantity of radicals and molecular fragments is produced from the substrate. In the absence of oxygen these fragments attack and convert part of the primary yields to other compounds. In the unscavenged substrate, then, the observed yields are the actual yields less the fraction which has been destroyed. Added oxygen suppresses the concentration of the radiolytic fragments and thus protects the primary yields. This protection accounts for the trend of increase in the labelled ethylene and acetylene yields in the systems examined.

Similar maxima were not observed in either the ethane/oxygen or the propane/oxygen system.[1c] Their absence was considered due to possible

self-scavenging in the higher hydrocarbons in the absence of oxygen.[20] The sharp rise in the yield of carbon monoxide observed in the methane system recurred in the ethane and propane systems[1c] and was attributed to an efficient scavenging reaction of the thermalized fraction of carbon atom and carbon fragment precursors. The ethylene and acetylene yields from the ethane and propane systems behaved quite differently with increasing oxygen compared to those from the methane system. Instead of a rapid rise, they dropped sharply within the first few percent oxygen. This was considered the result of the elimination of the thermal fraction of the precursors. The yield trend of these products was thus the complement of the carbon monoxide yield trend. In the oxygen concentration region above 2-3% a gradual linear decrease of ethylene and acetylene yields and a similar increase of the carbon monoxide yield were observed. These trends were held to arise from competition by the oxygen with the substrate for the hot carbon atoms.

The results of the present study will be examined for similarities to the systems described and to test the adequacy of the proposed reaction model. To organize the treatment of the results, a formal division of the range of oxygen concentration is made into low, medium, and high concentration regions.

2. The Low Oxygen Concentration Region

Yield trends in this region seem related to radiation effects and precursor scavenging.

a. Radiation effects. In the present study the carbon monoxide and ethylene yield trends (Figures 21, 22, 24, and 25) behave in the regions closest to the ordinate as would be expected, based on the previous observations (Figures 5 and 6).

The acetylene yield does not (Figures 20 and 23). Instead of dropping rapidly as the ethylene yield does, it climbs to a small maximum and then descends. Similar disparate sensitivities to scavenger of ethylene and acetylene yields were observed by Clark and Voigt in liquid phase systems.[89] The appearance of a maximum is considered below, but it is of interest whether the region of rapid descent between one and two percent oxygen is real or an artifact.

In the *n*-butane system (Figure 23) the best linear fit of the eight data points in the competition region from 2% to 60% oxygen falls very significantly below the close pair of points at ½% and 1% oxygen. This is a clear suggestion that the region between 1 and 2% oxygen is the vestige of a scavenging of the acetylene precursor similar to that observed previously[1c] and in this work for ethylene but far less pronounced. The trends in the acetylene yield from the isobutane system (Figure 20) are less clear in the same oxygen concentration region. A linear plot could accommodate all of the data from 1% to 50% oxygen with the exception of the point at 2%. However, such a line misses the best value of the yield at 4.5% oxygen by about 1½% yield. This best value is very well established (see Table 8) and one of the most reliable data in the entire work. Consequently the plot as drawn fitting the best datum at 4.5% oxygen and the point at 2% seems the best choice. As a result the graph suggests a small region of steep acetylene yield decline comparable to that in the normal butane system. The flat region from about 2½% to 10% oxygen has not been observed in other systems and has no apparent theoretical basis. Therefore it will not be discussed further. The conclusion is therefore that there is at least a short range over which acetylene yield declines as the ethylene yield does. The magnitude of the drop in yields of acetylene and ethylene is discussed after the maximum in the yield trends is considered.

The small maxima at low oxygen concentration in the ethylene and acetylene yield graphs (Figures 20, 21, 23, 24) are a new observation. The

maxima occur at about 1% oxygen in the yields of ethylene and acetylene from the isobutane system and acetylene from the n-butane system. The ethylene from the n-butane system seems to reach its local maximum at 2% oxygen, but considering the spacing of the data points the peak could actually be closer to 1% oxygen; this is not essential to the arguments. The peaks in acetylene yield and ethylene yield appear to be about 1% yield high. The fact that these small maxima appear from independent measurements on two different systems is a powerful indication that the effect being observed is real. This is the first reliable report of yield fluctuations of such small magnitude from recoil carbon systems. The maxima and local maxima appear quite different in size and location from the maxima observed in the methane system. Nevertheless, they too seem to stem from radiation damage.

The effects of oxygen and other additives on systems under irradiation will now be considered briefly. The results of the present study can be explained on the basis of chemical protection. A number of substances are known which inhibit radiolytic reactions if added in small amounts to a substrate before radiolysis. These protective agents may act in two fashions, which have been termed protective agents may act in two fashions, which have been termed chemical and physical.[103] A physical protective agent works by draining energy from the substrate molecules which have been activated by the absorption of the radiation. Radiolysis of the substrate is thus diminished by deactivation of the substrate molecules before they can decompose. The protection is accomplished either by promotion of energy dissipating processes like internal conversion in the substrate or by the acceptance by the protector of energy from the substrate. The protective agent, if very stable, may lose the excess energy in collision so that the radiation energy is degraded into heat. Alternatively, if the protective agent is mostly decomposed upon assumption

of the excess energy, the action is known as sacrificial protection.[103]

Chemical protection is actually another name for what is most commonly called scavenging. The action of scavengers has been described (section I E3); it depends on reactions with and removal of the chemically active fragments by the additive. The fact that oxygen, ethylene, and acetylene, all well-known radical scavengers, act to suppress radiolysis effects has suggested that the action of these substances in recoil carbon systems is chemical protection.[20] Results of the present study give additional support to this belief.

The maxima and local maxima observed in the acetylene and ethylene yields may be understood as arising from two trends in opposite directions. These are a decrease in yield due to scavenging of the thermal fraction of the ethylene and acetylene precursors and an increase in yield due to protective action. The results suggest that the effect should also pertain in the ethane and propane systems. Failure to observe it may be a result of its much diminished magnitude in these systems (compared to the methane system) and the likely occurrence of the effect at a higher oxygen concentration. The question naturally arises, what is the source of the different yield behaviors in the methane system compared to the other aliphatics? The answer, it turns out, is of help in unraveling the differences between the behavior of the ethylene and acetylene yields from the butanes.

The effects of radiation on the systems of interest will now be considered. Radiolysis will produce hydrogen atoms and other radicals in hydrocarbons. Several factors suggest that the concentration of these fragments will be higher in methane than in the butanes. First, a higher concentration of hydrogen atoms would be expected in methane because

of bond energy considerations.[104-107] Thrush has calculated the energy of activation for reactions of the type $H + RH \rightarrow R + H_2$. For RH = methane, the value is 14.0 kcal/mole; for RH = normal butane, it is 8.4 kcal/mole.[108] This disparity results from the fact that the C–H bond dissociation energy is significantly higher for methane than for the butanes.[104-107] Second, a higher total concentration of radicals will be expected in methane. This is because the alkyl radicals left from the abstractions in the butanes can recombine more effectively than the hydrogen atoms in methane (which recombination would require a third body to carry off the excess energy). Third, the total initial yield of unsaturates radiolytically produced in the butanes must be much greater than that in methane on account of the greater number and simpler processes for unsaturate formation in the C_4 compounds. The unsaturates produced would function by scavenging to further reduce the radical activity in the butanes.[70,71] Indeed, in methane the G-value for acetylene is found to fall almost exponentially and then level off close to and approaching zero with increasing dose,[109] a result consistent with rapid acetylene consumption towards exhaustion. In fine, the radical concentration should be much greater in the methane system than in the butane systems. Under these conditions one would expect methane to be more sensitive to added oxygen than the butanes.

This description provides a good qualitative explanation of the observations. The methane system is seen to be more sensitive to small amounts of added oxygen than any of the C_2 to C_4 alkane systems, the protection effect reaching saturation in methane at oxygen concentrations about a tenth those in the other cases. A comparison of the data of Stöcklin et al.[20] on the methane system with the results of the present investigation is revealing. For the first time, a quantitative demonstration of the higher activity of destructive fragments in methane can be made. However, a fairly elaborate train of reasoning is necessary.

Since a given ^{11}C-labelled unsaturate will act as a tracer for the larger amounts of the same compound produced from the substrate by radiolysis, it will be useful to compare the fraction of yield lost by radiolysis in the various systems. If, for example, the same quantity of unlabelled ethylene is produced in methane and butane, we anticipate that a larger fraction of it would be converted to secondary products in methane due to the high fragment concentration and fragment reactivity in that substrate.

However, it must be borne in mind that the rise to the maximum ethylene and acetylene yields actually reflects the difference between two slopes – the slope of protection with increasing oxygen concentration minus that of depletion due to thermal precursor scavenging. Naturally the scavenging of the precursors may progress to different extents in different substrates depending on factors like the moderation efficiency of the substrate, the excitation distribution of the carbon atoms in the substrate, and so forth. It is therefore conceivable that the shallow maxima of about 1% yield of the ethylene and acetylene in the butanes are really the vestiges of a large protection effect masked by a larger thermal yield depletion. Thus the heights of the maxima (yield at the maximum minus yield at the preceding minimum) represent only a lower limit of the protection contribution.

A calculation may be made of the labelled acetylene destroyed in unscavenged methane. The 17.7% yield of ^{11}C-acetylene from neat methane rises to a maximum of 32.3% yield in the presence of 0.1% added oxygen.[20] The fraction destroyed is therefore at least (32.3 – 17.7)/32.3 = 45%. Similarly, at least (30.5 – 12.4)/30.5 = 59% of the ^{11}C-ethylene formed in the unscavenged substrate is destroyed by radiolysis.[20] That these proportions are indeed greater than the

proportions of the same substances destroyed in the unscavenged butanes can be demonstrated by a reductio ad absurdum argument. Assume that in neat n-butane 45% of the acetylene formed is destroyed. Hypothetically, the production of labelled acetylene would be the observed yield divided by the factor (1−0.45) or 27.4/0.55 = 49.8% of the total induced volatile activity. Similarly, if 59% of the ethylene formed had been destroyed in the absence of scavenger, a 17.2/0.41 = 42.0% yield of the compound was hypothetically formed. From Table 5, a 4.6% radiochemical yield of methane is formed in the absence of oxygen, as are yields of 13.0% propylene, 1.2% ethane, and small quantities of other compounds.[110] Summing these real and hypothetical yields except the last-mentioned gives 110.6% recovery, which is to say the total product formation exceeded the amount formed. Therefore, there must be more destruction of ethylene and acetylene in methane than in n-butane. Applying the same treatment to isobutane gives inferred radiochemical yields of 51.6% acetylene and 59.8% ethylene. Added to the observed 3.3% methane (Table 4) and the 1.4% ethane[110] these give a hypothetical total of 116.1%, showing that a greater porportion of the ethylene and acetylene formed is destroyed in methane than in isobutane. Using this conclusion it is possible to demonstrate the higher concentration of radiolytic fragments in methane by a second method.

Consider the relative total amounts of unsaturates available in the different substrates. G-values for ethylene production from methane, n-butane, and isobutane are 1.4,[109] 1.4, and 0.6,[71] respectively. A starker comparison is provided by the acetylene, however. In methane, $G_{C_2H_2} \leq 0.002$[111] at the dose rate in the bombardments used. For production of acetylene from n-butane and isobutane, G-values of 0.52 and 0.31, respectively, have been reported.[70] Thus smaller

concentrations of the unsaturates are being produced in methane. If the amount of destruction is proportional to the concentrations of both the unsaturate and the radiolytic fragments, the greater destruction of unsaturates in methane requires a greater concentration of fragments in that substrate than in the butanes.

b. Precursor scavenging. Up to here we have been concerned with the radiation effects as revealed in comparisons between methane and other saturated hydrocarbon systems. Now, having established the basis for the singularity of the methane system, we shift our attention back to the earlier-described differences in behavior between ethylene and acetylene yields with increasing oxygen concentration in the butanes. It is now possible to evaluate the relative amounts of labelled ethylene and acetylene protected at the maxima in the butanes. As mentioned, the apparent heights of the maxima in the graphs cannot be used to measure the total protection of the compound. However, although the apparent maxima for ethylene and acetylene are each of the order of 1% yield high, it is possible to decide for which of the two compounds the actual protection should be greatest. Knowledge of this comparison will in turn open the way to inferences about the precursor scavenging region.

As a first approximation, the most active species in the destruction of unsaturates is the hydrogen atom. In high-energy irradiations, the evidence is that atomic hydrogen detachment is one of the dominant processes.[112] Also, hydrogen atoms are known to have lower energies of activation for addition to ethylene than alkyl radicals[113, 113a]; the same condition applies for acetylene, the hydrogen addition being the lower energy process.[114, 115] In the following discussion hydrogen atoms are

considered the major agent responsible for attack on the acetylene and ethylene in the unscavenged recoil systems.

Michael and Weston have measured the rates of addition of hydrogen atoms to ethylene and acetylene and find both reactions first order with respect to the unsaturate.[116] Bimolecular rate constants were found to be $k = (1.8_4 \pm 0.14) \times 10^{-14}$ cc/molec sec and $k = (3.2_7 \pm 0.17) \times 10^{-13}$ cc/molec sec for acetylene and ethylene, respectively.

The total amount of acetylene destroyed depends on 2 factors: the amount produced and the rate at which the product is destroyed. The G-values indicate that less acetylene is produced than ethylene. The reaction rates indicate that destruction is slower for acetylene than for ethylene. Therefore, total destruction by radiolysis in the recoil systems is less for acetylene than for ethylene.

An additional fact supports this contention. The rate constants measured actually reflect the rate of reaction of hydrogen atoms with unsaturate, i.e., the rate of disappearance of hydrogen atoms. In the case of acetylene (but not ethylene) there is ample evidence that one mode of hydrogen atom attack does not lead to the destruction of acetylene.[117-119] The reaction seems to proceed via $C_2H_2 + H \longrightarrow C_2H_3$; $C_2H_3 + H \longrightarrow C_2H_2 + H_2$,[119-121] the net effect being a catalytic recombination of the hydrogen atoms. The absence of ethylene from the products of the reaction of hydrogen atoms with acetylene and recovery of most of the starting materials[118,122-124] support the proposed reaction scheme.

On all counts, less of the acetylene than of the ethylene is being destroyed. Consequently the protection effect of added oxygen for acetylene must be less pronounced than for ethylene. Reiterating, the slopes of the ethylene and acetylene yield curves in the range between 0% oxygen and the maximum or local maximum are the sums of the slopes of the

thermal precursor scavenging diminution and the protection effect increase. Therefore the slopes or peak heights as seen in the graphs cannot be taken as direct measure of the comparative slopes of thermal precursor scavenging with added oxygen. But, since the protection effect is less positive for acetylene, it must follow that the thermal precursor scavenging component is less negative for acetylene than for ethylene.

If, as seems correct from the position of the local maxima (Figures 20, 23), the protective scavenging reaction reaches saturation at 1% oxygen, and if, as seems likely from the preceding section, the acetylene precursor scavenging is still ongoing between 1% and 2% oxygen, then the negative slope side of the acetylene peak should give an approximate indication of the slope of acetylene precursor decrease with added oxygen. The slope then lies between 1% and $1\frac{1}{2}$% yield diminution per percent added oxygen, certainly far less than the 5% to 10% yield diminution per percent added oxygen which is the minimum slope of ethylene precursor scavenging between 0% and 1% oxygen.

Several different inferences may be drawn from the apparent differing sensitivities of the thermal ethylene and acetylene precursors to oxygen. The implications for the mechanisms and other factors governing ethylene and acetylene production are considered. This section is the most speculative, since it relies solely on the slim fact that the slope of ethylene precursor scavenging with added oxygen is greater than that for acetylene in the low oxygen concentration range.

One possibility consistent with the results is that the ethylene and acetylene have the different precursors proposed. If acetylene proceeds from carbon atoms,[61] as seems well established, and if

ethylene arises by the reaction of methyne, as has been suggested,[82] the different precursor scavenging rates could arise from different oxygen sensitivities of the two precursors.

An alternative possible set of precursors is singlet and triplet carbon atoms. The singlets may be less oxygen sensitive than the triplets, since they have no unpaired electron, which suggests that the singlet is the acetylene precursor. However, this result is inconsistent with the hypothesis that triplet carbon is the acetylene precursor.[46]

Another interesting possibility is that the acetylene and ethylene are formed from the same precursor, carbon atoms, but that the production cross sections are different for the two products in different energy ranges. On the theory that the thermal range carbon is being suppressed in the low oxygen concentration region, the implication is that the acetylene is predominantly produced in the higher energy range. This inference would appear to agree with Skell's findings that no acetylene is produced by thermal carbon atoms.[58]

Finally, the proposal of Dubrin et al. that carbon atoms are the precursor of both ethylene and acetylene[80] may be considered. The proposed ethylene production mechanism proceeds via a vinyl radical

$$^{11}C + RCH_3 \longrightarrow RCH_2{}^{11}CH^* \longrightarrow R\cdot + CH_2={}^{11}CH\cdot$$

which is asserted to abstract hydrogen from the medium to form ethylene.[80] The vinyl radical intermediate might be expected to heighten the ethylene yield sensitivity to oxygen.[125] However, abstraction to form ethylene seems the least likely fate of any vinyl radicals which might be formed. Such a species would be most likely to react very rapidly with oxygen, entirely suppressing labelled ethylene formation.

Fessenden and Schuler have measured the reactions of vinyl radicals with ethylene and find the activation energy for the addition to

be 3.3 kcal/mole.[126] The activation energy for the abstraction from butane by vinyl is not known, but addition to the radiolytically produced unsaturates would be likely to compete with abstraction. Considering the very probable scavenging by oxygen to elimination and the possible competition of addition and radical recombination reactions, vinyl radicals appear unlikely to abstract and form ethylene under the conditions of recoil experiments. However, the possibility still exists that the oxygen sensitive fraction of the ethylene yield arises via a thermal vinyl radical and the remainder is formed either from hot vinyl radicals or by some other mechanism.

3. The Middle Oxygen Concentration Region

In the middle range of oxygen concentration, interesting breaks may be observed in the slopes of the carbon monoxide and acetylene yield curves (Figures 20, 22, 23, 25). This is the first observation of such an effect in recoil carbon systems. In the isobutane system, the acetylene yield curve appears to break at about 70% oxygen, the carbon monoxide curve at about 80% oxygen. In the normal butane system the breaks occur at about 70% oxygen for the acetylene yield and about 60% oxygen for the carbon monoxide. These numbers are representative of a region in which the slope seems to change rapidly. Data in the high oxygen concentration region are spaced rather far apart, and accuracy is limited by the lower attainable activities. Within the limitations of the data the breaks may well occur at the same oxygen concentration, especially as the changes in carbon monoxide and acetylene yields go in opposite directions and seem complementary. The linearity of the ethylene curves in the same oxygen concentration region is persuasive that the apparent breaks in the other curves are real and that their source does not affect ethylene production.

Something seems to be interfering with the production of acetylene which also results in a corresponding increase in carbon monoxide production. The occurrence of a threshold effect – a sudden rather than gradual slope change – is surprising, since the properties of the medium are expected to be changing continuously. However, an energy threshold phenomenon probably governs the energy requirement for acetylene production. At very high concentrations, the oxygen may assume the function of a moderator, shifting the energy spectrum of the carbon atoms downward. Indeed, Urch and Welch observed an apparent soft-sphere moderation of recoil tritium atoms by oxygen, setting in at about 70% oxygen.[127] The evidence in this system was deduced using a complex kinetic treatment not applicable to carbon systems. If moderation is in fact occurring in the carbon systems, the acetylene production could show a sudden depletion when the tail of the energy distribution shifted below the threshold for acetylene production. The fraction of the carbon carried below the threshold would, of course, be in the lower energy range, and this would be consistent with the carbon atoms having insufficient energy to pick up a hydrogen atom and form methyne. Thus, assuming that methyne is involved in ethylene production, the operation of oxygen as a moderator at high concentrations would result in a depletion of the acetylene yield, an increase in the carbon monoxide yield, and no effect on the ethylene yield.

If the changes in slopes observed are indeed moderator effects as postulated, the finding must serve warning to experimenters who work with high concentrations of oxygen and nitrogen in recoil carbon systems. Experiments have been made in which nitrogen gas was used as the source of ^{11}C via the $^{14}N(p, \alpha)^{11}C$ reaction.[18,19,83] The high concentrations of nitrogen or nitrogen plus oxygen which partly composed the mixtures irradiated were either close to or into the region at which moderation would set in.

4. The High Oxygen Concentration Region

As the concentration of oxygen approaches 100%, the ethylene and acetylene productions approach nil (Figures 20, 21, 23, 24). This is reasonable and consistent with the absence of sufficient carbon to form C_2 fragments in pure oxygen. The carbon monoxide yields do not approach 100% at 100% oxygen (Figures 22 and 25). In isobutane the approximate extrapolation based on only 2 points gives a value about 96%; in normal butane a better extrapolation gives a value about 89%. It is possible that if accurate data were available at concentrations above 90% oxygen, they would show an upturn towards a carbon monoxide yield value closer to 100% at 100% oxygen. No more than a few percent of the missing activity could be carbon dioxide (which would not have been detected under the conditions of the experiments), considering the results of other experimenters. MacKay et al. observed (98±1)% carbon monoxide and 2% carbon dioxide from pure oxygen.[76] Dubrin et al. found 97% carbon monoxide from a substrate of 98.8% oxygen, 0.6% carbon monoxide and 0.6% carbon dioxide.[66] Stöcklin and Wolf made two experiments using $^{16}O(p, pn\alpha)^{11}C$, and their corrected results indicate about 2% carbon dioxide is formed.[102] Based on these data, one would expect yields of carbon monoxide approaching 100% at 100% oxygen in the butanes. However, the better extrapolation in the n-butane system does not support this supposition. Interesting questions remain unanswered. In what chemical form is the missing activity to be found? What factor is unique to the n-butane system? These questions were not investigated because the Brookhaven accelerators do not produce adequate activity in the high oxygen-concentration substrates.

B. The Structure Dependence Series; Yields of Hot Ethylene and Hot Acetylene

The oxygen used in this alkane series was added with the intention of obtaining yields representative of hot processes. Previously, other experimenters had chosen to work at 4.5% oxygen with this aim.[1c, 18, 82, 83] The same percentage oxygen was chosen for use in the present work. Figures 5, 6, 7, and 20-25 all indicate that yields measured at this fraction of oxygen appear to be out of the range of the large yield fluctuations near 0% oxygen, yet close enough to the ordinate to be little altered by competition.

The alkane-series data have been examined for underlying patterns by several methods. Attempts have been made to reaffirm with corrected data the yield correlations shown in Figures 2-4. The attempt to fit acetylene yields to a structure dependence like that shown in Figure 2 resulted in a poor fit. Defining the parameter A as the ratio of the number of primary carbons to the total number of carbons in the compound, we find that methane and ethane at A = 1 have acetylene yields near 31%. Neopentane at A = 0.8 (or A = 1.0, vide infra) has an acetylene yield near 32% as does cyclopentane for which A is zero. A large majority of the other compounds studied with A between 0.33 and 0.75 have acetylene yields below 27%, and n-heptane with an A = 0.29 yields only 21.3% acetylene. An examination was also made for a possible relationship between acetylene yield and the parameter B, defined as the ratio of the number of primary hydrogens to the total number of hydrogens in the molecule; but no correlation appeared here either.

With ethylene, however, the reverse was the case; most of the data cluster along a line if percentage ethylene yield is plotted against either A or B. While ethylene yield had formerly been correlated with B (Figure 3), it seems more reasonable that carbon atoms would collide with or interact with particular carbon-hydrogen groups like methyl, methylene, etc., rather than with specific hydrogen atoms. This supposition is consistent with the finding of Ache and Wolf that carbon atoms appear to interact with such groups within the substrate molecule.[18] Consequently a plot was made for ethylene yields against the parameter, A, Figure 28. The least-squares plot is seen to be a good fit for nine of the data, but five others are considerably removed from the line. (The same type of result is obtained for a plot against B.) It is worthwhile noting that the 4° carbon in neopentane and 2,2 dimethylbutane is undoubtedly not a direct participant in productive interactions. Two facts support this premise. First, access to the central carbon is extremely hindered. Second, insertion by carbon atoms into C–C single bonds has not been observed.[42] If the central carbon is dropped from consideration as a participant, the A values for neopentane and 2,2 dimethylbutane are 1.0 and 0.8, respectively. Ghost points are shown for these values in Figure 28 which fall much closer to the least squares plot.

The relationship between percentage carbon monoxide yield and C, the reciprocal of the number of hydrogen atoms in the molecule (Figure 4), was re-examined with the corrected data. A simple linear plot no longer seems like a complete expression of the relationship between these two parameters. For example, neopentane, n-pentane, and isopentane, all with C = 0.083, give carbon monoxide yields of 21.2%, 18.0%, and 15.5%, respectively. There is an even larger spread for the isomeric hexanes: 2,2 dimethylbutane, n-hexane, and 2,3 dimethylbutane.

The yields from the hydrocarbon series have also been tested for

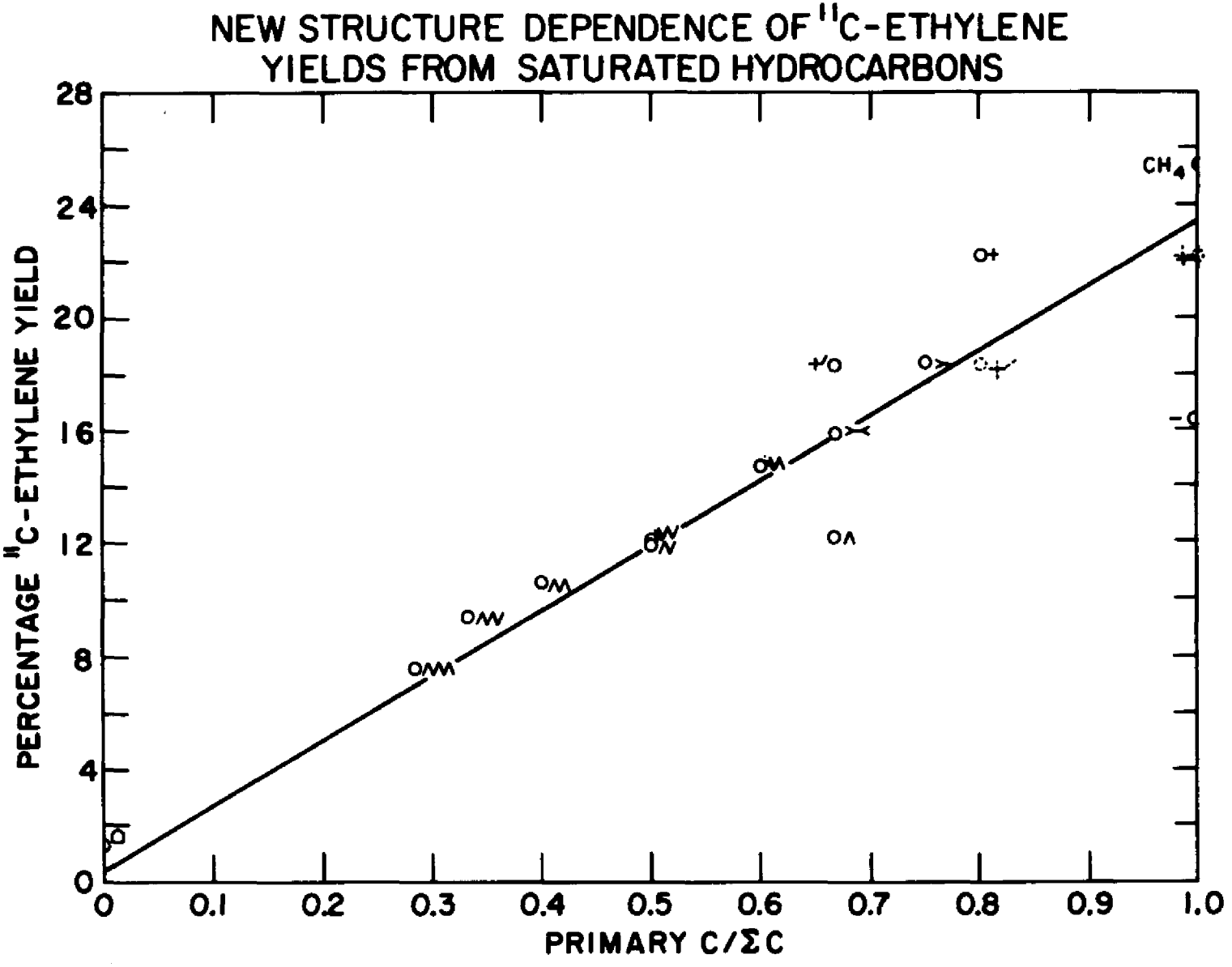

NEW STRUCTURE DEPENDENCE OF ^{11}C-ETHYLENE YIELDS FROM SATURATED HYDROCARBONS
PERCENTAGE ^{11}C-ETHYLENE YIELD
PRIMARY C/ΣC
0
4
8
12
16
20
24
28
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
CH_4

FIG. 28

fit by expressions of the type proposed by Rack et al.[84] and Clark and Voigt.[89] The latter authors used expressions of the type

$$\% \text{ Yield} = Ax + By + Cz$$

in which x, y, and z are the fractional amounts of hydrogen respectively in CH_3, CH_2, and CH groups of the substrate molecule. A, B, and C are empirically determined constants. The expressions were used to represent acetylene yield and ethylene-ethane combined yield from a variety of liquid hydrocarbons. It was found that acetylene yields in the present study could not be represented satisfactorily by the type of equation above. Either negative constants or wide deviations resulted from all combinations of compounds selected to evaluate the constants. However, a different set of parameters in the same expression was found to give acceptable agreement. Instead of considering the type of hydrogen in the substrate, we define the parameters, r, s, and t, to represent the fraction of carbon as CH_3, CH_2, and CH, respectively. In calculating these parameters for compounds containing the neo configuration, the central carbon is to be ignored for the reasons cited above. Thus for neopentane, $r = 1$, $s = t = 0$ and for 2,2 dimethylbutane, $r = 4/5$, $s = 1/5$, $t = 0$. These parameters are used in the expression

$$\% \text{ Yield Acetylene} = \alpha r + \beta s + \gamma t$$

in which α, β, and γ are again empirically determined constants. Parameters like r, s, and t were used by Rack et al.[84] to calculate the yield ratio $(\%C_2H_4 + \%C_2H_6)/\%C_2H_2$ for several liquid compounds in an attempt to demonstrate that ^{11}C insertion tends to be statistical in saturated hydrocarbons, a thesis which has not stood up well. The parameters used, however, did not include the important stipulated ignoring of 4° carbons.

In the present study, α, β, and γ are evaluated using the acetylene yields from the compounds ethane, n-butane, and isobutane, respectively.

The value 30.3 for α comes directly from the acetylene yield from ethane since there are only methyl groups in this compound. Inserting the value of α into the above equation for the substrate n-butane

$$\%C_2H_2 \text{ Yield} = 26.5 = (30.3)(2/3) + (\beta)(1/3) + (\gamma)(0)$$

gives $\beta = 22.6$. Similarly, $\gamma = 22.0$ is obtained from isobutane. Acetylene yield values calculated from these constants and the parameters r, s, and t are set forth in Table 9 for the other eleven compounds. Reasonable agreement is seen for all compounds except cyclopentane, for which the calculated value is nearly 30% low. The obvious difference between this compound and all the others is its cyclic structure.

The values of the constants α, β, and γ give a reflection of the acetylene production from the different groups. The methyl group is seen to be a considerably but not overwhelmingly stronger acetylene producer than the other two groups. The large value of γ – nearly the same as β – is somewhat surprising in view of the more complicated mechanism necessary to form acetylene from attack at a tertiary carbon. The accepted route for acetylene production involves attack at a carbon bonded to 2 or more hydrogen atoms.[61] The ratio of acetylene production from methyl versus methylene groups has been found to be ~1.9 by two different methods.[18] (However, one of these methods is inconclusive when re-evaluated with corrected data. See section IV D.) The above treatment of the present results is more consistent with a ratio $\alpha/\beta = 1.3$ to 1.4. The value of α/γ which describes the ratio of acetylene production from methyl versus tertiary C–H is the same. The approximations and limitations inherent in such ratio calculations have already been discussed in section I F. In the present calculations the choice of compounds for computing the constants is arbitrary. Acetylene yields from methane or neopentane could have been chosen to define α with very little change in the values. The

Table 9

COMPARISON OF ACTUAL AND CALCULATED YIELDS OF ^{11}C-ACETYLENE FROM SCAVENGED SATURATED HYDROCARBON SYSTEMS

Substrate	Percentage ^{11}C-Acetylene Yield	
	Experimental	Calculated
Methane	31.2	30.3
Propane	23.8	27.7
n-Pentane	25.4	25.7
n-Hexane	25.7	25.2
n-Heptane	21.3	24.8
Isopentane	26.6	25.1
Isohexane	24.5	26.4
Neopentane	32.3	30.3
2,2 Dimethylbutane	30.8	28.7
2,3 Dimethylbutane	26.7	27.5
Cyclopentane	31.9	22.6

butanes were chosen to compute β and γ, since the values of the yields were precisely determined for these compounds in the oxygen dependence study.

A different situation prevails for the ethylene yields, which can be fitted fairly well by either the carbon-fraction parameters or the hydrogen-fraction ones. The former parameters are used both for consistency and because carbon atom attack on entire groups seems to have been verified.[18] The ethylene yields are calculated from the equation

$$\% \text{ Yield } C_2H_4 = \delta r + \epsilon s + \zeta t \ .$$

The constant δ was evaluated from the ethylene yield from neopentane to be 22.2. (This choice was made simply because more measurements were made on neopentane than on either methane or ethane. However, the differences in ethylene yields for these three compounds are far outside of experimental error.) ϵ was determined to be 1.3 using cyclopentane. (If n-butane had been used to define ϵ, 1.8 would have been its value, substantially the same, and changing the over-all agreement between calculated and experimental values in Table 9 by less than 1%.) The value of ζ, 6.8, was again found by using the ethylene yield from isobutane. The yield values calculated using these constants are given in Table 10.

The values of δ, ϵ, and ζ indicate that ethylene production stems most pronouncedly from the methyl groups of the substrate, about 17:1 compared to methylene and 3.3:1 compared to tertiary C–H. This suggests that there should be substantial fit between ethylene production and the fraction of carbon as methyl in the substrate – already demonstrated in Figure 28. It would be surprising if any ethylene were produced from tertiary carbons. Perhaps methylene is responsible for at least this fraction of the ethylene yield. Alternatively, perhaps the presence of tertiary carbons in the substrate molecule promotes ethylene production in-

Table 10

COMPARISON OF ACTUAL AND CALCULATED YIELDS OF ^{11}C-ETHYLENE FROM SCAVENGED SATURATED HYDROCARBON SYSTEMS

Substrate	Percentage ^{11}C-Ethylene Yield	
	Experimental	Calculated
Methane	25.5	22.2
Ethane	16.4	22.2
Propane	12.2	15.2
n-Butane	12.0	11.8
n-Pentane	10.6	9.7
n-Hexane	9.4	8.3
n-Heptane	7.6	7.2
Isopentane	14.7	15.0
Isohexane	12.1	12.6
2,2 Dimethylbutane	18.3	18.1
2,3 Dimethylbutane	15.9	17.1

directly, for example by weakening some of the bonds in the molecule. The C–C bond dissociation energy is less if one of the carbon atoms is tertiary than if only primary or secondary atoms are involved.[127a] The amount of yield in question is small, though; since all the molecules examined with tertiary C–H's have at least 3 methyl groups, 10% of the total ethylene yield is the maximum that could arise from the tertiary group.

A new interesting correlation exists between Figure 28 and Table 10. The compounds in the table with the greatest deviation between actual and calculated yields – ethane, propane, and especially methane – give the poorest fit to the least squares plot in the figure, with similar relative deviations. The reason for the poor agreement of these three compounds is not evident, but a comment below about methane may be applicable (vide infra).

C. New Descriptions of Total Hot Hydrocarbon Production

Finally, a parameter has been sought which will correlate some property of the substrate with the total hydrocarbon production in the systems. For this endeavor, a partial return to first principles was made. The parameter was developed as follows. Hydrocarbon products are considered to arise from the interactions of carbon atoms in the reactive energy range with hydrocarbon molecules. Carbon monoxide arises from the interactions of thermal carbon atoms with oxygen. Since the systems studied are preponderantly composed of hydrocarbon, most collisions of the energetic atoms will be with the hydrocarbon molecules. These collisions will be of two general types: moderating collisions in which the carbon atom is released from the collision complex at a lower kinetic energy, and reactive collisions which result in the formation of some isolable hydrocarbon product. The moderating collisions will tend to produce carbon monoxide by lowering the kinetic energy of the carbon atoms towards thermal, where they

will be scavenged in the presence of 4.5% oxygen. (Carbon monoxide production from the reaction of energetic carbon atoms with oxygen may be neglected on statistical grounds.)

Since those substrates which are better moderators will promote production of more carbon monoxide, a measure of moderating power is needed. In the energy range where the fate of the carbon atom is being determined, soft sphere collisions must be a principal mode of energy loss. Accordingly, the total number of degrees of freedom of the molecules, 3N (where N is the number of atoms in the molecule), was chosen as proportional to the energy absorbing capacity and therefore the moderating power of the compound. If (100% -%CO) is used as a measure of the total hydrocarbon production, then this quantity should be inversely proportional to the number of degrees of freedom. One additional property of the substrate affects the fraction of carbon atom-hydrocarbon molecule interactions that have the potential for hydrocarbon production. Naturally, grazing or glancing collisions will have little likelihood of giving rise to hydrocarbon products, although energy can be transferred in such collisions. Moreover, different sized hydrocarbon substrate molecules will have different ratios of what might be termed "reactive core" to "unreactive shell."

Two approaches have been made to finding a parameter based on the above considerations. In the first of these, the gross volume of the molecule is used as a measure of the reaction cross section for hydrocarbon production. Such a choice is based on an implicit assumption that the "unreactive shell" is more like a fixed thickness rather than a fixed proportion of the thickness of the molecule. The resultant relationship may be expressed as

$$(100\% - \%CO) = \frac{b}{f} \Sigma$$

where b represents the volume of the molecule, f is its number of de-

grees of freedom, and Σ is the constant of proportionality. Σ has been evaluated from this expression for the substrates studied (Table 11). The molecular volume measure used in the calculations is the covolume, b, from the van der Waals equation of state. (The value of b is actually equal to four times the volume of the molecules in a mole since it takes account of the excluded volume.) The covolume was found to be a good measure of molecular size for hot atom collision cross sections by Root.[128] The values of the covolume were computed from the critical temperatures and pressures of the hydrocarbons using the relationship $b = RT_c/8P_c$.[129] The calculated covolumes are set forth in Table 12. The values of the critical constants were obtained from the American Petroleum Institute Research Project 44.[130] The constancy of Σ for the various substrates tests the validity of the assumptions. The results for the hydrocarbons studied may be seen in Table 11. The values of Σ are relatively constant, considering the many simplifying assumptions made in the derivation of the expression. The value for methane might be expected to agree poorly with the other values, since methane is the first member of the homologous series. The value for cyclopentane also shows some difference from the others. There are too many places in which the validity of the simplifying assumptions could break down to attempt a diagnosis of the source of the deviation.

The second approach to finding a collision parameter follows more classical treatments. Assuming spherical particles, the collision cross section for a moving particle in a stationary gas (a good model where the velocity of the carbon atom is much greater than the velocity of the substrate molecule) will be proportional to $(r_1 + r_2)^2$ where r_1 and r_2 represent the radii of the moving and stationary particles, respectively.[131] Considering that grazing collisions do not con-

TABLE 11

Σ-VALUES FOR SCAVENGED ALKANE SUBSTRATES

Substrate	$\Sigma \times 10^{-3} (\frac{\text{mole}}{\text{liter}})$
Methane	25
Ethane	29
Propane	29
n-Butane	29
n-Pentane	29
n-Hexane	29
n-Heptane	28
Isobutane	30
Isopentane	30
Isohexane	30
Neopentane	29
2,2 Dimethylbutane	29
2,3 Dimethylbutane	31
Cyclopentane	33

TABLE 12

COVOLUMES

Substrate	b (liters/mole)
Methane	0.04271
Ethane	0.06500
Propane	0.09037
n-Butane	0.1163
n-Pentane	0.1447
n-Hexane	0.1743
n-Heptane	0.2052
Isobutane	0.1163
Isopentane	0.1438
Isohexane	0.1706
Neopentane	0.1408
2,2 Dimethylbutane	0.1637
2,3 Dimethylbutane	0.1656
Cyclopentane	0.1179

tribute to the cross section for hydrocarbon production we again make the assumption that the sum $r_1 + r_2$ should be diminished by some fixed quantity. The following procedure was used. The radii of the substrate molecules were calculated from the values of b, assuming the molecules to be spherical. The constant of proportionality, Γ, was evaluated in the expression

$$(100\% - \%CO) = \Gamma \frac{(r_1 + r_2)^2}{f}$$

for ten of the 14 substrates studied. Values used for r_1 ranged from +0.77 Å (the covalent radius of the carbon atom) to −1.1 Å to allow for overlap. Then the average deviation divided by the average was calculated for each set of Γ's corresponding to an r_1. This quantity reached a minimum of 1.9% for a set of Γ's with $r_1 = -0.7$ Å. The set of Γ's for all the substrates studied using this value of r_1 appears in Table 13. Taken at face value, the −0.7 Å value of r_1 supports the premise that glancing collisions have a very low probability of leading to reaction. In fact, the implication seems to be that the substrate molecule must suffer a substantial collision with the hot carbon atom if the encounter is to yield hydrocarbon products. The same comments made about the Σ-values apply here. Both sets of results seem to indicate that the number of degrees of freedom of the substrate is a measure of moderating power of the medium.

This result has an important implication for the structure-yield theories. The moderating power of the medium determines the energy spectrum of the carbon atoms in that medium. The treatment above demonstrates that in addition to the various structural parameters, the energy distribution of the carbon atoms changes with different substrates. Taken in conjunction with the accepted theory that the production cross sections are energy dependent, it implies that the additional factor, moderation, is contributing to determination of the yields. It is clear that refined structure-yield theories will have to include a factor for

TABLE 13

Γ-VALUES FOR SCAVENGED ALKANE SUBSTRATES

Substrate	$\Gamma \times 10^{-2}$ ($\AA^{-2}$)
Methane	13
Ethane	14
Propane	14
n-Butane	14
n-Pentane	14
n-Hexane	14
n-Heptane	14
Isobutane	14
Isopentane	14
Isohexane	15
Neopentane	14
2,2 Dimethylbutane	14
2,3 Dimethylbutane	15
Cyclopentane	16

moderation power. In the present type of experiments, it is difficult to separate the variables. One method of circumventing the difficulty would be experiments involving accelerated beams of isoenergetic carbon atoms.

D. Implications of the Density Effect

The density effect described in section III B has apparently long gone unrecognized and affected the results of a number of workers. In addition to the comparative data cited[3] in the case of isobutane, other results of Stöcklin et al.[20] and Stöcklin[15] seem appreciably low, judging from the yield values at 4.5% oxygen. Clark and Voigt[89] have used a method which entails passage of macroscopic quantities of ^{11}C-carbon dioxide through a counting chamber. The results of the assay were used in the normalization of product yields. If the counting apparatus used was of the same geometry as previously shown[132] the observed carbon dioxide activity would be incorrectly high. Finally, consider the plot of acetylene yield versus the ratio of total methyl groups to total carbon atoms in the substrates,[18] made before the density effect was discovered. This plot was extrapolated to the ordinate to obtain a ratio $\cong$1.93 of acetylene production from methyl versus from methylene. If the graph is replotted, the data do not fit a straight line as well as they did before. In addition, when a straight line is used to fit the data, the best line has a lower slope and the production ratio becomes 1.3 to 1.6. This range agrees better with the mathematically determined value of the ratio, 1.3-1.4 (section IV B), than the one, 1.88, from a more direct and elegant method, using specifically deuterated propanes[18] (see section I F).

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BIOGRAPHICAL STATEMENT

The author, Peter Lieberman, was born in Brooklyn, New York, in 1937 and raised there. He attended Public School #208 and then Midwood High School from which he was graduated magna cum laude in 1955. Between 1955 and 1959 he was a student at Oberlin College, Oberlin, Ohio, receiving an A. B. with a major in chemistry in 1959. He spent the academic year 1959-1960 at Columbia University assisting in research on isotope separation. In the fall of 1960 Mr. Lieberman accepted a position on the teaching faculty of Brooklyn College and was Lecturer in chemistry for the following two academic years. In the fall of 1962 he was awarded a National Defense Education Act Fellowship and entered the initiating doctoral program at the City University of New York. The research upon which this dissertation is based was performed at the Brookhaven National Laboratory Chemistry Department in the three years from September 1963 to September 1966 during which Mr. Lieberman was a Technical Collaborator at the Laboratory.