

REACTIONS OF ENERGETIC CARBON ATOMS  
PRODUCED BY  $^{12}\text{C}(p, pn)^{11}\text{C}$  IN ALKANES AND ALKYL CHLORIDES;  
MODERATOR EFFECTS AND DEUTERIUM ISOTOPE EFFECTS

by

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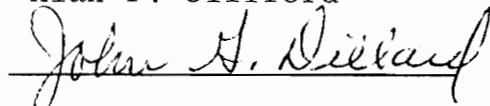
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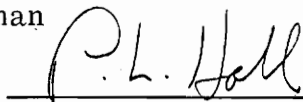
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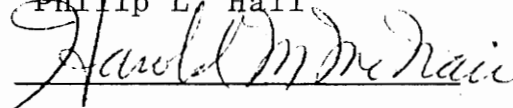
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This work is dedicated  
to my  
mother and father  
and to my husband,  
George.

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# CHAPTER I

## INTRODUCTION

### A. Preliminary Remarks

The chemical reactions of atomic carbon have been the focus of an increasing volume of experimental and theoretical activity. Although the study of this simplest of carbenes now proceeds by a variety of techniques, the bulk of present mechanistic information is based on product distributions in nuclear recoil systems. Recoil following nuclear transformation has proven to be an effective method for the preparation of free carbon species under controlled conditions. Little decomposition of substrate molecules occurs under these experimental conditions, so that mechanistic arguments are not complicated by carbon atom reactions with substrate fragments. Carbon atoms produced by nuclear recoil possess very high translational energies and are called "hot" atoms.

Hot atom chemistry is unique in at least two ways. Hot species exhibit unusually high reactive collision efficiencies, and are believed to react within ten collisions (and perhaps in the first collision) after reaching the reactive energy region. In addition, no Boltzman distribution of energies is present, so that hot atom reactions are not susceptible to a normal kinetic

analysis.

The concerns of hot atom chemistry are identical to those of other areas of chemical kinetics. Of interest are the microscopic pathways for reaction, the chemical intermediates and products formed, the electronic state and charge of the species involved, the energy of these species when reaction takes place, and the product distribution as a function of the energy of the reacting species.

#### B. Research Objective

This work was undertaken for the purpose of establishing the mechanism by which  $^{11}\text{C}$ -labeled ethylene is formed in the reaction between carbon-11 atoms generated by the nuclear reaction  $^{12}\text{C}(p,pn)^{11}\text{C}$  and hydrocarbon molecules. A second goal was to assess the electronic states of the carbon-11 species responsible for the formation of the major  $^{11}\text{C}$ -labeled products, such as carbon monoxide- $^{11}\text{C}$ , acetylene- $^{11}\text{C}$  and ethylene- $^{11}\text{C}$ .

Three series of experiments were performed. In order to evaluate the mechanism of ethylene- $^{11}\text{C}$  formation, a number of specifically-deuterated ethanes and propanes were irradiated and the resulting deuterated ethylenes- $\text{d}_0$ ,  $\text{d}_1$ ,  $\text{d}_2$ ,  $\text{d}_3$  and  $\text{d}_4$  were separated by gas chromatography. Once separated, the  $^{11}\text{C}$ -labeled ethylenes were measured by gas phase proportional counting. The distribution of

products was expected to shed light on the mechanism of ethylene formation in hydrocarbons. The observed results were used to test two proposed mechanisms for ethylene production.

A second investigation was carried out with the objective of producing evidence concerning the electronic states of the carbon atoms undergoing reaction. Rare gas additives have been used extensively as moderators to study the kinetics of hot reactions in tritium and halogen recoil chemistry. However, there is also the possibility that these rare gases may interact with the reacting species by inducing spin changes. Very little is known presently about how this latter type of interaction may affect the products and mechanisms involved in carbon-11 recoil reactions in the gas phase. Xenon has been shown<sup>1</sup> to be quite effective in promoting intersystem crossing between low-lying electronic states of carbon. The present experiment was undertaken to compare the effect of xenon on the product yields with those reported previously in helium and neon,<sup>2</sup> which have been found to be much less efficient spin converters. Ethane containing 4.5% O<sub>2</sub> scavenger was chosen as the substrate in order to be directly comparable to the previous study.

A third set of experiments was designed to elucidate the effect of the presence of halogen on product formation in the reactions of hot carbon atoms with a variety of

substrate molecules. Previous studies of carbon-11 reactions in alkyl halides<sup>3,4</sup> have demonstrated the sharp reduction in ethylene-<sup>11</sup>C yield caused by substitution of halogen for hydrogen in the substrate molecules. For example, ethylene yield is 25% of the gas phase activity in methane, but only 8% in methyl fluoride.<sup>5</sup> Thus, in this set of experiments carbon-11 atoms were reacted with equimolar mixtures of protonated and perdeuterated alkyl chlorides containing oxygen scavenger. Distribution of the isotopic deuterated ethylenes was expected to provide information concerning the electronic species of carbon involved in ethylene formation.

### C. Principles of Hot Atom Chemistry

Hot atom chemistry concerns itself with those reactions induced by the high translational energy of one of the reactants, and encompasses the entire chemically-interesting energy range from approximately one to twenty electron volts. Processes at extremely-high energies are not of interest, since they involve non-specific methods of energy loss, such as ionization and excitation of the medium and not chemical, i.e., bond formation, processes.

Hot atom chemistry enlarges the field of chemical kinetics to include reactants which are not at thermal equilibrium. Reactions are studied where sufficient energy is available to open many pathways other than the minimum

energy pathway along the potential energy surface. This leads to a variety of products not observed in systems at thermal equilibrium. This energy is provided by a single hot species, which may be produced by photolysis, pulse radiolysis, in an arc, or as a consequence of nuclear transformation. The following discussion will be limited to the method of nuclear recoil, which was the technique used in this work.

Numerous reviews of hot atom chemistry have now appeared.<sup>6-12</sup> In addition, reviews of some related<sup>13,14</sup> topics contain information pertinent to this subject.

There are two chief advantages of nuclear recoil as a source of hot atoms. Nuclear reactions affect only a small number of molecules directly, so that they can provide hot atoms without serious decomposition of the medium. This is an important consideration, since carbon atoms may react efficiently with any molecular fragments and seriously alter the product spectrum. In recoil systems the carbon atom is a truly isolated reactant. In a typical sample containing  $10^{20}$  molecules of hydrocarbon, only  $10^9$  molecules may be altered in the production of carbon-11. Furthermore, the carbon atom will react in an area well-removed from the site of its birth, so that chances of its reacting with radicals formed in the same process are vanishingly small.

Another advantage of recoil systems is that hot atoms produced in this way are generally radioactive. Methods of

detection of radioactive species are extremely sensitive, so that for example, only  $10^7$  molecules of  $^{11}\text{C}$ -labeled product can be identified in the presence of  $10^{20}$  molecules of substrate.

Unfortunately, no precise evaluation is possible of the energy at which each reaction takes place. Instead, one obtains data over the integrated energy scale of many collisions, starting at some defined high energy and extending into the thermal region.

Table I shows various nuclear reactions for the production of carbon-11 and the carbon recoil energies. This kinetic energy is a consequence of conservation of momentum during the emission of particles or gamma-rays by the nucleus. In most cases the recoil energy of the product nucleus is well in excess of chemical bond energies. The species will ionize rapidly by losing all electrons with Bohr orbital velocities less than the translational velocity of the hot species. Energy is lost by collisions of the resulting ion with the medium. As the particle velocity decreases to that of electrons in a given orbital, electron exchange collisions become important. The equilibrium charge of the recoil species gradually decreases until it becomes neutral. Further energy loss continues by collision with the medium until reaction occurs.

A considerable fraction of the atoms may reach thermal energies before reacting, and it is desirable to be able to



TABLE I  
Some Nuclear Reactions for Carbon-11 Production<sup>6</sup>

Reaction	Incident particle energy	Recoil energy of <sup>11</sup> C
<sup>12</sup> C(p,pn) <sup>11</sup> C	>20 MeV	1.8 MeV (mean)
<sup>12</sup> C(n,2n) <sup>11</sup> C	>18 MeV	1.1 MeV (max)
<sup>12</sup> C(γ,n) <sup>11</sup> C	>27 MeV	0.4 MeV (mean)
<sup>14</sup> N(p,α) <sup>11</sup> C	> 6 MeV	2.1 MeV (max)
<sup>16</sup> O(p,pnα) <sup>11</sup> C	2-3 GeV	-

distinguish the products of these reactions. Various properties have been recognized by which high energy reactions can be distinguished from their thermal analogs:

1) Small amounts of known radical scavengers will attenuate or eliminate the yields of thermal products, but have little effect on hot product yields. This property is a result of the high collision efficiencies of hot species, which are orders of magnitude greater than those observed in thermal systems. The scavenger will not significantly affect hot reactions, since a hot atom is unlikely to encounter it during the few collisions of its chemically effective existence. Figure 1 shows the variation in yield of the major labeled products in the methane-oxygen system. Carbon monoxide is formed from the reaction of carbon atoms with oxygen because the heat of reaction to form carbon dioxide in this reaction ( $-265$  kcal/mol) is greater than the sum of the dissociation energies of two C-O bonds ( $254$  kcal/mol).<sup>17</sup> In other words, the carbon dioxide molecule cannot contain the energy produced by its formation. The curves indicate that oxygen is an effective scavenger for thermal carbon atoms at concentrations of a few percent oxygen. But oxygen also reacts efficiently with energetic carbons, and concentrations must be kept low in order to avoid competing with the hydrocarbon for hot reaction. The presence of a scavenger serves the additional function of

$^{15}\text{C}$  PRODUCT YIELDS FROM  
METHANE / OXYGEN SYSTEM

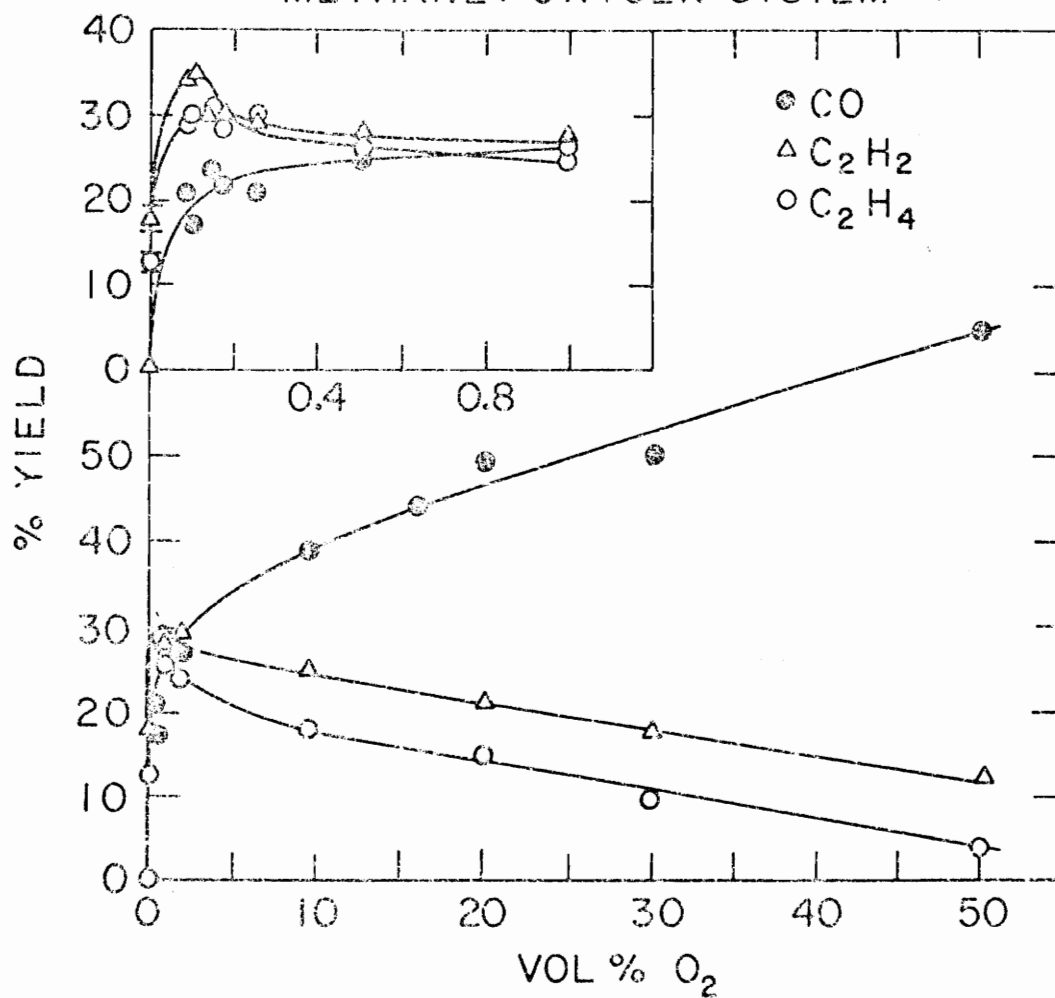
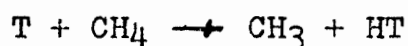


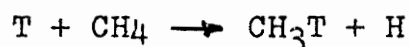
FIGURE 1

removing hydrogen atoms and other radicals produced by the radiation field. These radicals may react efficiently with the unsaturated primary recoil products and affect their yields.

2) One of the most noticeable features of hot reaction systems is the appearance of products not formed in thermal reactions. These are the result of the availability of higher-energy pathways across the potential energy surface. An excellent example is the reaction of hydrogen atoms with methane.<sup>8</sup> The only product of thermal reaction is hydrogen abstraction, which occurs at and above the 8-kcal threshold:



However, at energies greater than two electron volts (46 kcal/mol), substitution becomes an important competing process:



3) Because the bulk of the energy necessary for hot reaction is supplied by a single species, product yields are comparatively insensitive to temperature. This is not true if the stabilized hot product can undergo a secondary temperature-dependent reaction.

4) Hot product yields are sensitive to the presence of inert substances. Since the energetic atom cannot undergo reaction until it enters the range of chemical bond energies, it must lose energy by countless collisions

with molecules in its environment. If the ratio of inert molecules to reactive molecules is high, the hot atom has a better chance of reaching low energies without reacting. This has the effect of enhancing yields of thermal products and attenuating hot product yields. This is the classical way of looking at energy moderation. Since the subject is of considerable importance in this work, it will be expanded upon at some length.

#### D. Moderators

The purpose of a moderator is to reduce the number of reactive collisions occurring in the hot zone. According to classical mechanics, the maximum energy that a recoiling atom can transfer in an elastic collision with another atom is:<sup>6</sup>

$$E_M = \frac{4m_1m_2}{(m_1+m_2)^2} E_I$$

where,  $E_M$  = maximum energy transferrable to the struck atom

$E_I$  = kinetic energy of the incident atom

$m_1$  = mass of the incident atom

$m_2$  = mass of the struck atom

Because the energy transfer reaches a maximum at  $m_1 = m_2$ , it is evident that the recoiling atom will undergo fewer collisions during the slowing-down process in a medium in which its mass is similar to that of the surrounding atoms.

For this reason, and because noble gases tend not to form permanent bonds, the best moderator has been considered to be a noble gas whose mass is most similar to that of the hot atom. Thus, helium was used in tritium systems, and neon was used with fluorine-18 and carbon-11.

A moderator may influence the product spectrum further by collisional stabilization of excited products and intermediates. For example, it has been suggested that the unexpectedly high ratio of  $HT/C_2H_5T$  in recoil tritium-ethane experiments with helium moderator is due to superior energy transfer during collisions of excited  $HT$  with helium.<sup>16</sup> Generally speaking, the hydrocarbon substrate furnishes better moderation for excited intermediates, so that the introduction of a noble gas (at constant total pressure) results in less energy loss per collision, and higher yields of fragmentation rather than stabilization products.

Furthermore, a moderator may alter the distribution of electronic spin states among the hot atoms, thereby seriously affecting the product spectrum. For this process to be important, the hot atom must have relatively low-lying metastable states in which emission to ground is electric-dipole forbidden. This limitation arises from the requirement that the excited atom be sufficiently long-lived to undergo collisions and hence reaction, rather than be removed by radiation to the ground state. In hot atom chemistry the most familiar example of noble gas-facilitated

intersystem crossing has been that of the carbon atom. This aspect of moderator activity will be developed more fully in the Discussion part of this thesis.

#### E. Special Properties of Carbon

Carbon reactions constitute a special case in hot atom chemistry, partly because the very high heat of formation of atomic carbon (170.9 kcal/mol)<sup>17</sup> makes it an unusually reactive species, even at thermal energies. For example, the presence of 99.5% neon moderator in ethylene<sup>8</sup> fails to make more than quantitative differences in the product spectrum. This result in a system where carbon should be well thermalized indicates that carbon atoms which have reached thermal energies are still able to react by pathways similar to those of the hot species. Evidently, the threshold for these reactions is somewhere below the mean thermal energy.

Carbon cannot form final products via one-step reactions as can such monovalent species as tritium and chlorine. In most carbon reactions the primary adduct is a radical or carbene which must undergo further reaction before the final product is reached. Therefore, many reactive intermediates, such as CH, CH<sub>2</sub>, CH<sub>3</sub>, and others, must be considered in interpreting experimental results in terms of reaction mechanisms.

In as much as the recoil carbon is produced in a

highly ionized state, the possibility of its reaching chemical bond energies while still ionized must be taken into consideration. The adiabatic principle<sup>19</sup> offers a basis for predicting the charge state of such species which have undergone many charge-exchange collisions with the medium. This principle states that the probability of an electronic transition on collision is maximum when the time of the collision corresponds to the frequency ( $E/h$ ) of the transition. The relative velocity  $v_{\max}$ , for maximum cross section of a process characterized by an internal energy change  $\Delta E$ , is

$$v_{\max} = \frac{|\Delta E|a}{h}$$

where  $a$  is a dimension of the order of  $7 \times 10^{-8}$  cm,<sup>20</sup> and  $h$  is Planck's constant. Then  $E_{\max} = \frac{1}{2}mv_{\max}^2$ , and

$$E_{\max} = \frac{1}{2} m \frac{(\Delta E)^2 a^2}{h^2}$$

For carbon species where  $m = 11$ ,  $E_{\max} = 1600(\Delta E)^2$  eV. This principle has been applied by Marshall, et al.,<sup>18</sup> to recoil carbon in ethylene and in oxygen and they determined that, at least in these substrates, carbon is expected to react as a neutral atom. Table II shows similar calculations for carbon in ethane and in certain rare gases which suggest that in helium and neon, some fraction of carbons may reach the reactive energy range as  $C^+$ . For example, in ethane the ionization cross section for ground state carbon



Table II

## Application of the Adiabatic Principle to Carbon

Charge transfer process	M=C <sub>2</sub> H <sub>6</sub>		M=He		M=Ne		M=Xe	
	$ \Delta E ^*$ eV	$E_{\max}$ eV	$ \Delta E ^*$ eV	$E_{\max}$ eV	$ \Delta E ^*$ eV	$E_{\max}$ eV	$ \Delta E ^*$ eV	$E_{\max}$ eV
(1) C( <sup>3</sup> P)+M→C <sup>+</sup> +M+e <sup>-</sup>	11.2	2 × 10 <sup>5</sup>	11.2	2 × 10 <sup>5</sup>	11.2	2 × 10 <sup>5</sup>	11.2	2 × 10 <sup>5</sup>
(2) C( <sup>1</sup> D)+M→C <sup>+</sup> +M+e <sup>-</sup>	10.1	1.6 × 10 <sup>5</sup>	10.1	1.6 × 10 <sup>5</sup>	10.1	1.6 × 10 <sup>5</sup>	10.1	1.6 × 10 <sup>5</sup>
(3) C <sup>+</sup> +M→C( <sup>3</sup> P)+M <sup>+</sup>	0.4	2.8 × 10 <sup>2</sup>	13.3	2.1 × 10 <sup>5</sup>	10.3	1.3 × 10 <sup>5</sup>	0.9	9.7 × 10 <sup>2</sup>
(4) C <sup>+</sup> +M→C( <sup>1</sup> D)+M <sup>+</sup>	1.4	3.1 × 10 <sup>3</sup>	14.4	3.3 × 10 <sup>5</sup>	11.4	2.1 × 10 <sup>5</sup>	2.0	6.4 × 10 <sup>3</sup>

\*Ionization Potentials C<sub>2</sub>H<sub>6</sub> 11.65, He 24.48, Ne 21.56, Xe 12.13, C(<sup>3</sup>P) 11.23. From R.W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1965, and C(<sup>1</sup>D) 10.1 eV from Reference 18.

(reaction 1) begins to decline at energies below  $10^5$  electron volts, but the cross section for neutralization (reaction 3) reaches a maximum about 300 eV. In other words, the ions will have a high probability of being neutralized at very low energies where ionization is no longer probable. However, in the case where the medium is helium, the maximum probabilities for ionization and for neutralization occur at approximately the same energy. Where cross sections overlap in this fashion it is difficult to predict the final state of the hot species. Where some material of lower ionization potential (such as ethane) is present, a sufficient number of collisions may occur with the carbon to ensure neutralization. This probability can be calculated once the absolute cross sections are known. Electron capture and loss cross sections have been measured for carbon<sup>21</sup> with energies from 10 to 65 keV in collisions with rare gases and with hydrogen, nitrogen and oxygen. Massey's adiabatic criterion<sup>19</sup> was found to apply in all investigations of electron capture by fast particles which were tested. However, the energy range covered was not sufficient to show whether or not the cross section maxima occurred where predicted.

The electronic state of carbon also may be predicted using the adiabatic principle.<sup>8</sup> Such a treatment indicates that only relatively low-lying states such as the  $C(^3P)$ ,  $C(^1D)$  and  $C(^1S)$  would be expected to survive to the

chemically reactive energy range. Kinetic data have been reported for the interactions of these states of carbon with various hydrocarbons and small molecules<sup>22-26</sup> and with the rare gases.<sup>1</sup> The existence of these data for near-thermal reactions provides a foundation on which the results in hot systems can be interpreted.

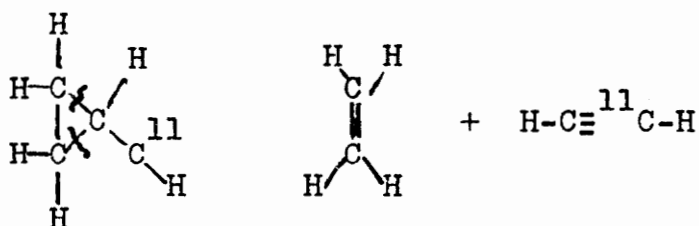
#### F. Review of Pertinent Literature

Dodson and Miller<sup>27</sup> first proposed that chemical (and not purely physical) interactions were responsible for the products observed in recoil systems. Since then a great volume of work has been performed to relate the products in recoil carbon systems to their mechanisms of formation.

Wolf, et al.,<sup>28</sup> first suggested that insertion reactions might play a part in hot carbon chemistry. They proposed that products might be formed by "the insinuation of a  $\text{CH}_2$ : between the methyl and carbonyl" carbons of acetamide. Support for the intermediacy of methylene in hot systems came from the finding of cyclopropane as a product of the irradiation of ethylene.<sup>29</sup> Further evidence was the report of Stöcklin and Wolf<sup>30</sup> of the production of one-carbon build-up products (for example, propane from ethane) by the insertion of methylene into carbon-hydrogen bonds.

MacKay and Wolfgang<sup>31</sup> explained the products observed in ten different hydrocarbons by the insertion of carbon atoms into alkyl carbon-hydrogen bonds. Convincing

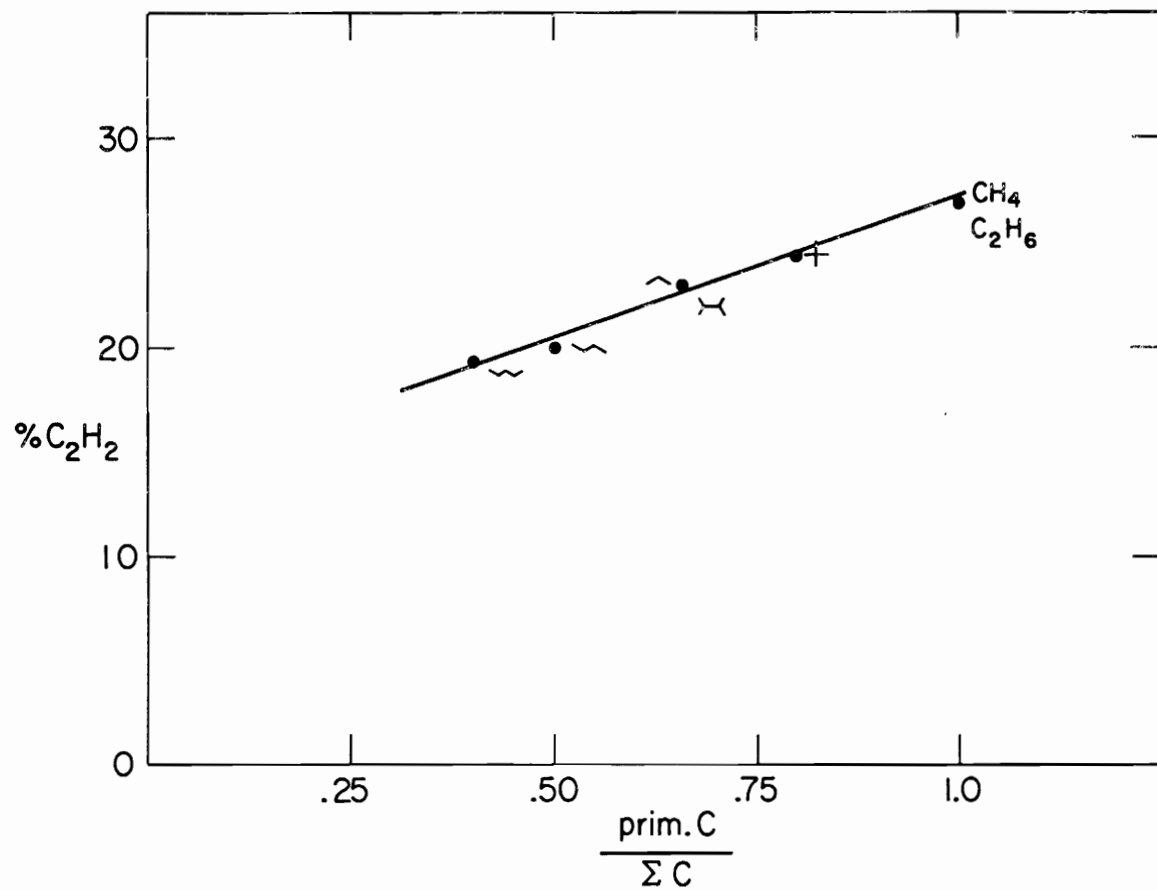
evidence for this mechanism was the unusually high yield of acetylene- $^{11}\text{C}$  found in cyclopropane. They argued that decomposition to acetylene should be particularly favored because stable products can be formed by simple electronic rearrangement of the excited intermediate with little nuclear motion.



This paper included the first mention of the spin state of the carbon undergoing reaction. Carbon was assumed to be in the ground state triplet.

Stöcklin and Wolf<sup>32</sup> reported the structure dependence shown in Figure 2 of the acetylene- $^{11}\text{C}$  yield in simple hydrocarbons. Carbon atoms were found to have an extremely high cross section for reaction with methyl groups. They concluded from competition experiments with hydrocarbon-oxygen mixtures that the reactivity of a non-thermal carbon with an oxygen molecule is about six times greater than the reactivity with a C-H bond.

An investigation of the isotopic composition of the acetylene- $^{11}\text{C}$  from a large variety of perdeuterated and specifically-deuterated compounds<sup>33</sup> produced results which were consistent with the insertion mechanism. Evidence was produced for a second pathway, involving high-energy

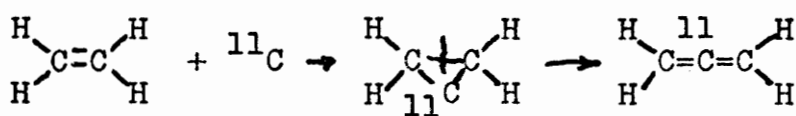


STRUCTURE DEPENDENCE OF THE ACETYLENE YIELD<sup>32</sup>

FIGURE 2

stripping to form  $^{11}\text{C}_2$  or some other intermediate. This finding was supported by the later work of Lambrecht, Furukawa and Wolf.<sup>34</sup>

MacKay, et al.,<sup>35</sup> first suggested that hot carbon may insert into carbon-carbon double bonds in 1961. They invoked a cyclic addition complex which ruptured at the



bond joining the two hydrogenated carbon atoms. Degradation of the labeled allene formed in ethylene<sup>18,36,37</sup> showed a high percentage of recoil carbon incorporated in the central position. The ratio of center-labeled to end-labeled allene- $^{11}\text{C}$  was 1.8 in the gas phase, demonstrating the preference of carbon for double-bond insertion compared to C-H insertion. In 95% neon moderator the ratio was 3.2, indicating the slightly greater selectivity of thermal carbon.

### C. Chemical Evidence for Methyne

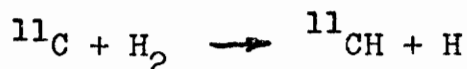
Very little is known about the chemistry of the methyne intermediate which, nevertheless, plays an important part in the discussion of the experimental results reported in this thesis.

Wolf<sup>38</sup> first suggested that methyne might take part in the reactions of recoil carbon. MacKay and Wolfgang<sup>35</sup> later

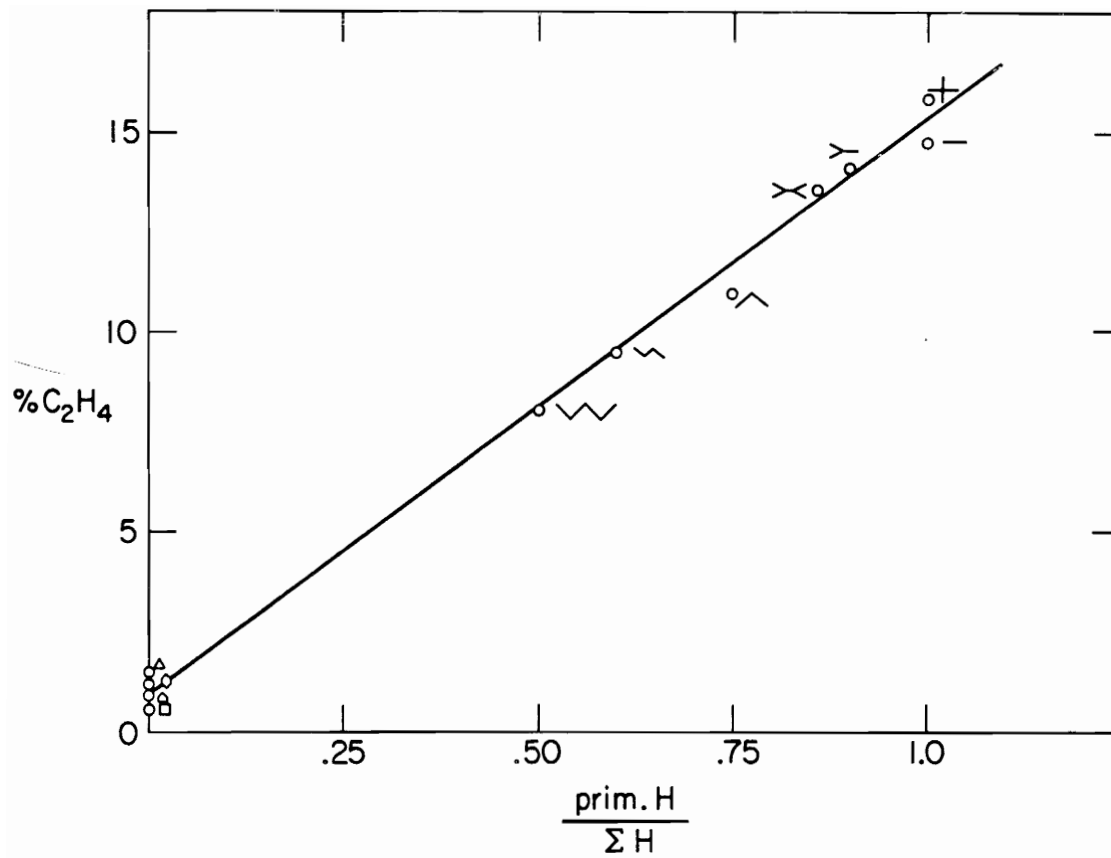
proposed methyne insertion as a possible route to acetylene- $^{11}\text{C}$ . Rack and Voigt<sup>39</sup> suggested this reaction might be a "hydrogen displacement" by methyne rather than an insertion. However, the methyne route to acetylene eventually was discarded<sup>33</sup> in favor of a direct carbon insertion as the major pathway.

Participation by methyne in ethylene- $^{11}\text{C}$  formation from hydrocarbons was postulated by Wolf<sup>6</sup> and by Stöcklin and Wolf,<sup>32</sup> who observed a proportionality between yields of ethylene and relative numbers of primary C-H bonds in the substrate (see Figure 3). Yields of ethylene from alicyclic substrates which contain no primary C-H bonds were found to be less than 1%, indicating a second and minor pathway. Absence of an isotope effect was attributed to the very high energy of the reacting species. An analogous reaction involving methyne insertion into secondary C-H bonds was postulated as the source of the smaller yields of propylene- $^{11}\text{C}$ .

MacKay, et al.,<sup>41</sup> presented evidence for the formation and reaction of methyne in hydrogen-ethylene mixtures and suggested the following pathway.



The only observed product which they did not ascribe to the reaction of C, CH<sub>2</sub>, or CH<sub>3</sub> with gaseous ethylene was pentene-1. According to the authors, addition of CH to an ethylene molecule should result in an allyl radical which



STRUCTURE DEPENDENCE OF ETHYLENE YIELD<sup>32</sup>

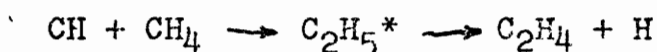
FIGURE 3



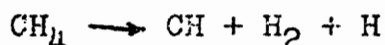
in turn is known to react with the ethyl radical to give pentene-1.<sup>42</sup> Apparently, they did not consider the possibility of methyne formation from the hydrocarbon.

The numerous accounts of methyne from flame studies generally have not included reports of its reactions with molecules. An exception is the work of Safrany, Reeves and Harteck,<sup>43</sup> who suggested that HCN was produced in their system by the action of methyne on ammonia.

A major contribution to our knowledge of methyne interactions comes from radiation chemistry and from photochemistry. In the flash photolysis of methane at 1236 Å, Ausloos, Rebbert and Lias<sup>44</sup> pointed out that CH, formed by the decomposition of internally excited CH<sub>2</sub> or CH<sub>3</sub> radicals produced in the primary process, could react to form ethylene:



Braun, Welge and McNesby<sup>45</sup> later observed methyne spectroscopically and obtained evidence for the reaction above. They found the rate of reaction of CH with methane to be quite fast and calculated the probability of a reactive collision to be approximately 1/100. Gordon and Ausloos<sup>46</sup> postulated the source of methyne at 1236 Å to be the reaction



Braun, McNesby and Bass<sup>47</sup> reported rate constants for reaction of methyne with methane and with H<sub>2</sub> and for the

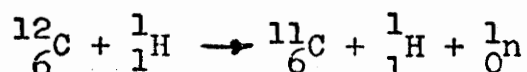
combination of two methyne radicals to produce acetylene. Bosnali and Perner<sup>48</sup> produced CH by the pulse radiolysis of methane and measured rate constants for reaction with various small molecules. They found similar rate constants for CH disappearance in oxygen ( $\leq 2.4 \times 10^{10}$  l/mol.s) and in methane ( $2.0 \times 10^{10}$  l/mol.s). This important result demonstrates that methyne would not be scavenged by oxygen before reaction with the substrate in our recoil systems containing only 4.5% oxygen.

In summary, the existence of reactive intermediates in recoil chemistry is based on experimental evidence. Such species cannot be observed directly. The product spectrum arising from these intermediates will depend on the energy and electronic state of the initial carbon insertion complex and the decay modes available to it.

CHAPTER II  
EXPERIMENTAL

A. Irradiation

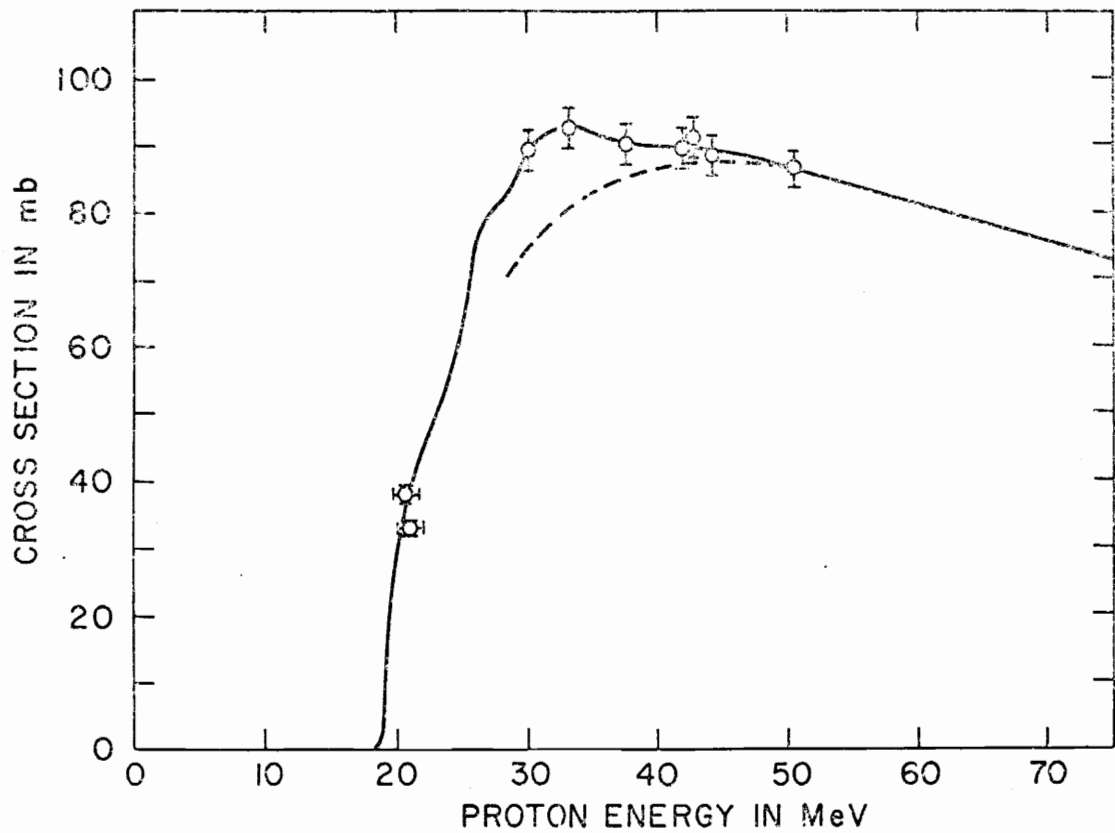
Carbon-11 was produced by high-energy protons from the Brookhaven 60-inch cyclotron. A proton energy of 33 MeV was employed to coincide with the maximum cross section<sup>49</sup> for the nuclear reaction:



The excitation function for this reaction appears in Figure 4. The detailed structure of this curve is based on additional experimental data discussed in reference 49.

The targets were bombarded typically with a one microampere proton beam for 50-100 seconds. The radiation dose absorbed by the sample under these conditions is  $7-15 \times 10^{-3}$  eV per molecule as determined by acetylene-to-benzene dosimetry.<sup>50</sup>

A well-collimated proton beam was directed to pass through the target by quadrupole magnets. The beam shape and position were checked by placing a one-inch long aluminum slug (the same diameter as the target) in the same position that the target would occupy during the irradiation. The slug was exposed to the beam for about



EXCITATION FUNCTION<sup>49</sup> FOR NUCLEAR REACTION  $^{12}\text{C}(p,pn)^{11}\text{C}$

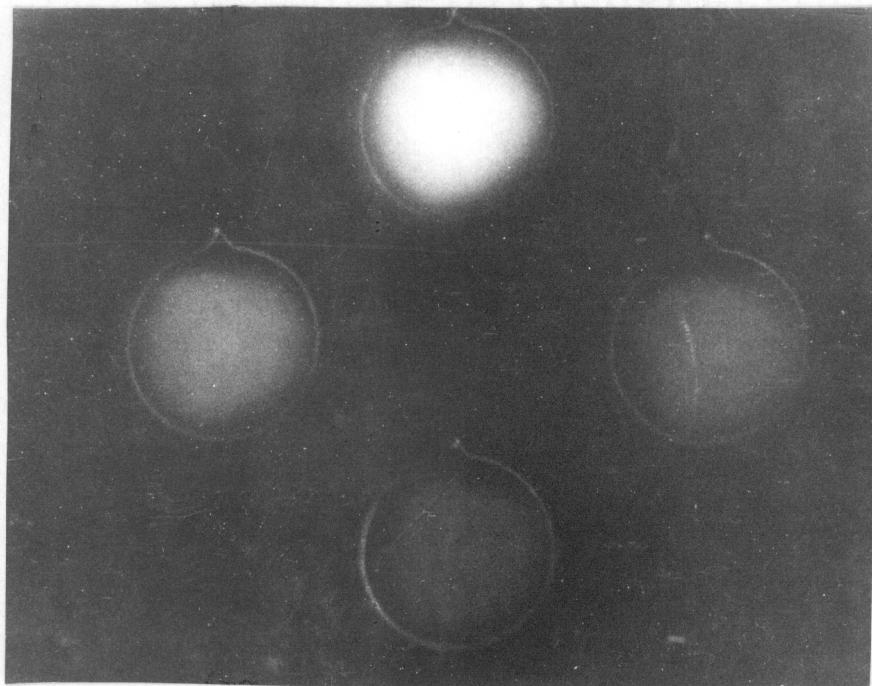
FIGURE 4

30 seconds, after which the face of the slug was placed against Polaroid film for 5-, 10-, 15- and 20-second intervals. A line was drawn around the perimeter of the slug so that when the rapidly-decaying aluminum exposed the film, the position of the spot relative to the line gave a clear indication of the shape and position of the beam. Figure 5 shows a typical autoradiograph prepared in this fashion. It shows a homogeneous beam of circular cross section which would pass through the front and back windows of the target without significant loss on the sides of the vessel.

Accurate placement of the target in the beam was assured by use of a target holder (Figure 6), machined from 2S aluminum, and keyed to fit precisely onto the cyclotron external beam pipe. The holder was built in two halves which completely enclosed the target vessel and contained holes for heaters. The heaters were cylindrical brass rods connected to a Variac, and provided for irradiations at elevated temperatures. The heaters were calibrated using an iron-constantan thermocouple (with one end in the gas inside the target vessel).

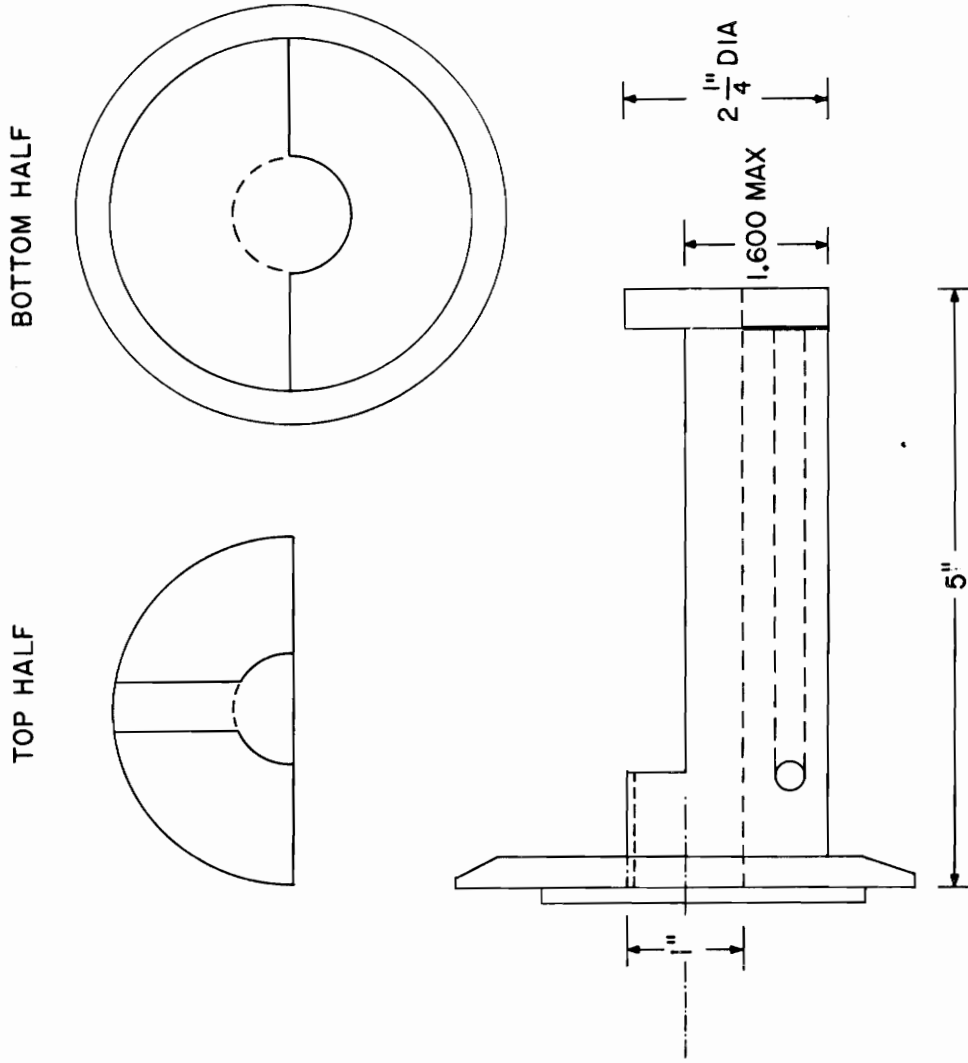
#### B. Target Vessels

Samples were irradiated in quartz cylinders (see Figure 7) fitted with teflon stopcocks (with Viton-A or silicon rubber o-rings) and suitable fittings for their



TYPICAL AUTORADIOGRAPH OF PROTON BEAM

FIGURE 5



TARGET HOLDER

FIGURE 6

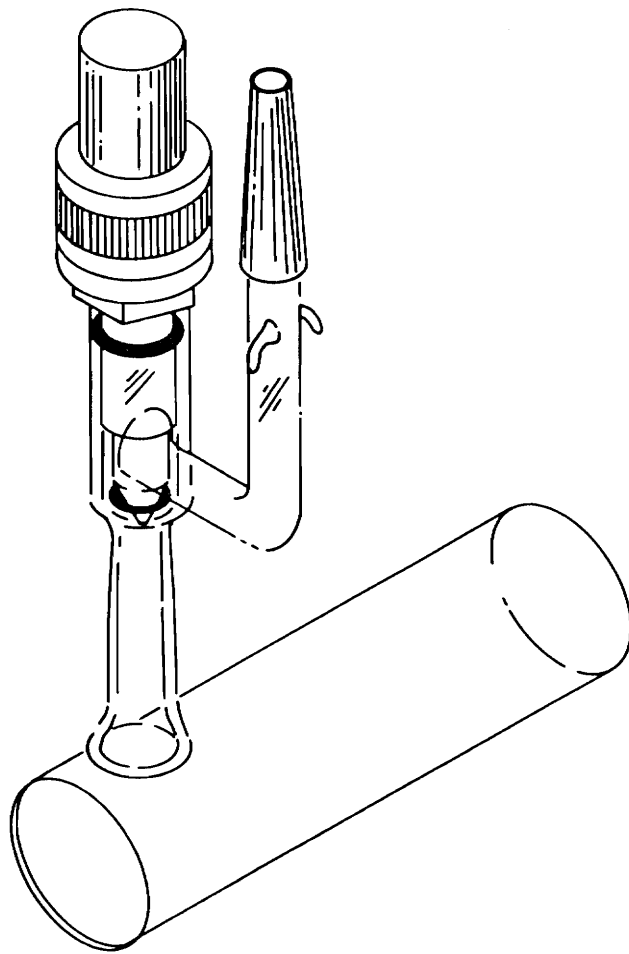
BEAM PIPE IRRADIATION VESSEL <sup>50</sup>

FIGURE 7



attachment to the vacuum line. These cylinders were constructed with thin (0.25 mm) quartz windows at either end to minimize energy degradation of the proton beam and to reduce the radiation exposure due to activation of the quartz.

These cylinders were of various sizes. Vessels used for the determination of absolute carbon-11 yield data were 7.6 cm long and 2.5 cm in diameter. When an analysis of the carbon-11 distribution in the various deuterium isotopes of ethylene was the goal, larger samples were required and irradiation was carried out in 3.8-cm diameter cylinders of 7.6- or 12.7-cm length.

### C. Loss Of Energy By The Beam

The energy degradation suffered by the proton beam on passing through the front window and through the sample can be calculated. The following discussion was adapted from reference 51. The formula below is applicable to protons, deuterons and helium ions with initial energies from 0.1 to 1000 MeV.<sup>51</sup>

For absorbers with  $Z > 10$ :

$$R_Z/R_a = 0.90 + 0.0275Z + (0.06 - 0.0086Z) \log_{10}(E/M) \quad (1)$$

where,  $R_Z$  is the range in element Z in  $\text{mg cm}^{-2}$

$R_a$  range in air of the same particle

M is the mass number of the particle

$Z$  is the atomic number of the absorber

$E$  is the initial particle energy in MeV

$R_a$  can be obtained from a plot of range versus energy.<sup>51</sup>

For absorbers with  $Z \leq 10$ , except helium and hydrogen:

$$R_Z/R_a = 1.00 + (0.06 - 0.0086Z) \log_{10}(E/M) \quad (2)$$

For helium and hydrogen absorbers, 1.00 is replaced by 0.82 and 0.30, respectively.

The range in a compound or homogeneous mixture can be calculated by substituting the results obtained in Formula (1) or (2), as applicable, for each element involved into the following equation:

$$1/R_C = w_1/R_1 + w_2/R_2 + \dots + w_i/R_i \quad (3)$$

where,  $R_C$  is the range in the compound or mixture

$w_i$  is the weight fraction of the element in which the particle has a range  $R_i$

$R_i$  is the particle range in element  $i$

By subtracting the absorber thickness (in  $\text{mg cm}^{-2}$ ) from the calculated range in the absorber, the residual range of the particle is obtained. By substituting this number back into Formulas (1) or (2) and then into (3) in an iterative procedure, one can calculate the energy of the particle that would have that range. Subtraction of this energy from the initial particle energy yields the

energy lost by the beam in the absorber.

It can be calculated by this method that a 33 MeV proton beam loses 0.6 MeV on passing through the 0.25 mm quartz window of the target vessel and the resulting 32.4 MeV beam loses 0.2 MeV on passing through a 12.7-cm long vessel filled with 700 mmHg of  $C_2H_5Cl$  at 25°C.

#### D. Materials

All fully-protonated hydrocarbons used in these experiments were Phillips Research Grade. Deuterated hydrocarbons, alkyl halides and alcohols were obtained from Merck, Sharp and Dohme, Ltd. Chemical purity in all cases was greater than 99%. Deuterium analyses were performed by Merck or at Brookhaven National Laboratory by mass spectrometry. Table III lists the isotopic purity for each compound. Normal butyl chloride was Fisher Chemical Company "Spectranalyzed" Grade, and ethyl chloride was Matheson USP Grade. These materials were degassed by normal vacuum line distillation, entailing cycles of freezing and melting.

Oxygen, hydrogen, krypton and xenon were Matheson Gas Products Analyzed Reagent and were used without further purification. Hydrogen- $d_2$  was supplied by Bio-Rad Laboratories and stated to be 99.998% chemically pure and 99.65 atom %D.

A few of the deuterated chlorides were prepared at

TABLE III

## Purity of Deuterated Compounds

Compound	% purity	Probable major impurity*	Place of analysis
CD <sub>3</sub> CD <sub>3</sub>	97.2	CHD <sub>2</sub> CD <sub>3</sub>	BNL
CH <sub>3</sub> CD <sub>3</sub>	97.1	CH <sub>3</sub> CHD <sub>2</sub>	Merck
CH <sub>2</sub> DCH <sub>2</sub> D	93.8	CH <sub>3</sub> CH <sub>2</sub> D	BNL
CHD <sub>2</sub> CHD <sub>2</sub>	95.5	CH <sub>3</sub> DCHD <sub>2</sub>	Merck
CD <sub>3</sub> CD <sub>2</sub> CD <sub>3</sub>	95.0	CHD <sub>2</sub> CD <sub>2</sub> CD <sub>3</sub>	Merck
CH <sub>3</sub> CD <sub>2</sub> CH <sub>3</sub>	98.0	CH <sub>3</sub> CHD <sub>2</sub> CD <sub>3</sub>	Merck
CD <sub>3</sub> CH <sub>2</sub> CD <sub>3</sub>	85.7	CHD <sub>2</sub> CH <sub>2</sub> CD <sub>3</sub>	Merck
CH <sub>3</sub> CH <sub>2</sub> CD <sub>3</sub>	94.0	CH <sub>3</sub> CH <sub>2</sub> CHD <sub>2</sub>	Merck
C(CD <sub>3</sub> ) <sub>4</sub>	95.9	C(CHD <sub>2</sub> )(CD <sub>3</sub> ) <sub>3</sub>	BNL
CD <sub>3</sub> CD <sub>2</sub> Cl	98.8	C <sub>2</sub> HD <sub>4</sub> Cl	BNL
CD <sub>3</sub> CH <sub>2</sub> Cl	95.3	C <sub>2</sub> H <sub>3</sub> D <sub>2</sub> Cl	BNL
CD <sub>3</sub> (CD <sub>2</sub> ) <sub>3</sub> Cl	92.3	C <sub>4</sub> HD <sub>8</sub> Cl	BNL

\*Impurities identified by cracking pattern in the mass spectrum.

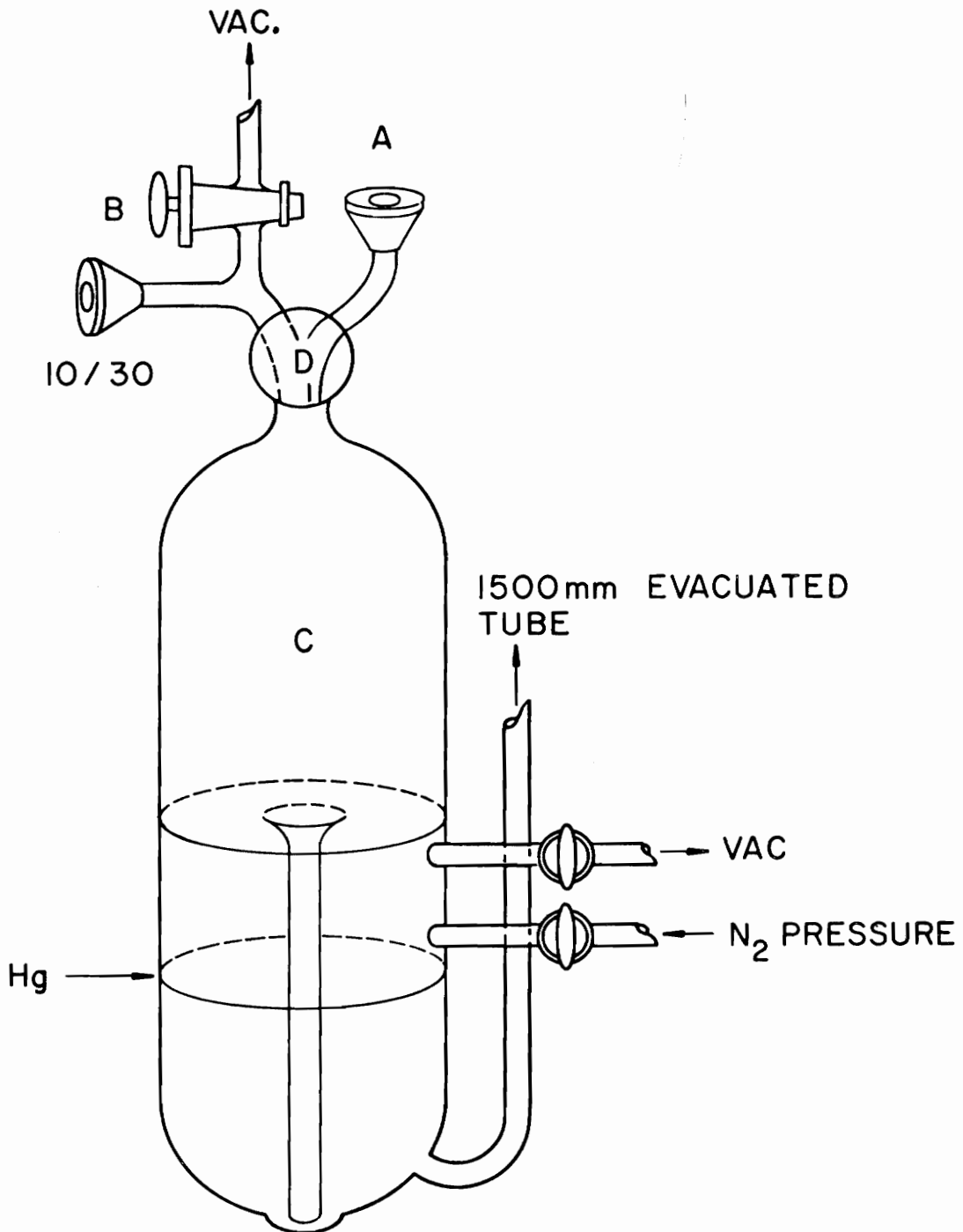
BNL from alcohols obtained from Merck, Sharp and Dohme. The tosylates of n-butanol-d<sub>10</sub>, ethanol-1,1-d<sub>2</sub> and ethanol-2,2,2-d<sub>3</sub> were prepared by the method of Edgell and Parts.<sup>52</sup> In each case 2 g of the tosylate was dissolved in 15 cc of diethyleneglycol and 2 g of potassium chloride was added.<sup>52</sup> The mixture was heated for 2 hours at 150°C under a helium atmosphere. The compound was distilled from the reaction mixture in vacuum and trapped in a liquid nitrogen cooled trap. Each chloride was then checked for purity on a 7.5 m, 6.4 mm o.d. polyethylene column packed with 25% DMS on Chromosorb W.

#### E. Sample Preparation

All samples were prepared for irradiation using standard vacuum line technique. Two basic procedures were followed. For preparation of a two-component gas mixture, the irradiation vessel was attached to the vacuum line and after a suitable evacuation period, the line was closed off from the vacuum pump and the desired pressure of the minor component gas was admitted. The vessel was closed off and the vacuum line and connection re-evacuated. Now the vacuum line was sealed from the pump again and the major component gas admitted. The pressure was increased until it exceeded the pressure of the first component; then the irradiation vessel was opened and the pressure quickly increased to the final desired pressure. The rush of the

second component entering the vessel kept the first component molecules from diffusing out. Pressures were measured on a mercury manometer. Samples were allowed to mix for several hours before irradiation. Analysis by mass spectrometer showed mixtures to be accurate within 1%.

The second method was used for multicomponent mixtures. This procedure was especially useful when all gases except one were condensable. Two vessels were attached to the vacuum line (in addition to the component gas reservoir). The desired pressure of each condensable gas was measured in turn in the target vessel (A) and then frozen into the second container (B). The non-condensable gas was then measured in A and the vessel sealed. Now A and B were attached to the specially-designed Töpler pump shown in Figure 8 and the entire system evacuated. Then the system was closed off from the vacuum pump and the gases in B were expanded into chamber C. The 3-way stopcock was turned so that raising the mercury level would force the gases into A. Vessel A was now closed off and stopcock D turned to admit more gas from B into chamber C. Once again the gas was forced into A. This was continued a sufficient number of times for 99.9% of the gas to be transferred into A. In those cases where the three-component mixture was composed of hydrocarbon, oxygen and rare gas, a mixture of 4.5% oxygen in hydrocarbon was prepared by the first



TÖPLER PUMP USED FOR SAMPLE PREPARATION  
FIGURE 8

method. After allowing time for mixing, the final mixture was prepared by the second method.

#### F. Sample analysis and Data Handling

The method of radiogaschromatography has proven to be generally useful in hot atom chemistry.<sup>53,54</sup> The sample to be analyzed is passed through a conventional gas chromatograph in order to separate the products of interest. The effluent then passes through a proportional counter, where only radioactive peaks are recognized. Decay occurring in  $^{11}\text{C}$ -containing molecules passing through the counter is recorded on paper printout and on magnetic tape for computer processing.

Samples were analyzed to obtain the absolute yields of products formed during irradiation and the relative yields of various deuterium isomers of ethylene. Procedures followed in the determinations were identical in principle, but differed sufficiently in detail so that each will be described independently.

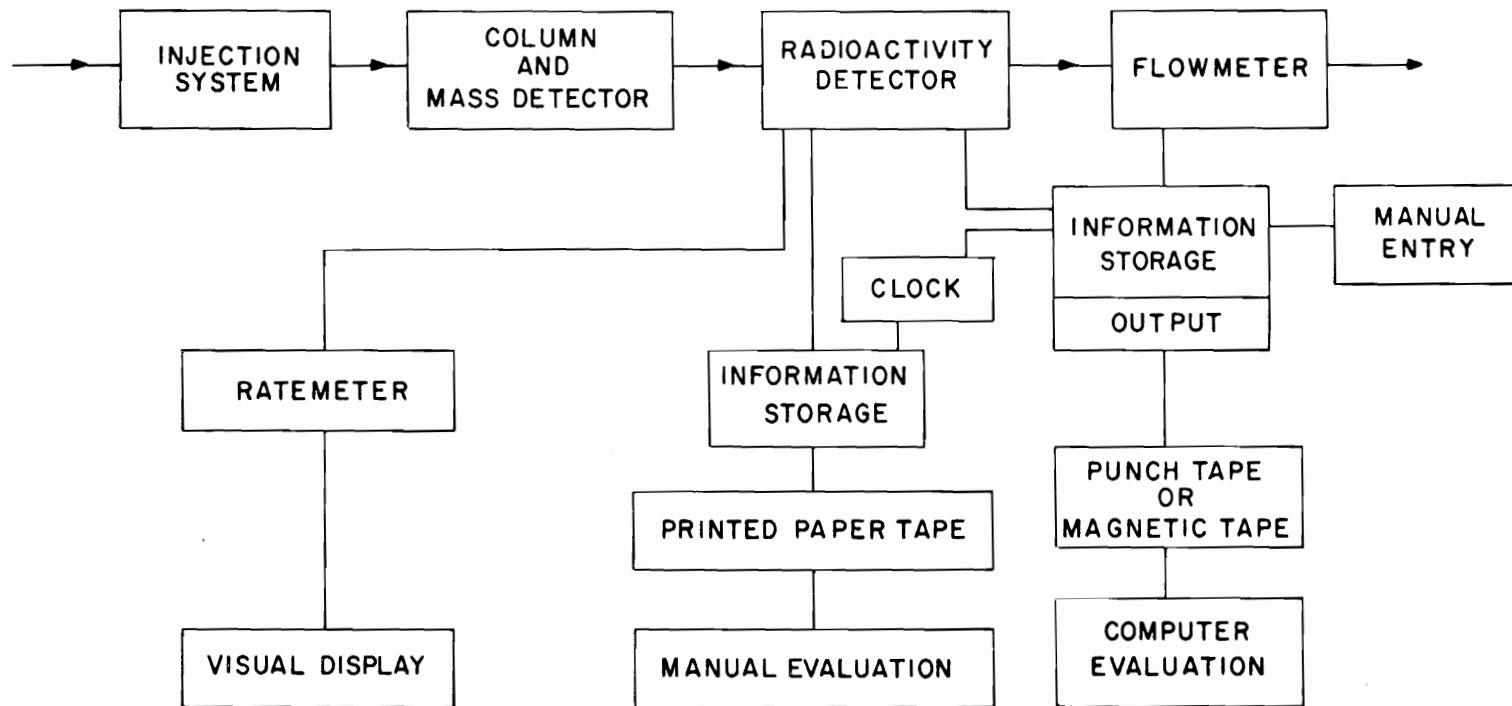
##### 1. Absolute Yield Determinations

Figure 9 shows a block diagram of the apparatus. Each basic element will be discussed in detail.

##### a. Injection System

The injection system ensured the injection of aliquots at accurately-known pressures, free from air contamination.





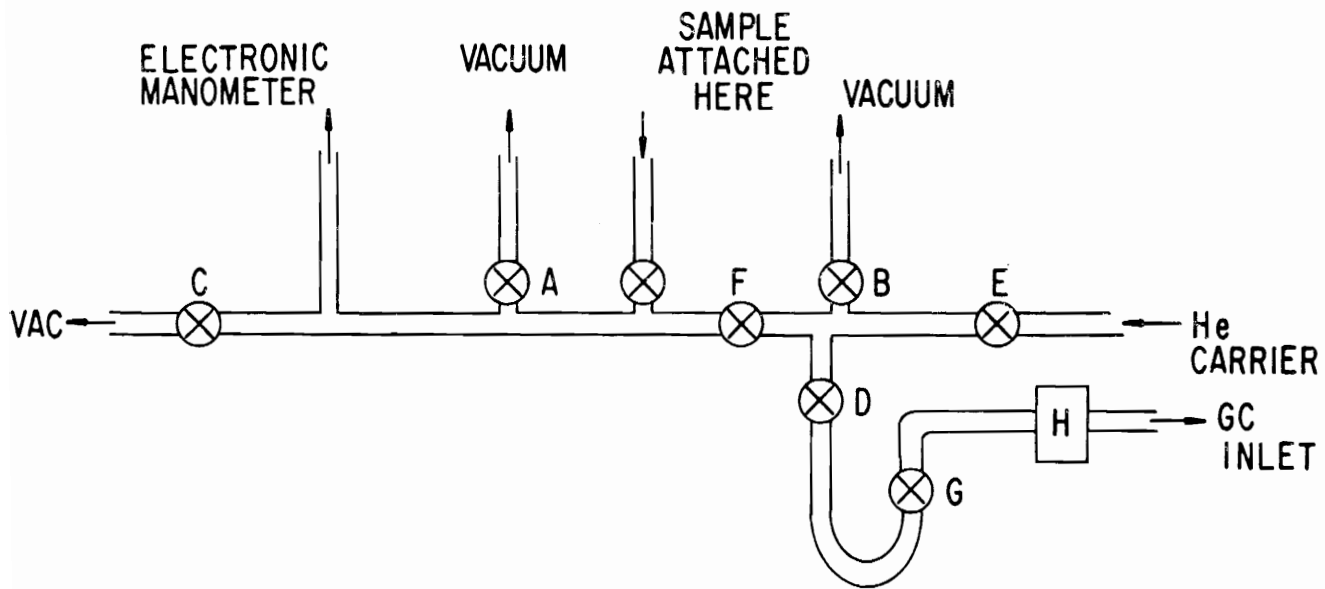
BLOCK DIAGRAM OF RADIOGASCHROMATOGRAPHIC EQUIPMENT<sup>55</sup>

FIGURE 9

The vessel containing the irradiated sample was attached to the vacuum line shown in Figure 10. After re-establishing the vacuum, the line was closed off at A, B and C, and the sample admitted. The pressure was read on a Barocel Type 1083 Electronic Manometer with a precision of 0.001 mmHg. Now stopcock D was closed and E opened to re-establish the vacuum. Then F was closed and E opened to pressurize the line with helium carrier gas. Once the flow rate into the gas chromatograph had returned to normal, stopcock D was opened to pressurize the sample in the trap whose volume was accurately known. When the flow rate had once again returned to normal, stopcock G was opened and solenoid valve H (Skinner Electric Valve Division, Type VH-7) was activated to divert the flow of helium through the trap and sweep the sample onto the chromatographic column. This sequence of steps insured that the aliquot was injected as a "plug," and did not mix with a large volume of helium, thus reducing resolution.

b. Gas Chromatograph

A Hewlett-Packard 7620A Series Chromatograph with dual-column oven, thermal conductivity bridge, strip-chart recorder, sub-ambient assembly and temperature programmer was used for the gas chromatographic separations. The programmer permitted multilevel programming from  $-70^{\circ}\text{C}$  to  $+500^{\circ}\text{C}$  by use of self-pressurized flow of liquid nitrogen.



VACUUM LINE GAS INJECTION SYSTEM

FIGURE 10

Injection could be made into either of the two columns by switching an 8-port microvolume valve supplied by Carle Instruments, Inc.

Two aliquots of each sample were taken and separated on different columns as a check on product identification and on precision. Columns were constructed of 6.4 mm o.d. pyrex tubing. Table IV shows the packings, operating conditions and retention times, relative to air.

### c. Counter

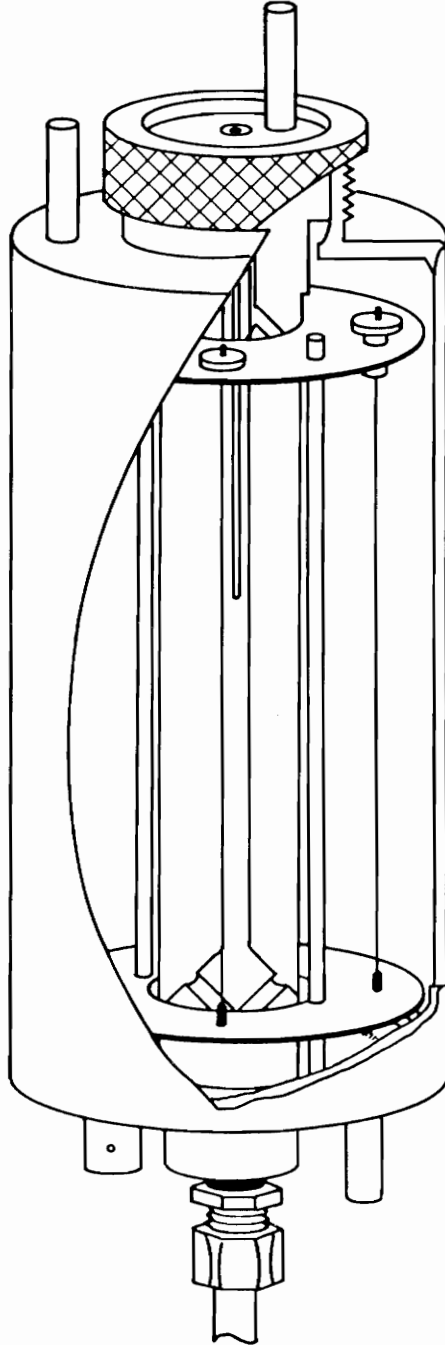
The window proportional gas counter used in these experiments has been described by Welch, Withnell and Wolf,<sup>55</sup> and is shown in Figure 11. This counter consists of two concentric cylinders. Effluent from the chromatograph passes through the inner cylinder which is constructed of one-mil Mylar film. For maximum efficiency, P-10 counting gas (90% argon, 10% methane) flows continuously through the outer cylinder. This counter has an active volume of 40 cc and counts carbon-11 with an efficiency of 34.6% at a flow rate of 100 cc/min.

The efficiency of this counter can be measured by the following procedure. A sample of high-specific-activity  $^{11}\text{CO}_2$  is counted in a static proportional counter of known volume and efficiency. Using the pressure of  $^{11}\text{CO}_2$  in the counter, the volume, efficiency and a decay correction, the

TABLE IV

## Column Packings and Operating Conditions

Packing material	Porapak R	3% Squalane on silica gel
Mesh	50-80	40-60
Length $\times$ i.d.	3m $\times$ 3mm	3m $\times$ 3mm
Flow rate (cc He/min)	75	60
Temperature program	-35°C (for 8 min) 20°/min to 25°C (8 min) 30°/min to 90°C	50°C (for 10 min) 20°/min to 70°C (15 min) 30°/min to 90°C
Relative retention times		
C $\equiv$ O	1.2	1.0
CO <sub>2</sub>	6.6	4.0
Kr	3.4	1.0
Xc	7.5	2.5
CH <sub>4</sub>	3.2	2.3
C <sub>2</sub> H <sub>6</sub>	9.3	8.8
C <sub>2</sub> H <sub>4</sub>	8.3	4.7
C <sub>2</sub> H <sub>2</sub>	9.7	8.8
C <sub>3</sub> H <sub>8</sub>	-	7.5
C <sub>3</sub> H <sub>6</sub>	-	14.3
C <sub>3</sub> H <sub>4</sub>	-	16.1



WINDOW FLOW PROPORTIONAL GAS COUNTER<sup>55</sup>

FIGURE 11

specific activity in dpm/cc of the material at end-of-bombardment can be calculated. An aliquot of the same material is expanded into the injection loop of the gas chromatograph. The volume of the loop is known; the pressure can be measured. The activity passing through the counter is recorded and corrected for decay. The ratio of the specific activity passing through the flow counter to that measured in the static counter is the efficiency.

Naturally, this static counter is a secondary standard. It was calibrated by comparing the specific activity produced in a gas to that produced in polyethylene foils during the same bombardment. The specific activity which can be produced in foils was determined using a Faraday cup. This device consists of a metal block thick enough to stop the beam entirely, supported on insulators inside an evacuated chamber. The proton flux can be determined by measuring the current flow to ground during a bombardment interval. Then, if the cross section for the nuclear reaction is known, the activity produced in the polyethylene foils can be calculated.

#### d. Flow Meter

Since the efficiency of the flow counter is directly proportional to the residence time of the radioactive material in the counter, it is critical that the flow rate

be known accurately. Aside from the expected perturbations in flow due to changes in column temperature, the elution of a mass peak can increase the flow rate due to the larger volume of gas which must pass through the counter. To remedy this difficulty a flowmeter has been developed<sup>56</sup> which will continuously monitor the flow and with digital output suitable for acceptance by the data acquisition system discussed below. A schematic of the flow meter appears in Figure 12 and a block diagram of the electronics in Figure 13. The device was connected in series with and as close to the counter as possible to minimize any time lag.

e. Data Acquisition

The data are collected and recorded onto magnetic tape by a Hewlett-Packard 2052A DYMEC Data Acquisition System (Figure 9). The DYMEC consists of a digital clock, two scalers which accept information from the counter and the flow meter, a manual data entry device, a magnetic tape recorder, and a paper printer. Every ten seconds the clock issues a pulse which resets the scalers and the flow meter. The information stored in the scalers during the previous ten seconds is recorded simultaneously on magnetic tape and on paper. This information is recorded as a twelve-digit word. The first five digits are the time in seconds from end-of-bombardment; digits six through ten are the number



56  
SCHEMATIC DIAGRAM OF "ABSOLUTE" FLOWMETER

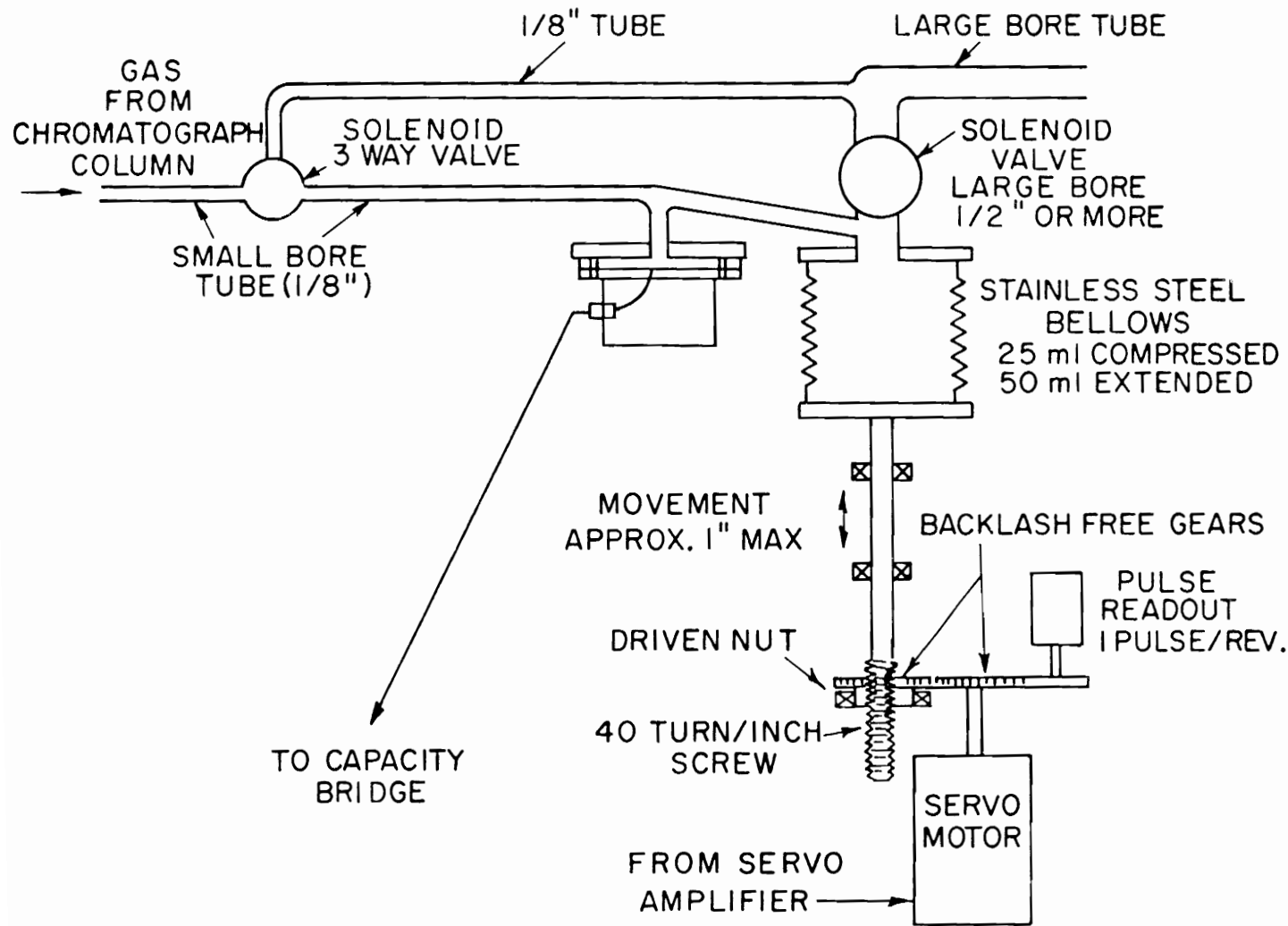


FIGURE 12



of counts observed during the ten-second interval; and the last two digits are the absolute flow rate in cc per minute. Code words must be entered manually onto the magnetic tape to permit computer manipulation of the data.

f. Data Handling

A sample of the data obtained appears in Figure 14. The number of counts recorded each ten seconds is indicative of the number of  $^{11}\text{C}$ -containing molecules within the active volume of the counter. The counter exhibits a finite background activity due to cosmic radiation, natural radioactivity in construction and shielding materials and electronic instability. This average background activity (about 13 counts) must be subtracted from each ten-second count. The data show a peak beginning to emerge at 2209 seconds and not returning to baseline until 2369 seconds. With a half-life of only 20.4 minutes, significant decay takes place during the analysis; and correction must be made for this decay.

These calculations can be done very efficiently by computer, using the computer program ORGATOM.<sup>57</sup> By testing for a slope change, this program is able to pick out the radioactive peaks, correct for background, flow rate and decay, and sum the area under each peak.

0	0	2	5	5	9	0	0	3	4	2	6	9
0	0	2	5	4	9	0	0	4	7	2	6	9
0	0	2	5	3	9	0	0	7	0	6	6	9
0	0	2	5	2	9	0	1	0	5	5	6	8
0	0	2	5	1	9	0	1	4	7	3	6	8
0	0	2	5	0	9	0	2	1	7	1	6	8
0	0	2	4	9	9	0	3	3	9	4	6	8
0	0	2	4	8	9	0	4	9	7	7	6	8
0	0	2	4	7	9	0	7	2	4	5	6	8
0	0	2	4	6	9	1	0	2	2	0	6	8
0	0	2	4	5	9	1	3	1	0	1	6	9
0	0	2	4	4	9	1	2	6	0	3	6	9
0	0	2	4	3	9	0	4	7	2	2	6	9
0	0	2	4	2	9	0	0	3	2	6	7	0
0	0	2	4	1	9	0	0	0	2	4	7	0
0	0	2	4	0	9	0	0	0	1	8	7	0
0	0	2	3	9	9	0	0	0	1	5	7	1
0	0	2	3	8	9	0	0	0	1	9	7	2
0	0	2	3	7	9	0	0	0	1	9	7	2
0	0	2	3	6	9	0	0	0	1	9	7	2
0	0	2	3	5	9	0	0	0	4	6	7	2
0	0	2	3	4	9	0	0	0	3	5	7	2
0	0	2	3	3	9	0	0	0	5	7	7	2
0	0	2	3	2	9	0	0	1	0	0	7	2
0	0	2	3	1	9	0	0	1	2	0	7	2
0	0	2	3	0	9	0	0	1	8	0	7	2
0	0	2	2	9	9	0	0	2	9	6	7	2
0	0	2	2	8	9	0	0	4	3	6	7	2
0	0	2	2	7	9	0	0	7	0	6	7	2
0	0	2	2	6	9	0	1	0	8	1	7	2
0	0	2	2	5	9	0	1	6	6	1	7	2
0	0	2	2	4	9	0	1	9	6	0	7	2
0	0	2	2	3	9	0	1	8	6	5	7	2
0	0	2	2	2	9	0	1	0	2	3	7	2
0	0	2	2	1	9	0	0	2	4	3	7	2
0	0	2	2	0	9	0	0	0	4	3	7	2
0	0	2	1	9	9	0	0	0	2	5	7	2
0	0	2	1	8	9	0	0	0	1	2	7	2
0	0	2	1	7	9	0	0	0	2	3	7	2
0	0	2	1	6	9	0	0	0	2	8	7	2
0	0	2	1	5	9	0	0	0	3	8	7	2
0	0	2	1	4	9	0	0	0	6	1	7	2
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0	0	2	1	2	9	0	0	1	2	0	7	2

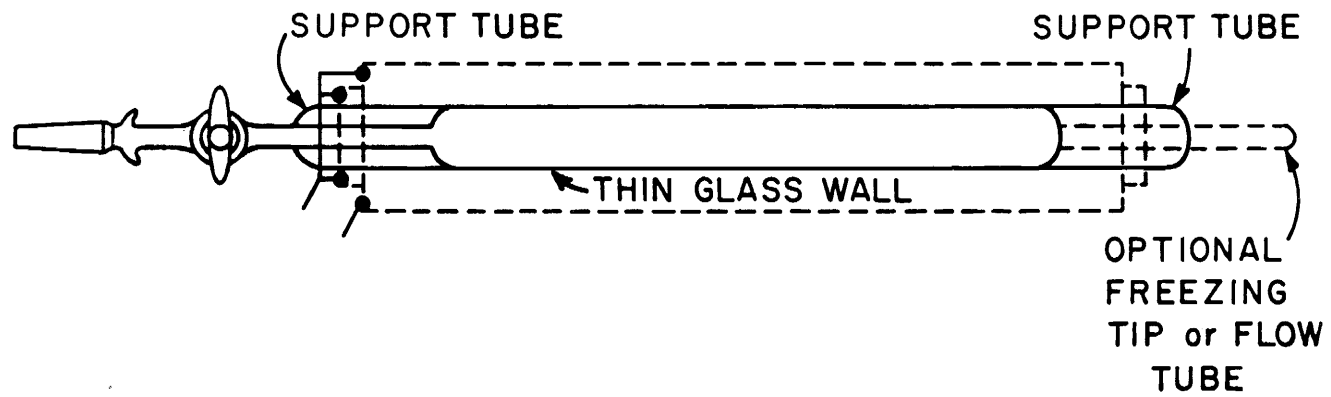
SAMPLE DATA

FIGURE 14

g. Total Activity Measurements

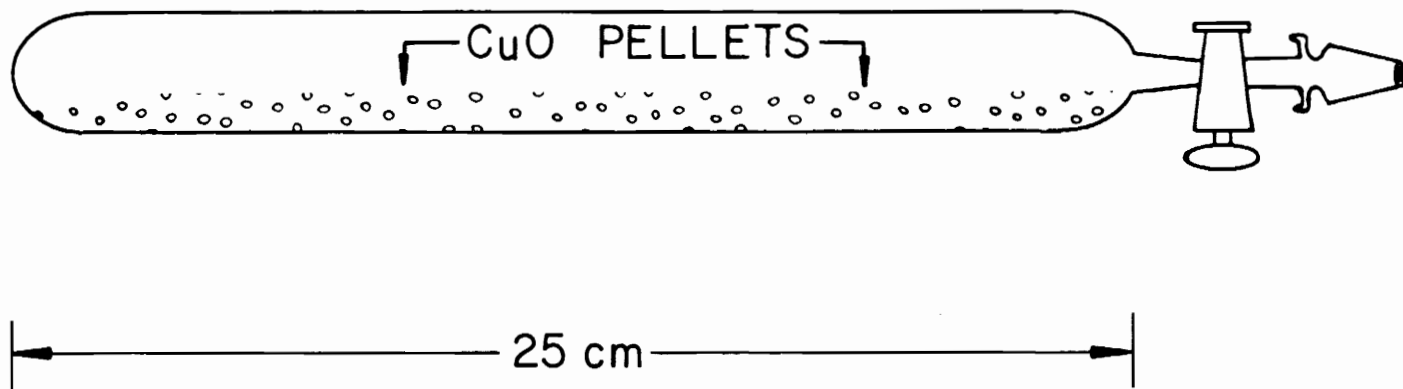
The data obtained in the chromatographic analysis can be transformed into absolute yields if the total activity produced in the gas phase is known. If only carbon-11 is present, an aliquot of the irradiated gas sample can be counted in a static proportional counter (see Figure 15) of known volume and efficiency. Correction for background and decay give the total gas phase carbon-11 activity produced at end-of-bombardment. This method is also useful if other nuclides are present. The resulting decay curve is a combination of first order reaction plots which can be resolved graphically or by a least-squares analysis. The more-objective least-squares method is facilitated by use of a computer program such as CLSQ Decay-Curve Analysis Program.<sup>58</sup>

In those experiments where xenon was present, a large number of radioactive nuclides were produced so that it was impossible to use the static counting method. In these cases, an aliquot of the gas was expanded into a quartz tube of 60 cc volume (Figure 16). Approximately 400 mm of oxygen were admitted to the tube, which also contained 0.5 gram of CuO pellets. The tube was heated at 700°C for 30 minutes to convert any hydrocarbon present into CO<sub>2</sub>. The gases then were pumped to vacuum through a 12-cm long tube of 1.3 cm diameter containing "Mallcosorb"



GLASS INSERT FOR STATIC COUNTER<sup>59</sup>

FIGURE 15



COMBUSTION TUBE FOR TOTAL ACTIVITY DETERMINATIONS

FIGURE 16

carbon dioxide absorber (supplied by Mallinckrodt Chemical Works). The solid Malleosorb was counted on a 12 cm diameter thallium-doped sodium iodide crystal with photomultiplier tube, obtained from Harshaw Chemical Company.

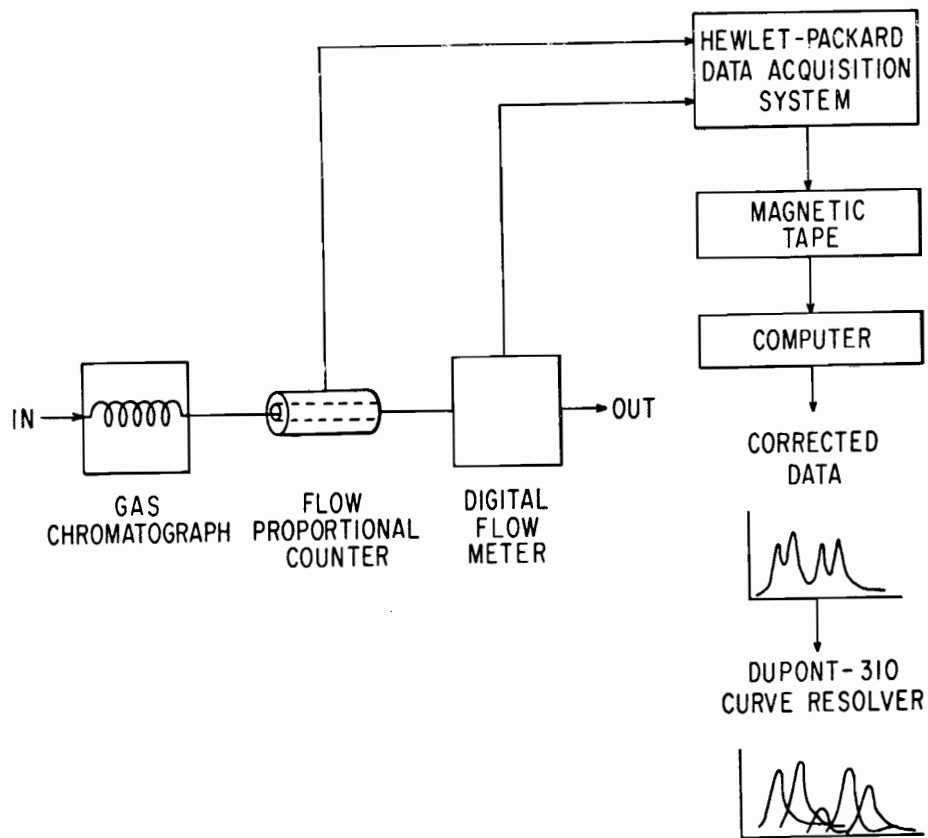
## 2. Relative Ethylene Yield Determination

A block diagram of this procedure appears in Figure 17.

### a. Preliminary Operations

Each sample which was analyzed for relative yields of the five mass isomers of deuterated ethylene- $^{11}\text{C}$  was analyzed also for absolute yields of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  using the method described previously. Therefore, the first operation with the irradiated gas was to remove an aliquot for this purpose. The next problem was to transfer the sample as quickly as possible to a loop suitable for injection into a gas chromatograph. All of these samples contained oxygen and some contained hydrogen so that the most practical way to condense them was to pump the entire sample to vacuum through a radiator trap which was immersed in liquid nitrogen. This trap was constructed of 3 m of 3.2 mm o.d. thin walled pyrex tubing. It was filled prior to the irradiation with a mixture of the deuterated ethylenes to a pressure of 5 mmHg, then attached





BLOCK DIAGRAM OF PROCEDURE FOR RELATIVE ETHYLENE YIELD DETERMINATIONS

FIGURE 17

to the vacuum line, the connections evacuated, and the ethylene frozen by immersion in liquid nitrogen. As the sample was pumped through this trap, the radioactive ethylene and other condensable gases were frozen out, while oxygen and hydrogen passed on through. The carrier ethylene served the double purpose of providing a mass peak for subsequent gas chromatographic detection and, in addition, offering extra surface area for condensation of the ethylene-<sup>11</sup>C which has a slight vapor pressure at 77°K.

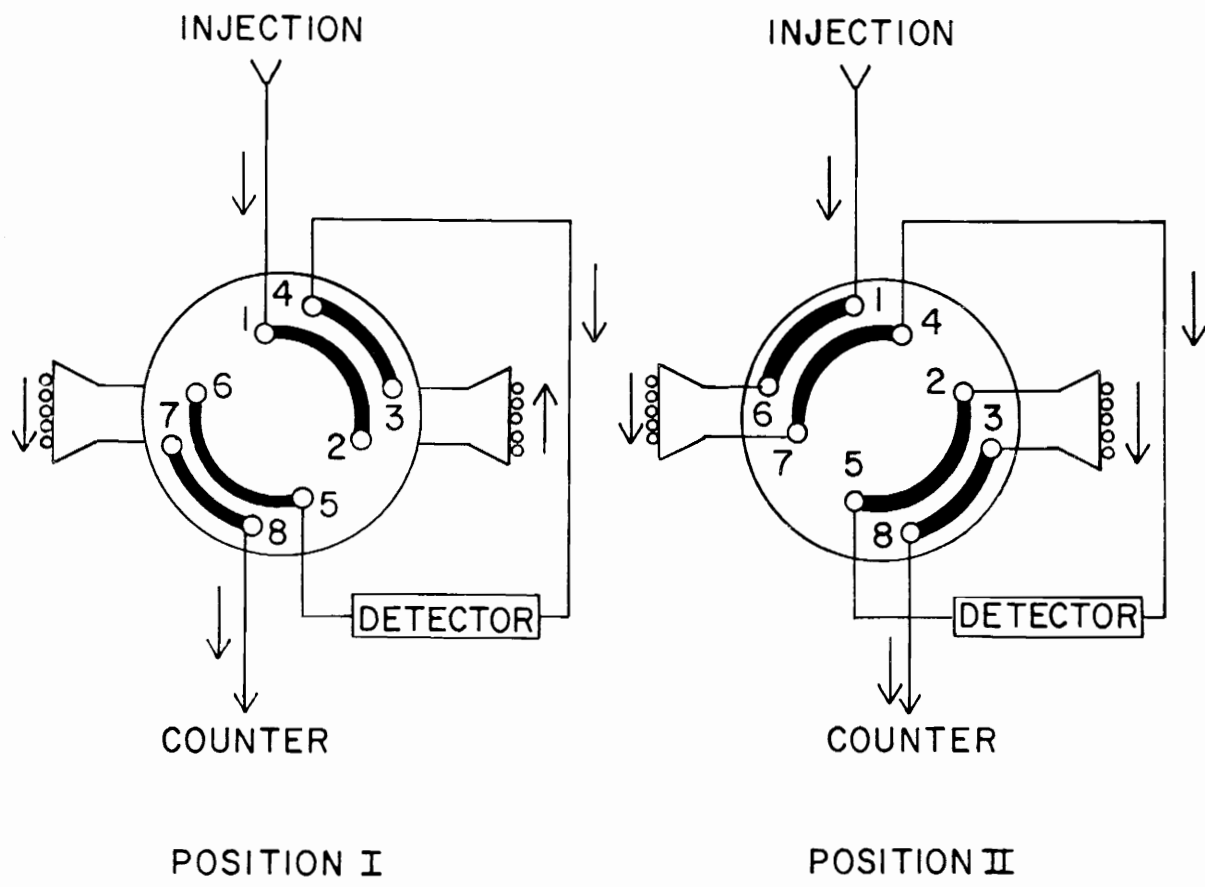
The radiator trap then was closed off from the vacuum line and rapidly thawed by immersion in hot water. This trap was used as the injection loop for a Scientific Industries, Inc., Mini 1 Gas Analysis Unit. This gas chromatograph accomplished the separation of the ethylene carrier from the bulk of the sample in approximately 10 minutes. The column was Porapak T (60-80 mesh), packed in 1.8 m of 6.4 mm o.d. polyethylene tubing, operated at room temperature and at a flow rate of 80 cc He/min. At the exit of the column was a trap of dimensions similar to that used for injection, but containing a few inches of glass wool to facilitate trapping of the low-boiling ethylene. This trap also was immersed in liquid nitrogen and connected to the column outlet by a 3-way stopcock. The effluent was allowed to pass to the hood until the ethylene peak was about to emerge. Then the stopcock was

turned and the helium stream directed through the trap. The trap then was closed off and attached to the vacuum line while still frozen in liquid nitrogen and the helium was pumped off. The trap, which now contained only carrier and radioactive ethylene, was closed off again, warmed to room temperature, and attached to the recycle chromatograph for separation of the deuterated ethylenes- $^{11}\text{C}$ .

The procedure from the end of the target irradiation to the point of this injection requires approximately 20 minutes. Every effort was made to streamline each operation, since the 20.4 minute carbon-11 half-life severely restricts the total time available for analysis.

b. Recycle Gas Chromatograph

This system has been modified slightly from that previously described by Ache and Wolf.<sup>60,61</sup> The columns are 25%  $\text{AgNO}_3$ -saturated ethylene glycol on 60-80 mesh Chromosorb P-AW, prepared essentially as described by Cvetanovic, et al.,<sup>62</sup> and packed in two 7.6-meter sections of 6.4 mm o.d. opaque polyethylene tubing. The recycle technique of Root, et al.,<sup>63</sup> was employed to shorten the analysis time and to reduce back pressure on the column. The two columns were connected through an 8-port microvolume switching valve (CV-8HT, supplied by Carle Instruments, Inc.) shown in schematic in Figure 18. One column was connected to ports 2 and 3; the other was

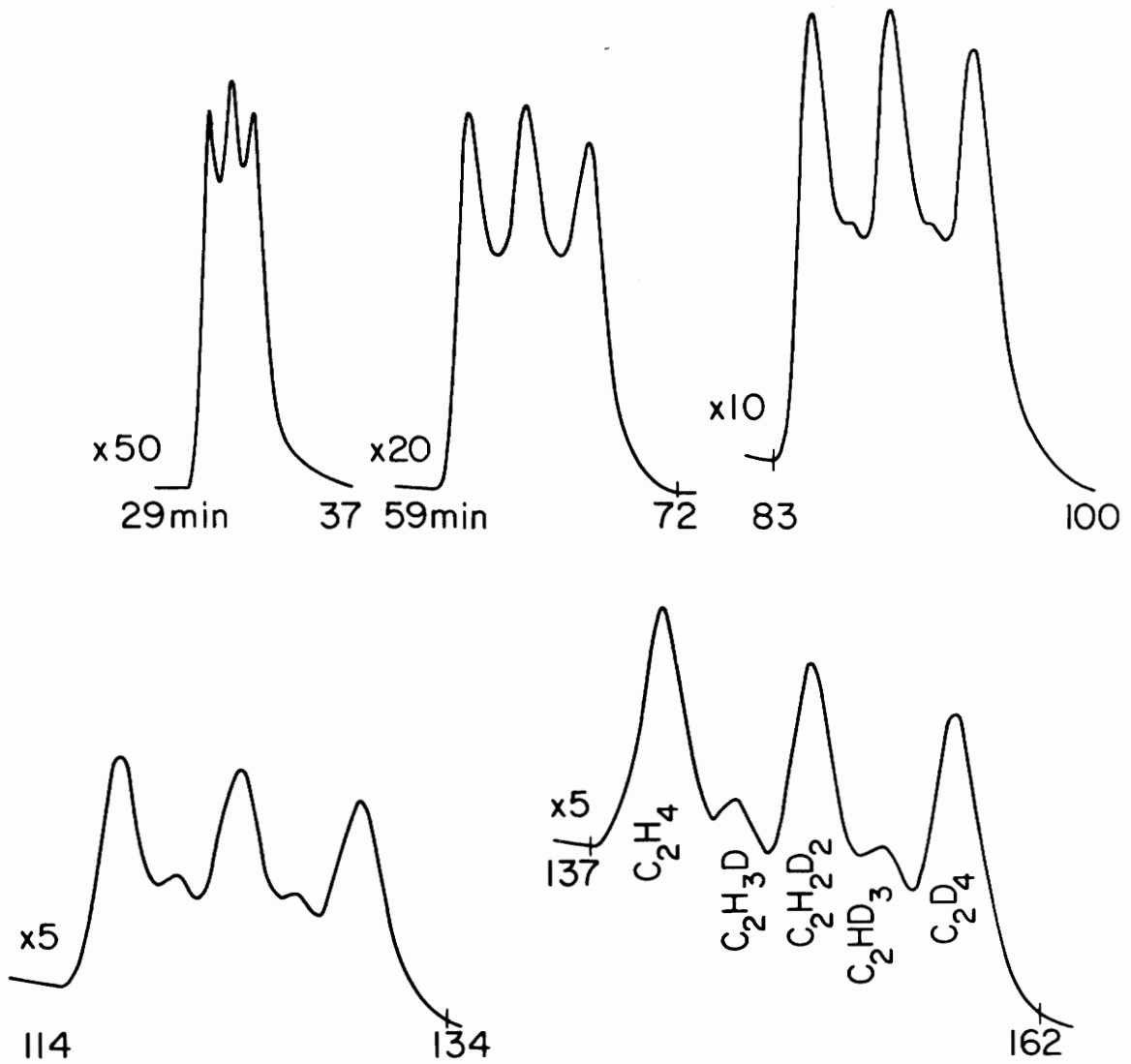


RECYCLE GAS CHROMATOGRAPH SHOWING DETAIL OF MICROVOLUME VALVE

FIGURE 18

connected to ports 6 and 7. The detector was a Carle Micro Detector, equipped with thermistors for maximum non-destructive response, and chosen for its small volume of 58 ul. All connections in this system were of 1.6 mm stainless steel tubing, made as short as possible to minimize any loss of resolution during the many passes through valve and detector. The resolution possible with a recycle system is limited by two factors. The first derives from the normal spreading of a peak while moving through the column, valve and connections. The limiting situation, when the sample occupies one entire length of column, occurs with these ethylenes after passage through 5 lengths (38 m) of column. The second restriction applies only to a radioactive system. Recycling must be terminated before decay has reduced the counting rate below a few hundred counts per 10-second interval. For compounds which produce a 15% yield of carbon-11 labeled ethylene, the practical limit is 3.5 hours after end-of-bombardment. For compounds with 3% yield the limit is about 2.5 hours.

The separation achieved by this chromatograph is illustrated in Figure 19. Retention times were determined by injection of  $C_2H_4$  (Matheson USP grade) and ethylene- $d_1$ ,  $d_2$ ,  $d_3$  and  $d_4$  obtained from Merck, Sharp and Dohme, Ltd., Montreal, Canada. The first peak off the column is  $C_2H_4$ , followed by the other isomers in order of increasing mass.



CHROMATOGRAPHIC SEPARATION OF DEUTERATED ETHYLENES

FIGURE 19

### c. Counter and Flow Meter

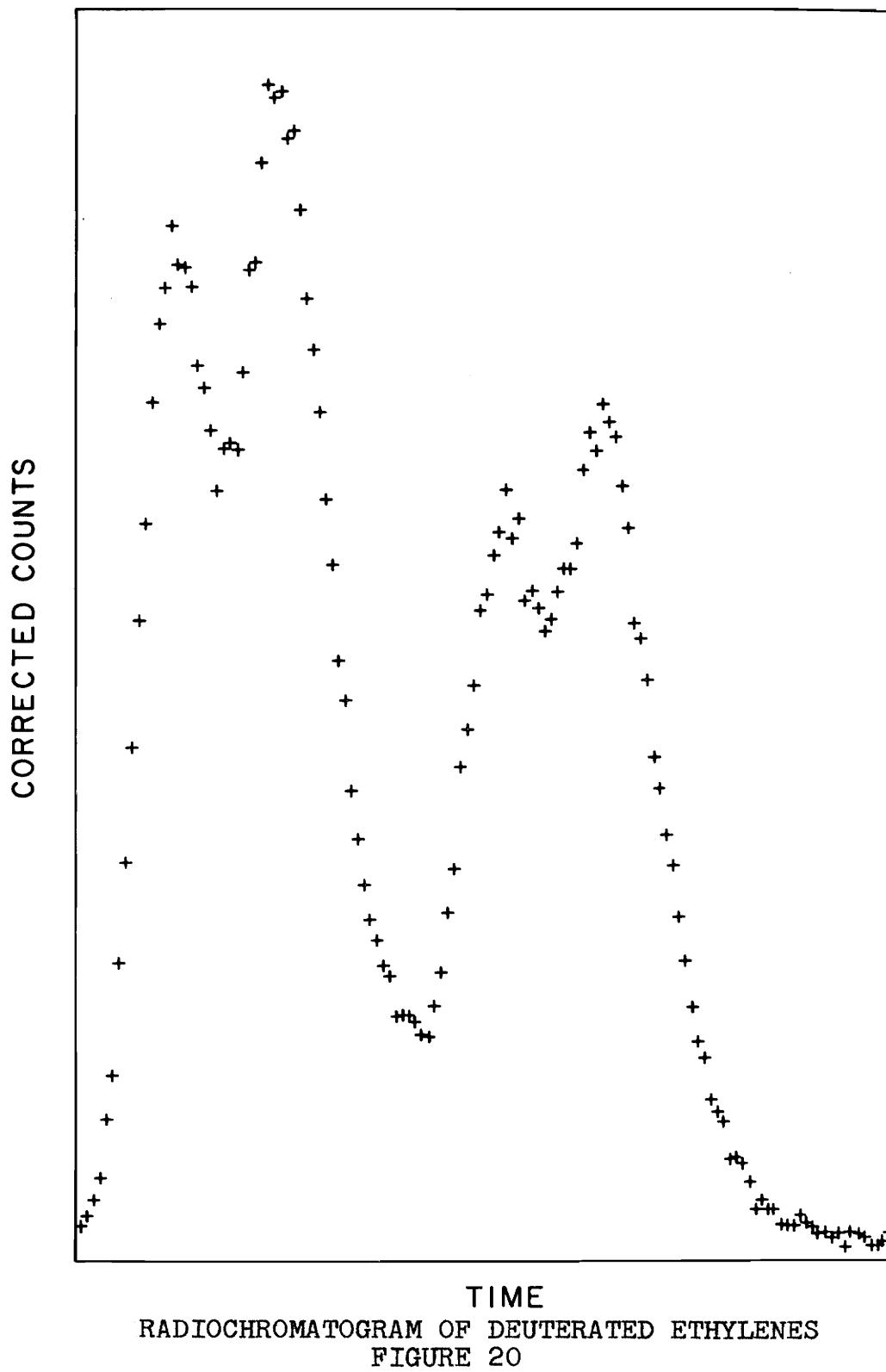
After the final pass through the  $\text{AgNO}_3$  columns the ethylenes exited through the valve (Figure 19) into a window flow proportional counter. This counter was in every way identical to that discussed previously, except the active volume was 25 cc instead of 40 cc in order to minimize loss of resolution in the counter. Since the counter efficiency is proportional to active volume, it is not surprising to find the counter efficiency to be only 21%.

The digital flow meter was identical to that described above.

### d. Data Handling

Data were recorded by the same Hewlett-Packard Data Acquisition System as described previously. The computer program ORGATOM<sup>57</sup> was used to correct the data for background, flow rate and radioactive decay, but the areas under peaks were not calculated. Instead, each number was plotted with respect to time, as shown in a typical plot in Figure 20. Each point represents the number of counts (corrected) during a 10-second interval. The actual number of counts recorded during a 10-second interval at the peak maxima was approximately 1500.

The relative area under each component peak was found using a Dupont 310 Curve Resolver. This instrument is a

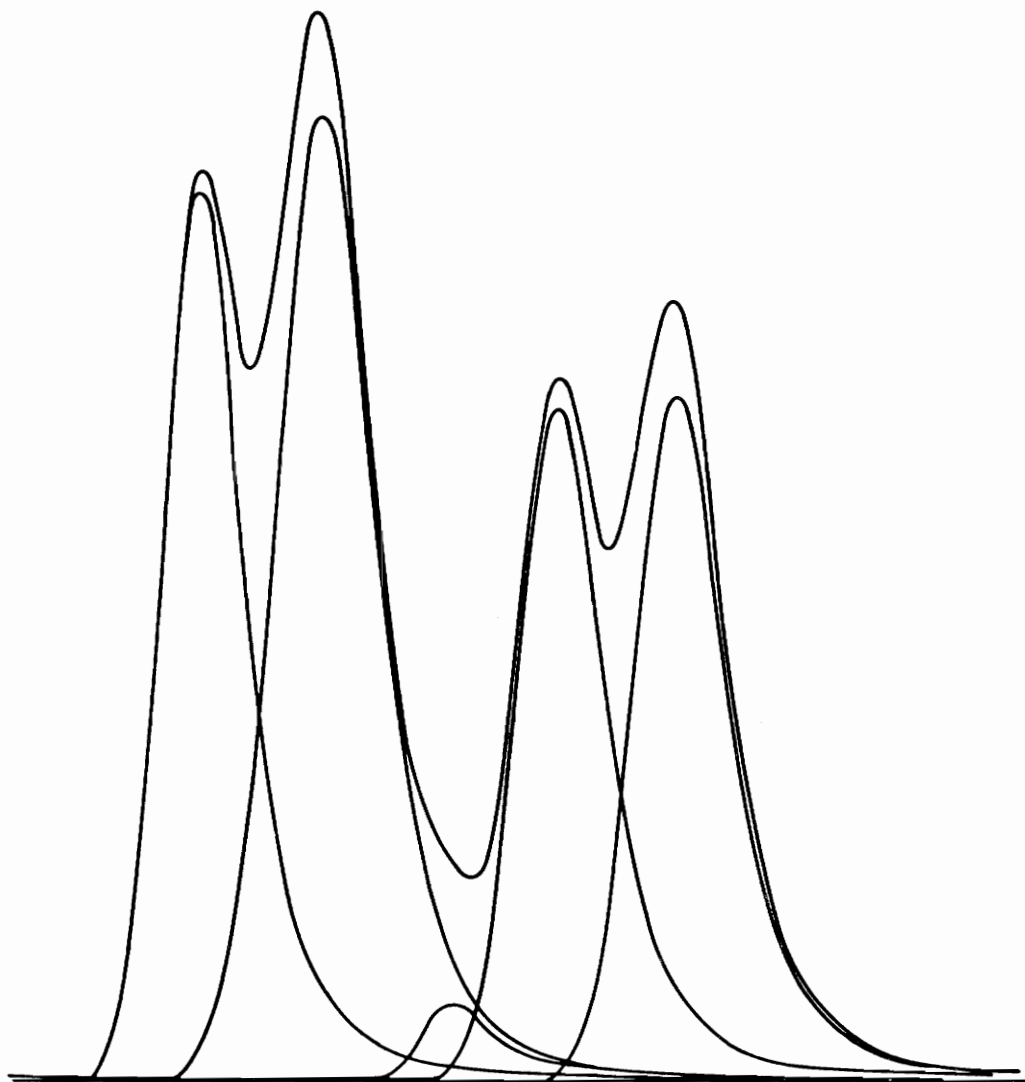




small analog computer which requires input of the actual curve shapes which are to be resolved from a complex curve. It was necessary to have the activity peaks since they are expected to differ somewhat from the mass peaks seen by the thermal conductivity cell. This is because additional spreading of the peaks occurs in the relatively large volume of the radioactivity detector after they have passed through the thermal conductivity detector and been recorded.

To obtain the standard shape for the first peak, propane gas was irradiated to produce a single radioactive ethylene peak:  $^{11}\text{C}_2\text{H}_4$ . Similarly, propane- $\text{d}_8$  was irradiated to produce  $^{11}\text{C}_2\text{D}_4$ . Unfortunately, the propane- $\text{d}_8$  contained enough impurity propane- $\text{d}_7$  to give a small shoulder of  $^{11}\text{C}_2\text{HD}_3$  on the rising part of the ethylene- $\text{d}_4$  peak. Since the shoulder was so small, the shape of the ethylene- $\text{d}_4$  peak could be estimated in this region with little difficulty. The first and last peaks proved to be good approximations of skewed gaussians. The intervening peaks (ethylene- $\text{d}_1$ , ethylene- $\text{d}_2$  and ethylene- $\text{d}_3$ ) were assumed also to be skewed gaussians and to elute in order of increasing mass. A typical set of resolved curves is shown in Figure 21.

Peak areas were corrected for the non-isotopic purity of the substrate in the following way. Consider the



RESOLUTION BY DUPONT-310  
CURVE RESOLVER

FIGURE 21

example of  $\text{CH}_3\text{CD}_3$  which was reported to be 97.1% pure, with the major impurity assumed to be  $\text{CH}_3\text{CHD}_2$ . When this compound was irradiated the resulting  $^{11}\text{C}$ -ethylenes were distributed as follows:

24.0%  $\text{C}_2\text{H}_4$ , 32.3%  $\text{C}_2\text{H}_3\text{D}$ , 3.7%  $\text{C}_2\text{H}_2\text{D}_2$ , 19.8%  $\text{C}_2\text{HD}_3$ , and 20.2%  $\text{C}_2\text{D}_4$ .

If the ethane- $\text{d}_3$  had been 100% pure and there were no isotope effects operative, we would expect to see:

25.0%  $\text{C}_2\text{H}_4$ , 25.0%  $\text{C}_2\text{H}_3\text{D}$ , 25.0%  $\text{C}_2\text{HD}_3$ , and 25.0%  $\text{C}_2\text{D}_4$ .

If the  $\text{CH}_3\text{CD}_3$  were 97.1% pure and there were no isotope effect, we predict the ethylene distribution:

25.24%  $\text{C}_2\text{H}_4$ , 24.76%  $\text{C}_2\text{H}_3\text{D}$ , 0.77%  $\text{C}_2\text{H}_2\text{D}_2$ , 25.21%  $\text{C}_2\text{HD}_3$ , and 24.01%  $\text{C}_2\text{D}_4$ .

Therefore, we correct the experimental results as follows:

$$\% \text{C}_2\text{H}_4 = 24.0 (25.0)/(25.24) = 23.8$$

$$\% \text{C}_2\text{H}_3\text{D} = 32.3 (25.0)/(24.76) = 32.7$$

$$\% \text{C}_2\text{H}_2\text{D}_2 = 3.7 - 0.77 = 2.9$$

$$\% \text{C}_2\text{HD}_3 = 19.8 (25.0)/(25.21) = 19.6$$

$$\% \text{C}_2\text{D}_4 = 20.2 (25.0)/(24.01) = 21.0$$

Naturally, the correction is more important when the compound is less isotopically pure.

## CHAPTER III

### RESULTS

#### A. Specifically-Deuterated Compounds

The relative yields of the five mass isomers of deuteroethylene- $^{11}\text{C}$  produced during the proton irradiation of deuterated alkanes and alkyl chlorides are summarized in Tables V and VI, respectively. The assay technique used in this investigation can distinguish mass isomers of ethylene, but not positional isomers. For example,  $^{11}\text{CH}_2=\text{CD}_2$ ,  $\text{CH}_2=^{11}\text{CD}_2$ , *cis*- $\text{CHD}=\text{CHD}$ , and *trans*- $\text{CHD}=\text{CHD}$  cannot be distinguished. These data have been corrected for the non-isotopic purity of the substrate, as discussed previously, and represent the arithmetic mean of the results of at least three experiments. The error limits cited are one standard deviation.

Samples were irradiated at room temperature in the gas phase at a pressure of 700 mmHg, and in the presence of 4.5 mol % oxygen scavenger. There were the following exceptions: 1) Mixtures containing carbon tetrachloride and *n*-butyl chloride were heated to 80°C during the bombardment to render them gaseous. 2) The mixture of xenon, ethane and ethane- $\text{d}_6$  contained 2.25 mol % oxygen, although the ratio of ethane to oxygen was the same as in all other samples.

TABLE V

## Ethylene Yields in Specifically-Deuterated Alkanes

Substrate	% of total ethylene- <sup>11</sup> C					Absolute yields ethylene- <sup>11</sup> C
	<sup>11</sup> C <sub>2</sub> H <sub>4</sub>	<sup>11</sup> C <sub>2</sub> H <sub>3</sub> D	<sup>11</sup> C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	<sup>11</sup> C <sub>2</sub> HD <sub>3</sub>	<sup>11</sup> C <sub>2</sub> D <sub>4</sub>	
C <sub>2</sub> H <sub>6</sub> +C <sub>2</sub> D <sub>6</sub>	24.2±.8	33.9±.6	0.9±.7	19.4±.9	21.3±.5	16.6±2.3
CH <sub>3</sub> CD <sub>3</sub>	23.4±1.8	32.9±1.3	1.9±.7	19.3±.9	22.5±1.7	17.1±1.0
CHD <sub>2</sub> CHD <sub>2</sub>	—	—	28.0±1.0	72.0±1.1	—	18.0±.4
CH <sub>2</sub> DCH <sub>2</sub> D	—	63.7±1.8	36.3±2.4	—	—	15.9±0.8
C <sub>3</sub> H <sub>8</sub> +C <sub>3</sub> D <sub>8</sub>	25.3±1.7	29.2±.8	2.8±1.2	19.8±1.6	23.0±1.6	14.1±1.0
CH <sub>3</sub> CD <sub>2</sub> CH <sub>3</sub>	68.2±.5	32.0±1.1	—	—	—	13.7±2.0
CD <sub>3</sub> CH <sub>2</sub> CD <sub>3</sub>	—	0.7±.6	0.4±.6	26.8±1.3	72.1±1.0	13.2±1.2
CH <sub>3</sub> CH <sub>2</sub> CD <sub>3</sub>	34.0±1.8	23.8±.5	1.3±1.0	26.1±.9	14.8±.5	13.8±.9
CH <sub>3</sub> CD <sub>2</sub> CH <sub>3</sub> +CD <sub>3</sub> CH <sub>2</sub> CD <sub>3</sub>	24.2±.6	33.5±1.3	0.5±.3	20.2±1.0	21.6±.8	14.4±.3

TABLE VI

Ethylene Yields in Specifically-Deuterated Alkyl Chlorides and Miscellaneous Substates

Substrate	% of total ethylene- <sup>11</sup> C					Absolute yields ethylene- <sup>11</sup> C
	<sup>11</sup> C <sub>2</sub> H <sub>4</sub>	<sup>11</sup> C <sub>2</sub> H <sub>3</sub> D	<sup>11</sup> C <sub>2</sub> H <sub>2</sub> D <sub>2</sub>	<sup>11</sup> C <sub>2</sub> HD <sub>3</sub>	<sup>11</sup> C <sub>2</sub> D <sub>4</sub>	
C <sub>2</sub> H <sub>5</sub> Cl + C <sub>2</sub> D <sub>5</sub> Cl	29.1 ± .6	28.3 ± .3	0.4 ± .5	22.6 ± .8	19.5 ± 1.2	4.2 ± .5
n-C <sub>4</sub> H <sub>9</sub> Cl + n-C <sub>4</sub> D <sub>9</sub> Cl	31.4 ± 1.8	28.4 ± 1.8	0.6 ± .3	21.7 ± 1.2	17.9 ± 2.6	7.0 ± .6
14% CCl <sub>4</sub> + (C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> D <sub>6</sub> )	31.0 ± 2.0	29.8 ± .3	0.8 ± 1.0	20.6 ± .6	17.6 ± 1.5	11.8 ± .7
50% Xe + (C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> D <sub>6</sub> )	25.4 ± 1.3	32.4 ± 1.5	0.1 ± .9	19.7 ± 1.2	22.6 ± 1.6	13.8 <sup>a</sup>
CD <sub>3</sub> CH <sub>2</sub> Cl	1.7 ± .4	3.3 ± .7	1.0 ± .4	42.0 ± .7	52.0 ± 0.0	3.7 ± .1

<sup>a</sup>Only one determination.

When a substrate is listed in these tables as a mixture of deuterated and protonated components, this indicates an equimolar mixture of the two. For example,  $C_2H_6 + C_2D_6$  refers to a mixture of 334.3 mm  $C_2H_6$ , 334.3 mm  $C_2D_6$  and 31.5 mm oxygen. These tables also list the observed absolute yields of ethylene- $^{11}C$ , based on the total gaseous activity.

Tables VII and VIII show ratios of certain products ( $\pm$  one standard deviation) for each substrate listed in Tables V and VI. The significance of these ratios will be discussed later in regard to the probable intermediate in the mechanism of ethylene formation.

#### B. Xenon Moderator Experiments

Figure 22 shows the influence of xenon concentration on major product yields in oxygen-scavenged ethane. The data, including the yields of some minor  $^{11}C$ -labeled hydrocarbon products, appear in Table IX with error limits of one standard deviation.

Any small variations in the ratio of ethane to oxygen were avoided by preparing a standard mixture of 4.5%  $O_2$ -95.5%  $C_2H_6$  which was diluted with the proper amount of xenon to obtain the desired concentration of moderator. All samples were irradiated at room temperature in the gas phase at 700 mmHg pressure with a beam intensity of one microampere for 50 seconds. Data represent the

TABLE VII

Product Ratios in Ethylene-<sup>11</sup>C Formed in Alkanes

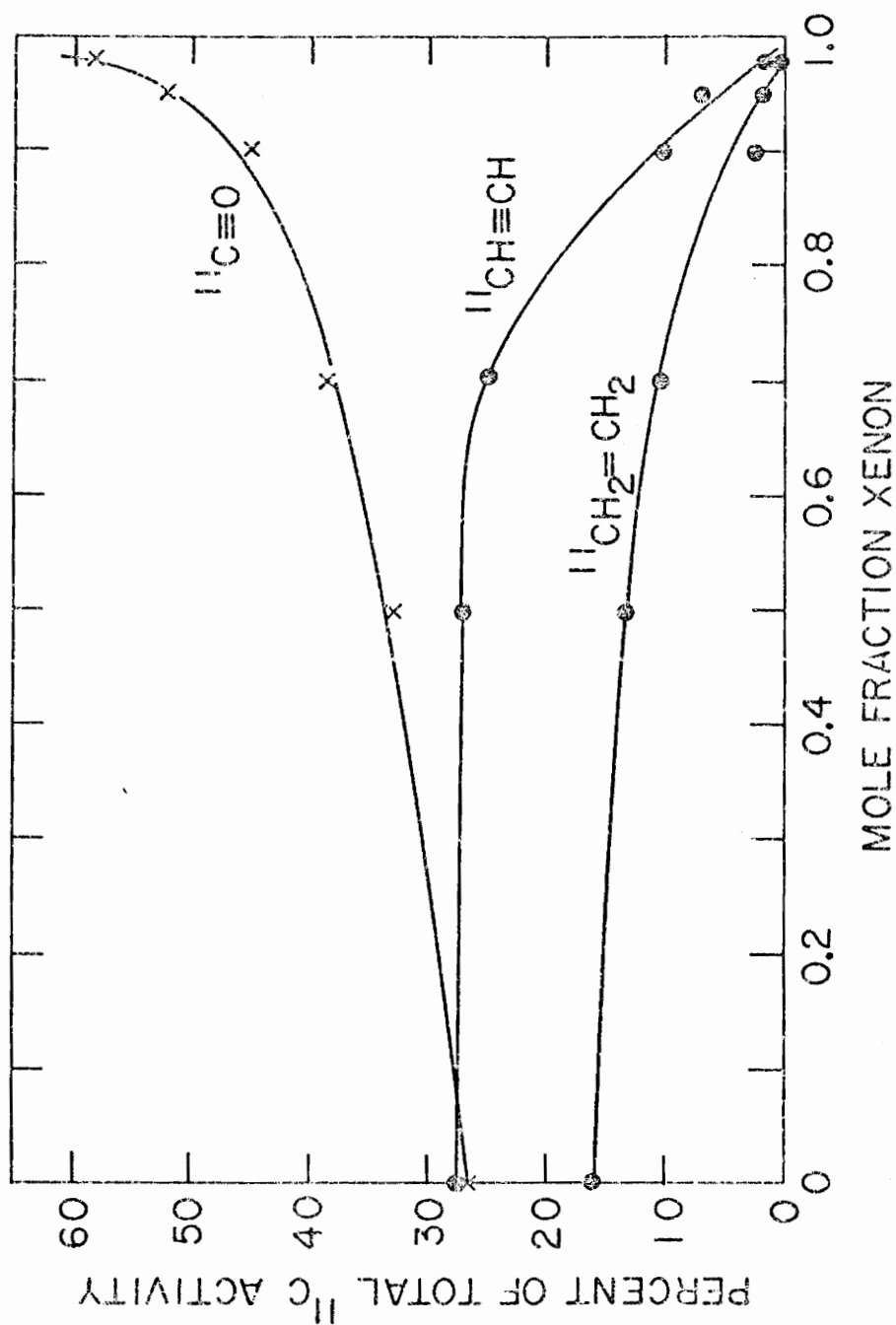
Substrate	$\frac{^{11}\text{C}_2\text{H}_4}{^{11}\text{C}_2\text{H}_3\text{D}}$	$\frac{^{11}\text{C}_2\text{HD}_3}{^{11}\text{C}_2\text{D}_4}$	$\frac{^{11}\text{C}_2\text{H}_4 + ^{11}\text{C}_2\text{HD}_3}{^{11}\text{C}_2\text{H}_3\text{D} + ^{11}\text{C}_2\text{D}_4}$	$\frac{^{11}\text{C}_2\text{H}_4}{^{11}\text{C}_2\text{HD}_3}$	$\frac{^{11}\text{C}_2\text{H}_3\text{D}}{^{11}\text{C}_2\text{D}_4}$	$\frac{^{11}\text{C}_2\text{H}_4 + ^{11}\text{C}_2\text{H}_3\text{D}}{^{11}\text{C}_2\text{HD}_3 + ^{11}\text{C}_2\text{D}_4}$
C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> D <sub>6</sub>	0.71 ± .04	0.91 ± .06	0.79 ± 0.05	1.25 ± .10	1.60 ± .07	1.43 ± 0.08
CH <sub>3</sub> CD <sub>3</sub>	0.71 ± .08	0.86 ± .11	0.77 ± 0.09	1.21 ± .15	1.46 ± .17	1.34 ± 0.16
CHD <sub>2</sub> CHD <sub>2</sub>	$\frac{^{11}\text{C}_2\text{H}_2\text{D}_2}{^{11}\text{C}_2\text{HD}_3} = 0.78 \pm .02$					
CH <sub>2</sub> DCH <sub>2</sub> D	$\frac{^{11}\text{C}_2\text{H}_3\text{D}}{^{11}\text{C}_2\text{H}_2\text{D}_2} = 0.88 \pm .17$					
C <sub>3</sub> H <sub>8</sub> + C <sub>3</sub> D <sub>8</sub>	0.86 ± .13	0.87 ± .08	0.86 ± .10	1.28 ± .19	1.27 ± .12	1.27 ± 0.16
CD <sub>3</sub> CH <sub>2</sub> CD <sub>3</sub>		0.87 ± .02	0.87 ± .02			
CH <sub>3</sub> CD <sub>2</sub> CH <sub>3</sub>	0.91 ± .09		0.91 ± .09			
CH <sub>3</sub> CH <sub>2</sub> CD <sub>3</sub>	0.77 ± .11	0.95 ± .12	0.84 ± .11	1.30 ± .11	1.61 ± .03	1.41 ± .10
CH <sub>3</sub> CD <sub>2</sub> CH <sub>3</sub> + CD <sub>3</sub> CH <sub>2</sub> CD <sub>3</sub>	0.72 ± .05	0.94 ± .08	0.81 ± .06	1.20 ± .09	1.55 ± .12	1.38 ± .11



TABLE VIII

Product Ratios in Ethylene-<sup>11</sup>C Formed in Alkyl Chlorides and Miscellaneous Substrates

Substrate	$\frac{^{11}\text{C}_2\text{H}_4}{^{11}\text{C}_2\text{H}_3\text{D}}$	$\frac{^{11}\text{C}_2\text{HD}_3}{^{11}\text{C}_2\text{D}_4}$	$\frac{^{11}\text{C}_2\text{H}_4 + ^{11}\text{C}_2\text{HD}_3}{^{11}\text{C}_2\text{H}_3\text{D} + ^{11}\text{C}_2\text{D}_4}$	$\frac{^{11}\text{C}_2\text{H}_4}{^{11}\text{C}_2\text{HD}_3}$	$\frac{^{11}\text{C}_2\text{H}_3\text{D}}{^{11}\text{C}_2\text{D}_4}$	$\frac{^{11}\text{C}_2\text{H}_4 + ^{11}\text{C}_2\text{H}_3\text{D}}{^{11}\text{C}_2\text{HD}_3 + ^{11}\text{C}_2\text{D}_4}$
C <sub>2</sub> H <sub>5</sub> Cl + C <sub>2</sub> D <sub>5</sub> Cl	1.03 ± .03	1.16 ± .11	1.08 ± .06	1.29 ± .07	1.45 ± .11	1.36 ± .09
n-C <sub>4</sub> H <sub>9</sub> Cl + n-C <sub>4</sub> D <sub>9</sub> Cl	1.11 ± .13	1.21 ± .24	1.15 ± .17	1.45 ± .16	1.59 ± .34	1.52 ± .25
14% CCl <sub>4</sub> + 86% (C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> D <sub>6</sub> + O <sub>2</sub> )	1.04 ± .08	1.17 ± .13	1.09 ± .10	1.51 ± .15	1.69 ± .16	1.57 ± .15
50% Xe + 50% (C <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> D <sub>6</sub> + O <sub>2</sub> )	0.78 ± .07	0.84 ± .12	0.82 ± .09	1.29 ± .14	1.43 ± .17	1.36 ± .16
CD <sub>3</sub> CH <sub>2</sub> Cl		1.21 ± 0.01	1.21 ± 0.01			



ABSOLUTE YIELDS OF MAJOR LABELLED PRODUCTS DURING  $^{12}\text{C}(p, n)^{13}\text{C}$  ON ETHANE-XENON MIXTURES

FIGURE 22

TABLE IX

Variation With Xenon Concentration of Major Labelled Product Yields  
in Oxygen-Scavenged Ethane

% Xe	% of total gaseous activity							
	$^{11}\text{CO}$	$^{11}\text{CO}_2$	$^{11}\text{CH}_4$	$^{11}\text{C}_2\text{H}_4$	$^{11}\text{C}_2\text{H}_2$	$^{11}\text{C}_3\text{H}_8$	$^{11}\text{C}_3\text{H}_6$	$^{11}\text{C}_3\text{H}_4$
0	$26.5 \pm 0.1$	$3.3 \pm 0.5$	$0.4 \pm 0.1$	$15.9 \pm 0.3$	$27.6 \pm 0.3$	$3.5 \pm 0.1$	$3.6 \pm 0.1$	$1.2 \pm 0.1$
50	$33.0 \pm 1.9$	$2.9 \pm 0.3$	$0.2 \pm 0.1$	$13.2 \pm 0.8$	$26.9 \pm 1.4$	$2.4 \pm 0.1$	$3.0 \pm 0.2$	$1.2 \pm 0.1$
70	$38.7 \pm 1.3$	$3.0 \pm 0.8$	$0.1 \pm 0.0$	$10.4 \pm 0.6$	$24.9 \pm 2.4$	$1.7 \pm 0.0$	$2.3 \pm 0.0$	$1.2 \pm 0.1$
90	$45.1 \pm 1.0$	$1.9 \pm 0.1$	$0.3 \pm 0.1$	$2.6 \pm 0.5$	$10.1 \pm 1.4$	$3.0 \pm 0.4$	$1.0 \pm 0.4$	$3.8 \pm 1.1$
95	$52.3 \pm 1.2$	$1.1 \pm 0.1$	$0.4 \pm 0.2$	$1.8 \pm 0.2$	$7.1 \pm 1.5$	$3.3 \pm 0.4$	$0.6 \pm 0.7$	$4.1 \pm 0.3$
98	$58.3 \pm 6.6$	$0.9 \pm 0.9$	$0.5 \pm 0.4$	$< 0.1$	$1.3 \pm 0.3$	$3.5 \pm 0.3$	$0.9 \pm 0.3$	$2.6 \pm 0.8$

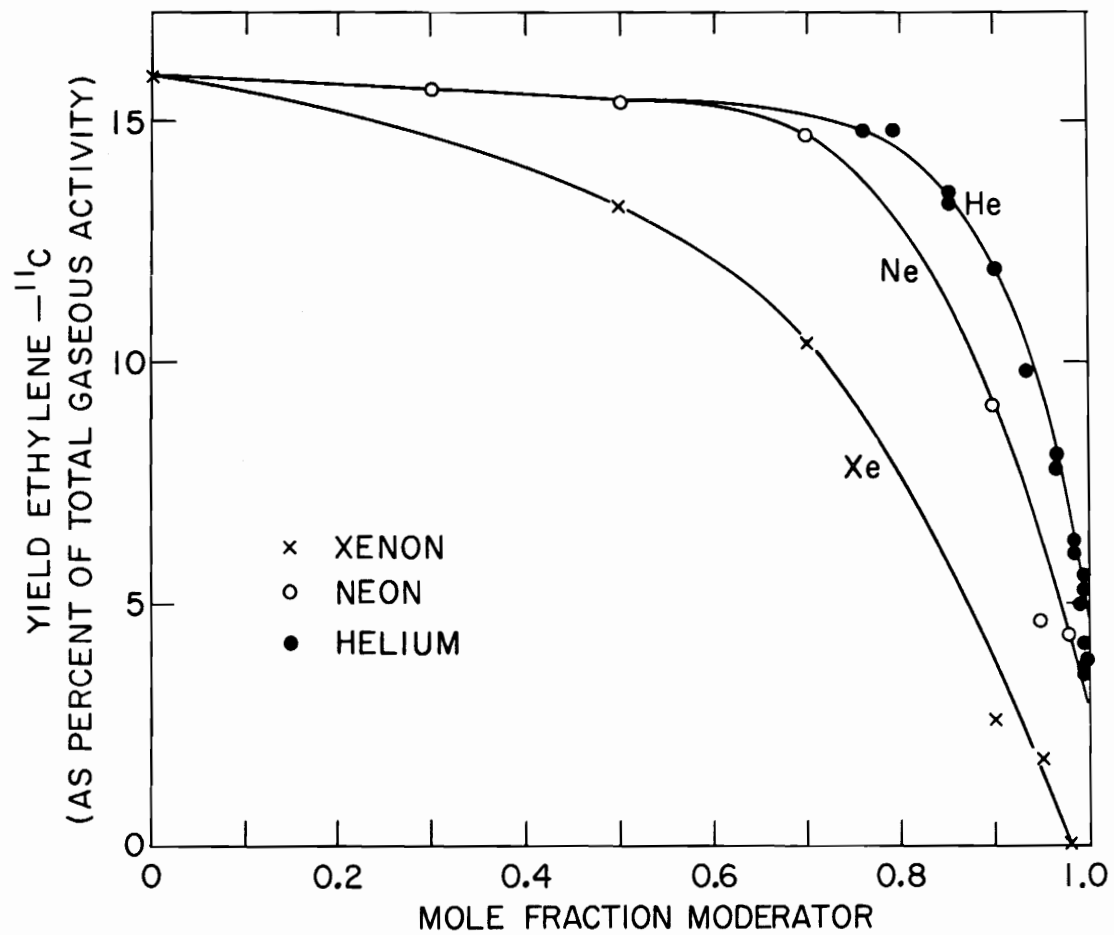
arithmetic mean of at least three experiments.

A comparison of these moderator curves with those determined by other investigators in helium<sup>2</sup> and neon<sup>64</sup> shows some surprising results. These experiments were performed under the same conditions, except the helium experiments were performed just once at each indicated concentration, and the samples were irradiated at a total pressure of 760 mmHg instead of at 700. Figure 23 shows the ethylene-<sup>11</sup>C yield as a function of moderator concentration for xenon, helium and neon. The acetylene-<sup>11</sup>C and carbon monoxide-<sup>11</sup>C yields in the same noble gases appear in Figures 24 and 25, respectively.

The final plots (Figures 26 and 27) show the variation with noble gas concentration of the ratio of the yields of the two most abundant products, acetylene and ethylene, and the ratio of the sum of carbon monoxide and acetylene to ethylene yield. These will be discussed as possible evidence for the spin states of carbon undergoing reaction.

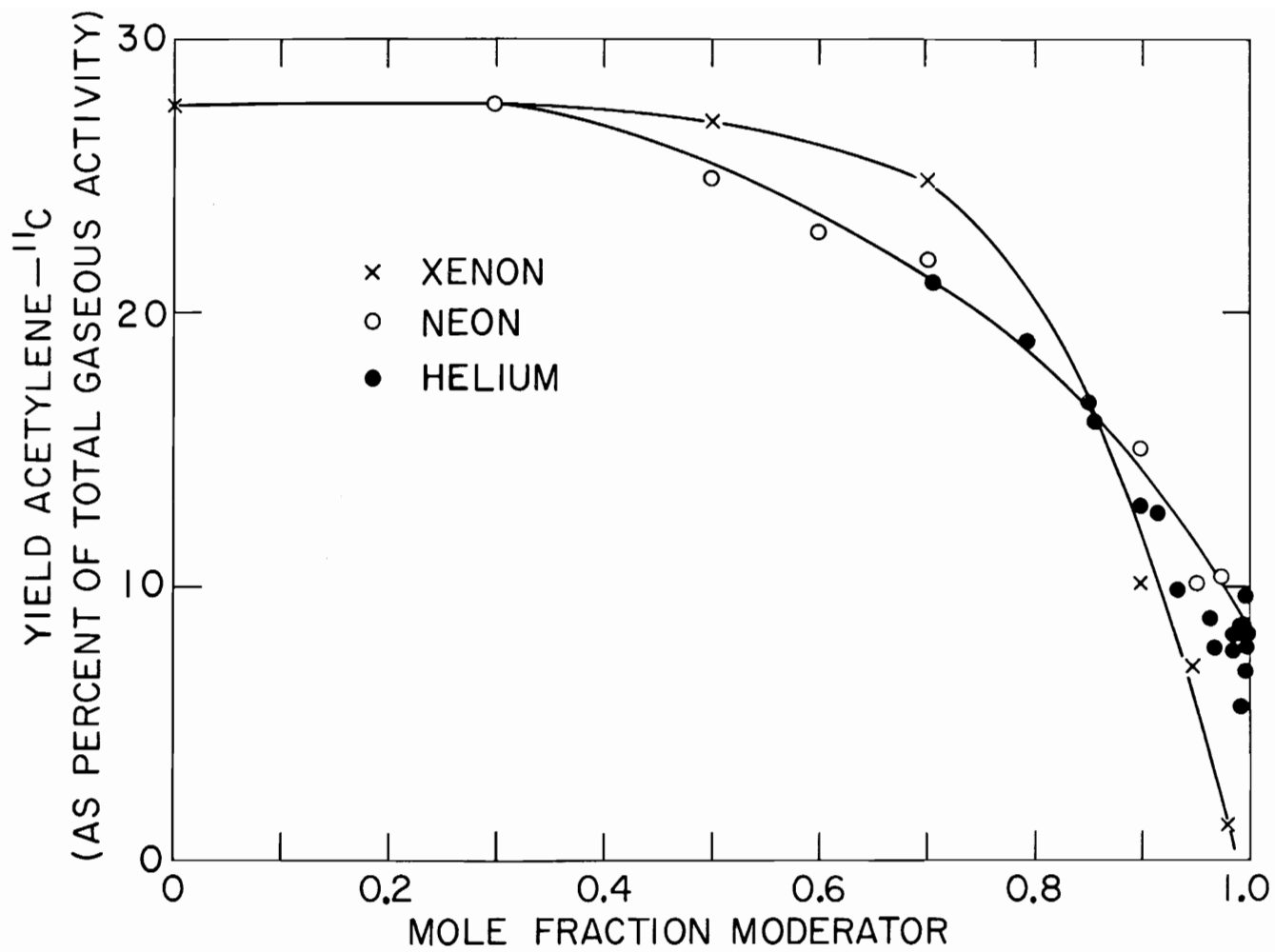
### C. Hydrogen-Alkane and Hydrogen-Alkyl Halide Mixtures

A series of experiments was performed in which hydrogen was mixed in varying ratios with ethane-d<sub>6</sub> and with neo-pentane-d<sub>12</sub> in the presence of 4.5 mol % oxygen scavenger. Other mixtures contained D<sub>2</sub>-ethane, D<sub>2</sub>-ethyl chloride and D<sub>2</sub>-ethyl fluoride. In such cases only two different deuterated ethylenes can be formed since ethylene



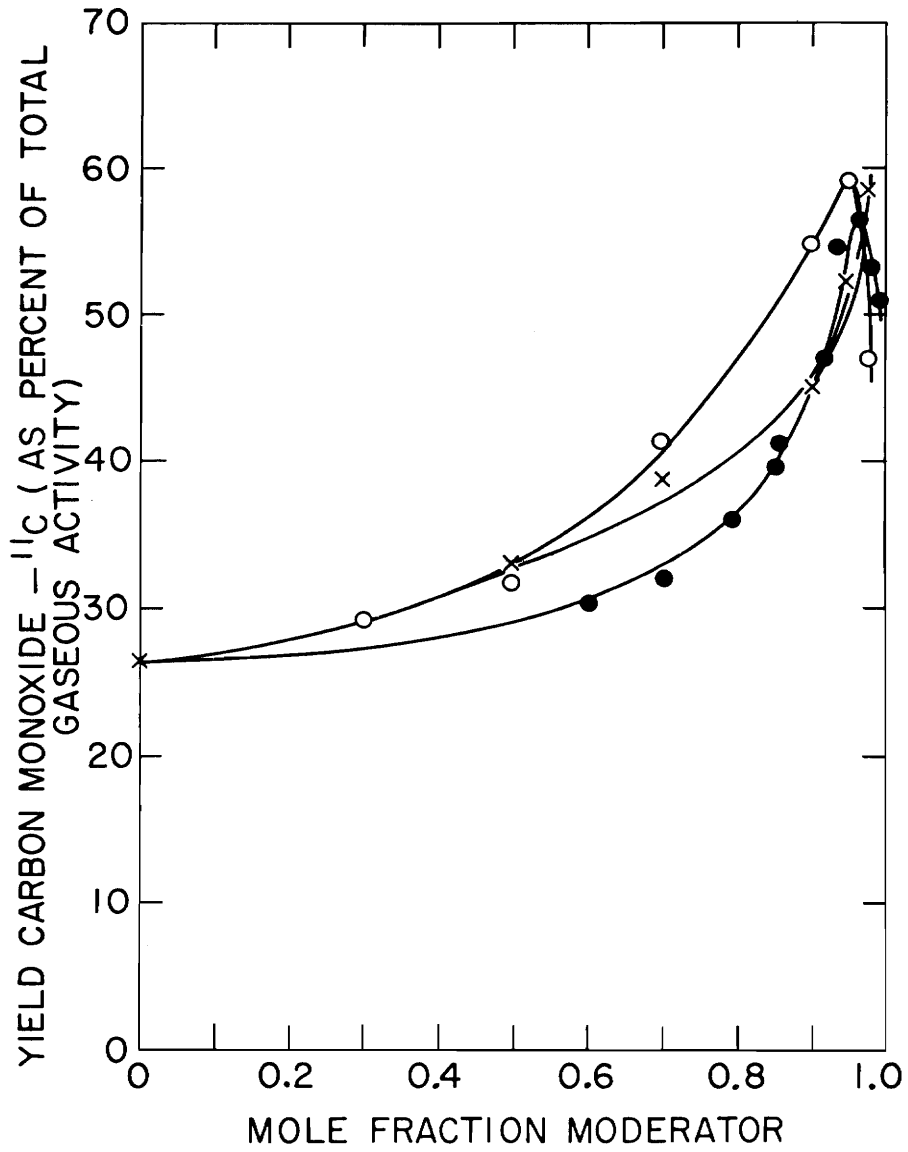
YIELD  $\text{H}_2=^{11}\text{C}\text{H}_2$  IN ETHANE vs MOLE FRACTION MODERATOR

FIGURE 23



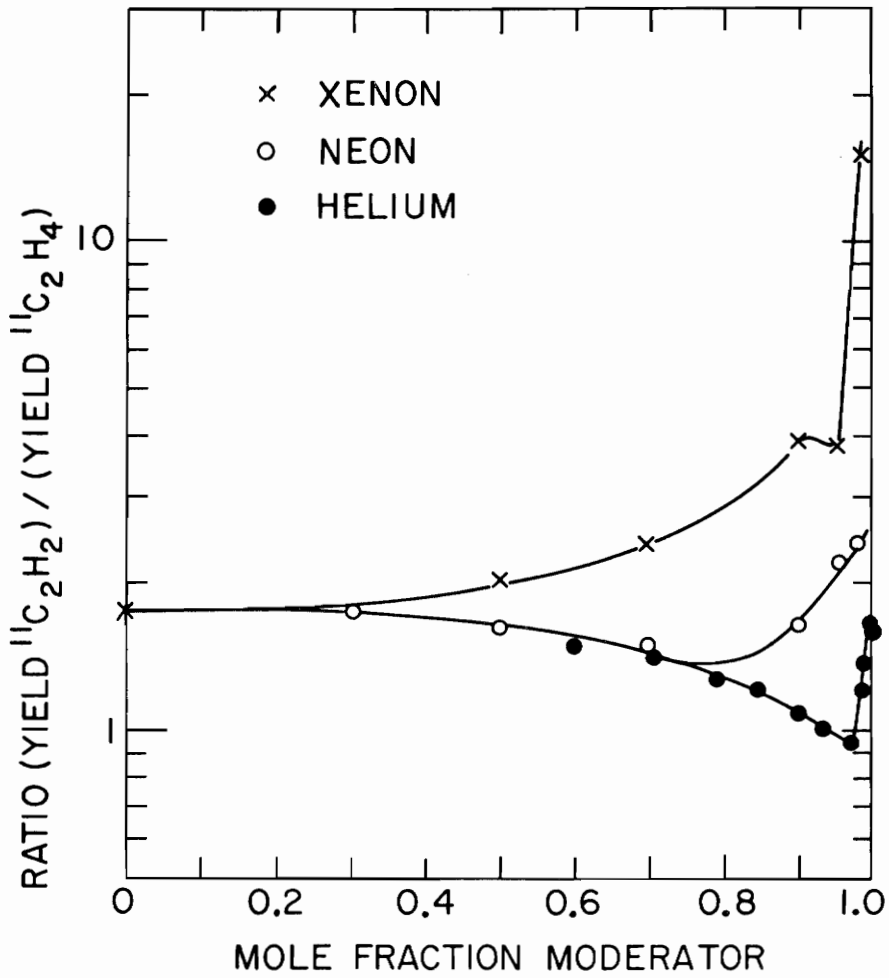
YIELD  $\text{HC}\equiv^{13}\text{CH}$  IN ETHANE vs MOLE FRACTION MODERATOR

FIGURE 24



VARIATION OF  $^{11}\text{C}\equiv\text{O}$  YIELD WITH MODERATOR CONCENTRATION

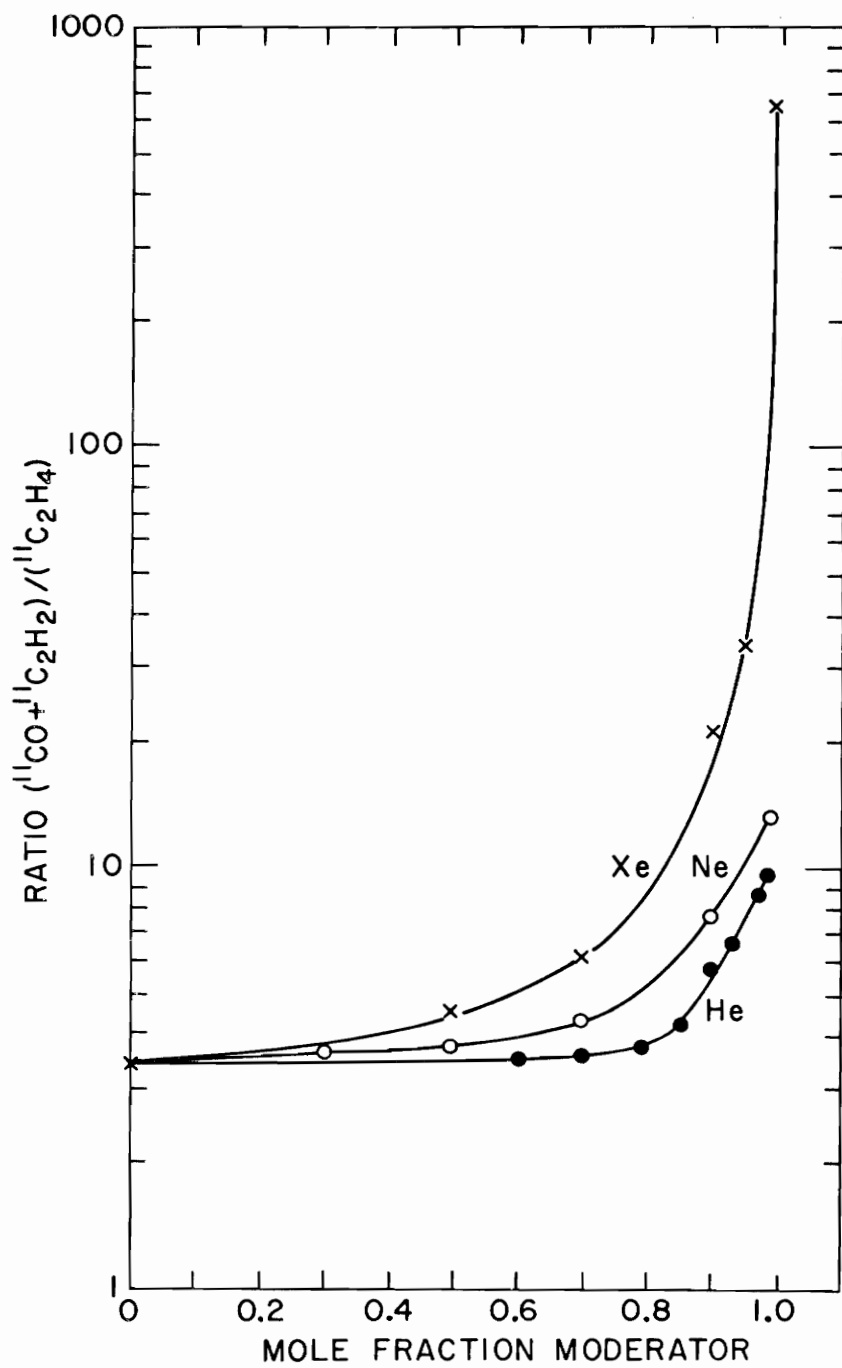
FIGURE 25



RATIO  $\frac{\text{ACETYLENE}-^{13}\text{C}}{\text{ETHYLENE}-^{13}\text{C}}$  vs MOLE FRACTION  
MODERATOR IN ETHANE

FIGURE 26





RATIO  $\frac{^{11}\text{CO} + ^{11}\text{C}_2\text{H}_2}{^{11}\text{C}_2\text{H}_4}$  vs MOLE FRACTION MODERATOR

FIGURE 27

must originate from the methyl group of the hydrocarbon. These systems produce quite different absolute yields of  $^{11}\text{C}$ -labeled ethylene as can be seen in Table X, however, the relative yields of the two deuterated ethylenes are surprisingly uniform. For example, the 1:3 mixtures of hydrogen- $\text{d}_2$  with ethane, ethyl fluoride and ethyl chloride, respectively, exhibit  $^{11}\text{C}$ -ethylene yields of 16, 10, and 4.5%, but their relative yields of  $^{11}\text{C}_2\text{H}_3\text{D}$  are 16.0, 14.5 and 15.3%, respectively. These relative yields are listed in Table XI and plotted in Figures 28 and 29 with respect to the collision fraction of  $\text{D}_2$  or  $\text{H}_2$  in the gas mixture.

The collision fraction of one component of a two component mixture is defined as:

$$(\text{C.F.})_1 = \frac{(\pi \sigma_{\text{C-1}})^2}{(\pi \sigma_{\text{C-1}})^2 + (\pi \sigma_{\text{C-2}})^2}$$

where,  $\sigma_{\text{C-1}}$  and  $\sigma_{\text{C-2}}$  are the collision diameters for rigid sphere collisions between carbon and components 1 and 2, respectively, and

$$\sigma_{\text{C-1}} = \frac{1}{2} (\sigma_{\text{C}} + \sigma_1)$$

The collision diameters used in this calculation appear in Table XII.

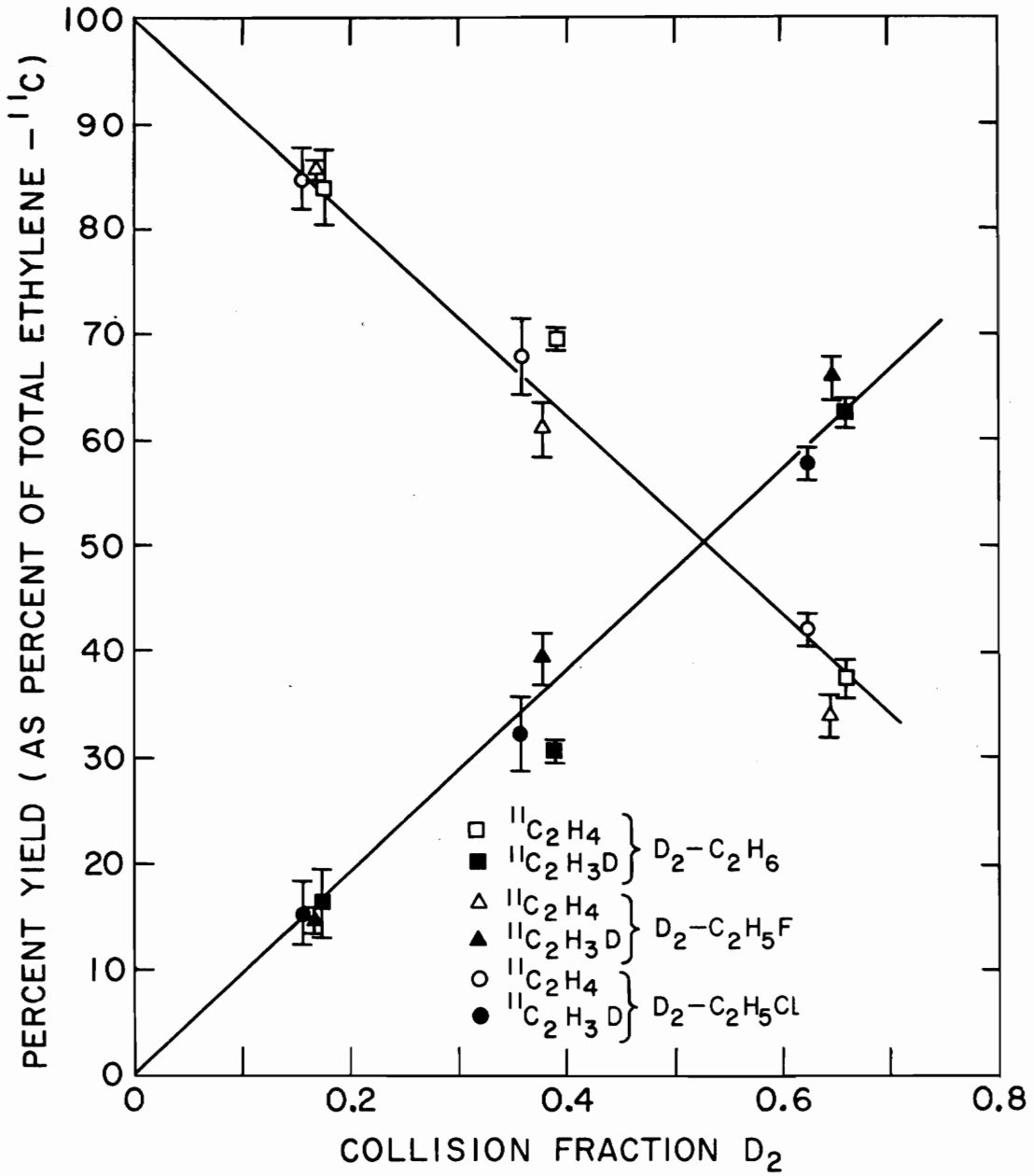
TABLE X

## Absolute Yields of Major Products in Hydrogen Mixtures

Substrate		% of total gas phase activity			
		$^{11}\text{CO}$	$^{11}\text{CO}_2$	$^{11}\text{C}_2\text{H}_4$	$^{11}\text{C}_2\text{H}_2$
$\text{D}_2 + \text{C}_2\text{H}_6$	(3:1)	$43.4 \pm 3.4$	$8.9 \pm 0.3$	$7.6 \pm 1.2$	$17.9 \pm 1.2$
	(1:1)	$33.7 \pm 2.4$	$7.7 \pm 1.6$	$12.5 \pm 1.4$	$25.9 \pm 0.8$
	(1:3)	$27.9 \pm 2.5$	$5.3 \pm 0.3$	$16.3 \pm 0.7$	$30.1 \pm 1.2$
$\text{D}_2 + \text{C}_2\text{H}_5\text{F}$	(3:1)	$35.0 \pm 0.7$	$13.8 \pm 0.4$	$4.9 \pm 0.2$	$16.2 \pm 1.0$
	(1:1)	$37.8 \pm 3.4$	$14.0 \pm 1.1$	$5.3 \pm 0.3$	$21.7 \pm 0.9$
	(1:3)	$28.6 \pm 0.1$	$12.2 \pm 0.1$	$10.1 \pm 0.1$	$25.0 \pm 0.1$
$\text{D}_2 + \text{C}_2\text{H}_5\text{Cl}$	(3:1)	$54.2 \pm 2.9$	$7.0 \pm 0.3$	$2.3 \pm 0.2$	$15.4 \pm 0.6$
	(1:1)	$45.0 \pm 5.0$	$5.0 \pm 0.4$	$2.8 \pm 1.1$	$18.7 \pm 0.7$
	(1:3)	$52.2 \pm 3.2$	$4.1 \pm 0.5$	$4.5 \pm 0.8$	$25.3 \pm 1.5$
$\text{H}_2 + \text{C}_2\text{D}_6$	(3:1)	$24.7 \pm 4.1$	$11.5 \pm 2.5$	$7.2 \pm 1.7$	$17.0 \pm 2.0$
	(1:1)	$29.7 \pm 3.9$	$9.3 \pm 1.4$	$13.0 \pm 1.7$	$26.3 \pm 3.8$
	(1:3)	$29.6 \pm 4.9$	$6.7 \pm 1.0$	$15.8 \pm 3.7$	$27.9 \pm 5.1$
$\text{H}_2 + \text{neo-C}_5\text{D}_{12}$	(4:1)	$29.0 \pm 0.8$	$7.3 \pm 0.6$	$12.4 \pm 0.8$	$21.7 \pm 0.7$
	(2:1)	$23.6 \pm 2.5$	$6.2 \pm 0.3$	$16.2 \pm 0.5$	$25.8 \pm 0.9$
	(1:1)	$21.4 \pm 0.3$	$5.1 \pm 0.1$	$18.4 \pm 0.9$	$27.8 \pm 0.8$

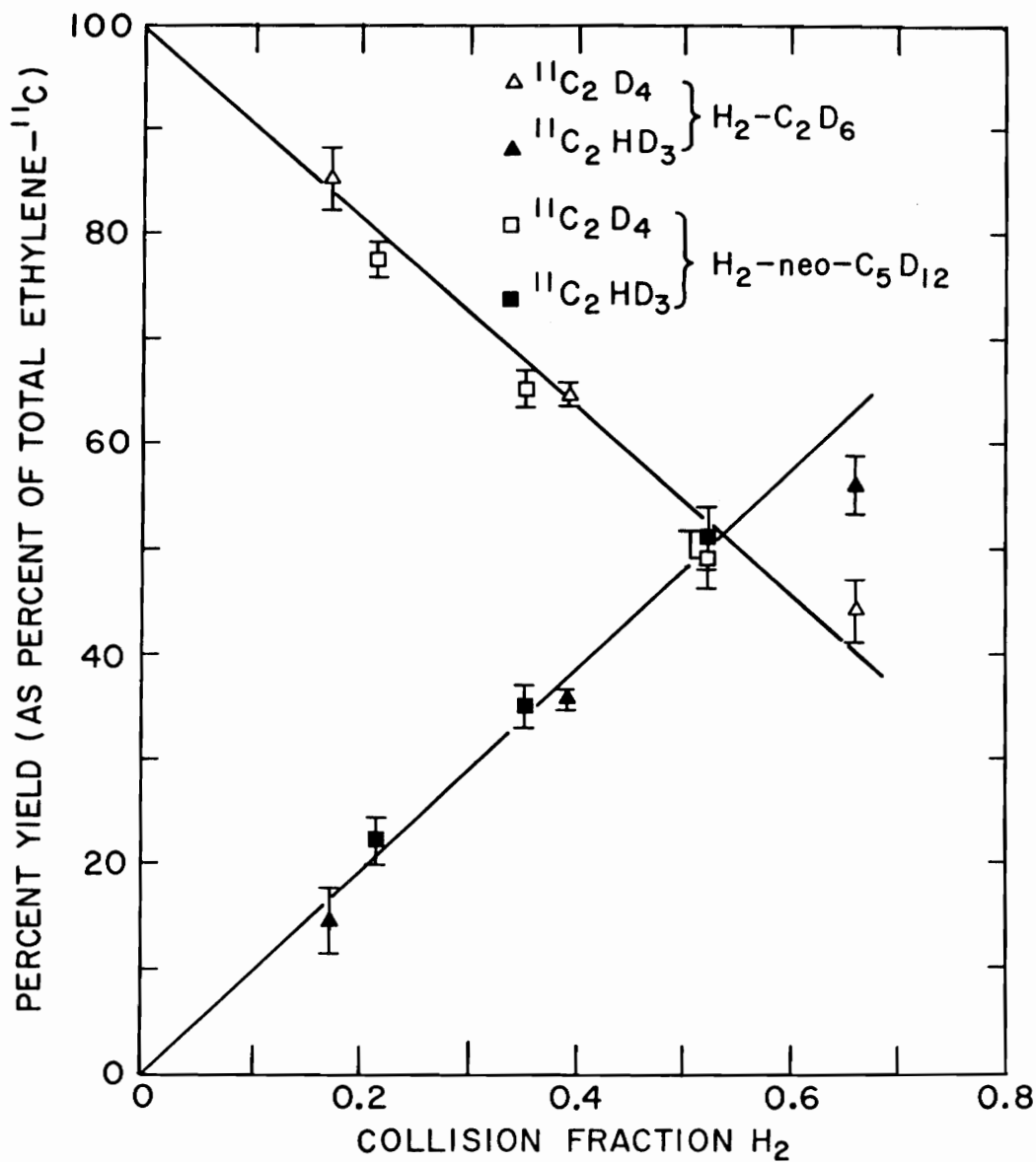
**TABLE XI**  
 Relative Yields of Deuterated Ethylene in Mixtures  
 of Hydrogen With Alkanes and Alkyl Halides

Substrate		% of total ethylene- <sup>11</sup> C			
		<sup>11</sup> C <sub>2</sub> H <sub>4</sub>	<sup>11</sup> C <sub>2</sub> H <sub>3</sub> D	<sup>11</sup> C <sub>2</sub> HD <sub>3</sub>	<sup>11</sup> C <sub>2</sub> D <sub>4</sub>
D <sub>2</sub> + C <sub>2</sub> H <sub>6</sub>	(3:1)	37.5 ± 1.8	62.5 ± 1.6	—	—
	(1:1)	69.4 ± 1.0	30.6 ± 1.1	—	—
	(1:3)	84.0 ± 3.4	16.0 ± 3.3	—	—
D <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> F	(3:1)	34.0 ± 1.9	66.0 ± 2.1	—	—
	(1:1)	60.5 ± 2.6	39.5 ± 2.4	—	—
	(1:3)	85.5 ± 1.0	14.5 ± 1.0	—	—
D <sub>2</sub> + C <sub>2</sub> H <sub>5</sub> Cl	(3:1)	42.2 ± 1.5	57.8 ± 1.5	—	—
	(1:1)	67.9 ± 3.4	32.1 ± 3.5	—	—
	(1:3)	84.7 ± 3.0	15.3 ± 3.0	—	—
H <sub>2</sub> + C <sub>2</sub> D <sub>6</sub>	(3:1)	—	—	56.0 ± 2.7	44.0 ± 3.0
	(1:1)	—	—	35.5 ± 0.5	64.5 ± 0.4
	(1:3)	—	—	14.7 ± 3.1	85.3 ± 3.1
H <sub>2</sub> + neo-C <sub>5</sub> D <sub>12</sub>	(4:1)	—	—	51.0 ± 3.1	49.0 ± 2.6
	(2:1)	—	—	35.0 ± 2.0	65.0 ± 1.8
	(1:1)	—	—	22.3 ± 0.7	77.7 ± 1.4



ISOTOPIC ETHYLENES FORMED IN HYDROGEN MIXTURES

FIGURE 28



ISOTOPIC ETHYLENES FORMED IN HYDROGEN MIXTURES

FIGURE 29

TABLE XII

Hard-Sphere Collision Diameters<sup>a</sup>

H <sub>2</sub>	2.968 Å
D <sub>2</sub>	2.948 Å
C <sub>2</sub> H <sub>6</sub>	4.383 Å
C <sub>2</sub> D <sub>6</sub>	4.376 Å
C <sub>2</sub> H <sub>5</sub> Cl	4.899 Å
C <sub>2</sub> H <sub>5</sub> F	4.6 Å <sup>b</sup>
neo-pentane	5.671 Å
C	2.8 Å <sup>c</sup>

<sup>a</sup>J.W. Root, Ph.D. Thesis, U. of Kansas, 1964, p. 538 ff.

<sup>b</sup>Estimated.

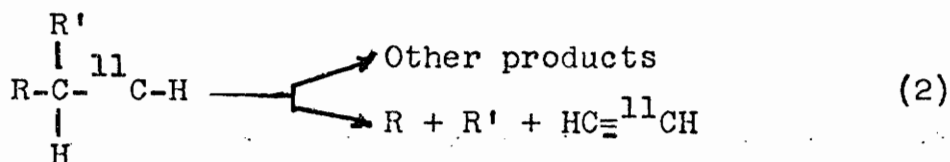
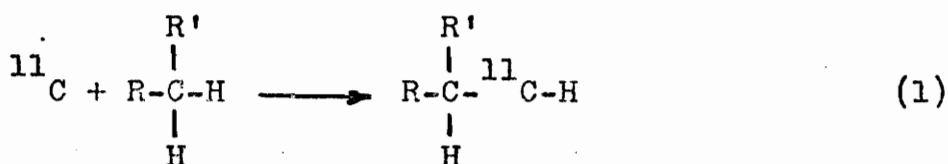
<sup>c</sup>Estimated to be equal to  $\sigma_{\text{Neon}} = 2.777 \text{ \AA}$

## CHAPTER IV

### DISCUSSION

#### A. Mechanism of Ethylene Formation

Numerous investigations<sup>65-68</sup> have shown acetylene and ethylene to be the major labeled products of the reaction of energetic carbon atoms with acyclic alkanes. Fifty-five percent of the gaseous activity in oxygen-scavenged methane can be accounted for by these two products, although this percentage decreases with increasing chain length of the substrate. Most workers<sup>29,69</sup> agree that the major pathway for acetylene formation involves insertion of the carbon atom into the C-H bond of a methyl or methylene group, followed by unimolecular decomposition of the excited carbene intermediate.



This mechanism has been slightly altered to accommodate the results of pressure-dependence studies of Welch and Wolf<sup>70,71</sup> who found that the yields of fragmentation



products (acetylene and ethylene) increased with increasing pressure. To explain this observation they postulated a collision complex of unspecified structure as the first interaction between carbon atom and substrate.

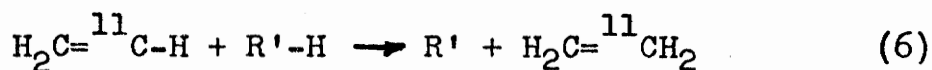
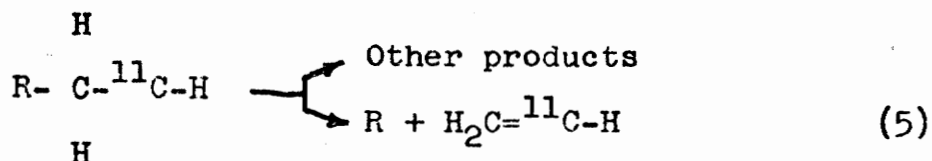
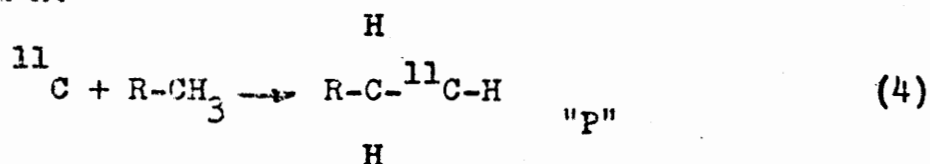


This complex has a sufficiently long lifetime to be stabilized by collisional energy transfer. The second step of the reaction is the actual insertion of carbon into a C-H bond, i.e., reaction (1).

A second pathway, perhaps involving initial formation of  $^{11}\text{C}_2$  or  $^{11}\text{C}_2\text{H}$ , is supported by the finding of mixed acetylene ( $^{11}\text{C}_2\text{HD}$ ) in substrates containing only per-protonated and perdeuterated compounds.<sup>33,34</sup> However, this is a minor route, in most cases accounting for less than ten percent of the labeled acetylene.

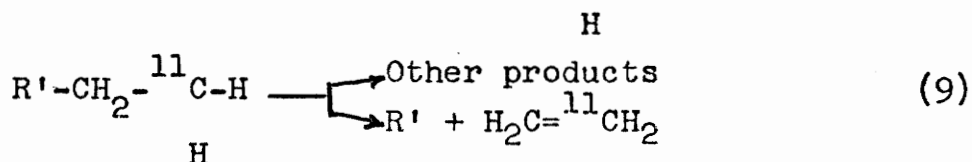
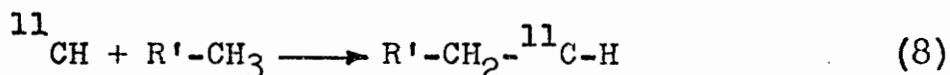
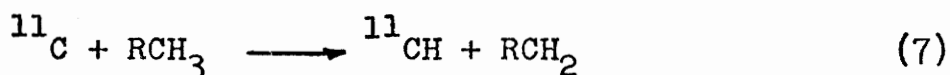
In contrast to the amicable state of affairs with regard to acetylene, the pathway to ethylene has been in considerable dispute. MacKay and Wolfgang<sup>72</sup> suggested that ethylene and acetylene share a common precursor, the product of C-H bond insertion by a carbon atom. This precursor (P in Equation 4 below) can decompose in a number of ways. One of these leads to acetylene, as above, and another leads to ethylene by intermediate formation of a vinyl radical.

Mechanism A:



Stöcklin and Wolf<sup>32</sup> argued that ethylene is formed exclusively by the insertion of methyne into primary C-H bonds of the hydrocarbon, followed by direct decomposition to ethylene.

Mechanism B:



These reaction differ primarily in the order of two steps: hydrogen pick-up and C-H bond insertion. Until recently there has been no definitive evidence which could support one of these mechanisms in preference to the other. One fact which placed the intermediacy of the vinyl radical

in question was that ethylene production occurs in the presence of oxygen, which is known to be an effective scavenger for thermal vinyl radicals.<sup>73</sup> Since one can only speculate as to the energy range in which vinyl radicals would be formed by this decomposition (Reaction 5), one might argue that they might be more reactive than similar thermal species and, thus, perhaps less easily scavenged by oxygen. However, one might in this case still expect to see a more distinct effect of oxygen addition on the ethylene yields.

Ache and Wolf<sup>3</sup> compared the yields of  $^{11}\text{C}_2\text{H}_2$  and  $^{11}\text{C}_2\text{H}_4$  in oxygen-scavenged ethane and fluoroethane. Their finding, that the substitution of one fluorine for hydrogen in ethane only slightly altered the acetylene- $^{11}\text{C}$  yield, but severely depressed the ethylene- $^{11}\text{C}$  yield, suggested that the two products could not share a common intermediate. This finding was not, of course, conclusive since fluoride substitution could alter the mode of decomposition.

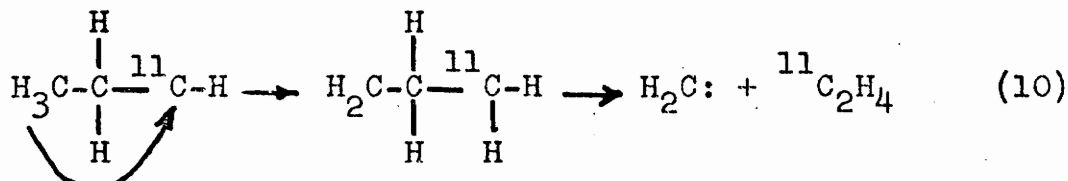
Lambrecht and Wolf<sup>4</sup> reported similar results with recoil carbon-11 in the series of homologous halomethanes  $\text{CH}_n\text{X}_{4-n}$  (where  $X = \text{H}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}, \text{I}$ ).

More convincing evidence was the failure of Ayres and Wolf<sup>74</sup> to find a significant yield of vinyl chloride in oxygen-scavenged methyl, ethyl, propyl, and butyl chlorides. If the vinyl radical is an important intermediate in the formation of ethylene as proposed in Mechanism A, we would

expect this radical to abstract chlorine more readily than hydrogen and form vinyl chloride in preference to ethylene. The low yield of vinyl chloride found in these systems (less than 1% in  $\text{CH}_3\text{Cl}$ ) discounts this alternative.

Additional evidence indicating the failure of the common precursor argument was supplied by the present investigation. Table V shows the distribution of isotopic  $^{11}\text{C}$ -labeled ethylenes produced in some specifically-deuterated ethanes and propanes.

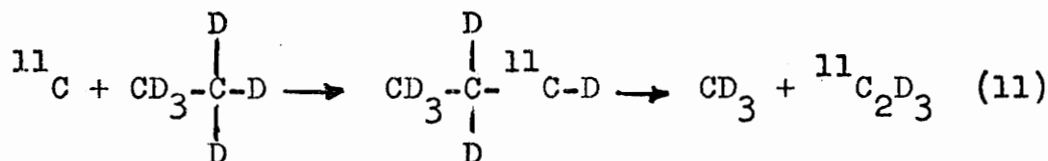
An obvious conclusion from the data in Table V is that ethylene is formed by an intermolecular process. Were this not the case, an equimolar mixture of  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{D}_6$  would yield only  $^{11}\text{C}_2\text{H}_4$  and  $^{11}\text{C}_2\text{D}_4$  and not the four different ethylenes actually observed. This result has been reported previously,<sup>75</sup> but does not help us to distinguish Mechanisms A and B, which both predict the mixture of products we observe. We can, however, rule out a purely intramolecular mechanism involving, for example, a hydrogen shift:



A second conspicuous feature of these data is the non-statistical nature of the product distribution. If each reaction step took place in a strictly random fashion either mechanism would predict a 25% yield of each of the

same four isotopic ethylenes:  $^{11}\text{C}_2\text{H}_4$ ,  $^{11}\text{C}_2\text{H}_3\text{D}$ ,  $^{11}\text{C}_2\text{HD}_3$  and  $^{11}\text{C}_2\text{D}_4$ . When the results for each compound listed in Table V are examined closely, a trend becomes apparent. In every case the monodeuterated product,  $^{11}\text{C}_2\text{H}_3\text{D}$ , occurs in higher yield than the fully-protonated  $^{11}\text{C}_2\text{H}_4$ ; and the perdeuterated  $^{11}\text{C}_2\text{D}_4$  always is favored over the  $^{11}\text{C}_2\text{HD}_3$ . For example,  $\text{CH}_3\text{CD}_3$  produces 32.9% ethylene- $\text{d}_1$  compared to 23.4% ethylene- $\text{d}_0$ , and 22.5% ethylene- $\text{d}_4$  compared to 19.3% ethylene- $\text{d}_3$ .

Let us consider again the example of the ethane-ethane- $\text{d}_6$  mixture. According to Mechanism A, the radicals ( $^{11}\text{C}_2\text{H}_3$  and  $^{11}\text{C}_2\text{D}_3$ ) would be formed following  $^{11}\text{C}$ -insertion and subsequent decomposition of the insertion complex.



The relative yields may, therefore, be subject to isotope effects involved in these reaction steps. The ratio of  $^{11}\text{C}_2\text{H}_4/^{11}\text{C}_2\text{H}_3\text{D}$  or  $^{11}\text{C}_2\text{HD}_3/^{11}\text{C}_2\text{D}_4$ , however, will be solely the result of the capability of the vinyl radicals to abstract hydrogen or deuterium from surrounding molecules. The observed ratios would indicate that H-abstraction is less favored than D-abstraction by a factor of 0.79 (see Table VII). To explain this observation one would have to assume preferential breakage of the stronger C-D bond,<sup>76</sup> an unlikely result. This evidence, together with the reduced

yield of ethylene in alkyl chlorides and the absence of substantial yields of vinyl chloride in these same substrates, suggest that the vinyl radical cannot be an important intermediate in this reaction. We, therefore, reject Mechanism A, and consider the results in the light of Mechanism B.

### B. Origin of the Isotope Effect

If we accept the methyne hypothesis, then  $^{11}\text{C}_2\text{H}_4$  and  $^{11}\text{C}_2\text{H}_3\text{D}$  can be viewed as the respective products of  $^{11}\text{CH}$  and  $^{11}\text{CD}$  insertion into a  $\text{CH}_3$  group of the hydrocarbon. Similarly,  $^{11}\text{C}_2\text{HD}_3$  and  $^{11}\text{C}_2\text{D}_4$  are the products of  $^{11}\text{CH}$  and  $^{11}\text{CD}$  insertion into a  $\text{CD}_3$ . Viewing the data in Table V in this way makes apparent two general trends. First, in every case, relatively more ethylene is formed by CD insertion than by CH insertion. And, second, relatively more ethylene is formed by insertion into  $\text{CH}_3$  groups than into  $\text{CD}_3$  groups. Consider the ethylene yields from an equimolar mixture of propane and propane- $\text{d}_8$  as illustration. The products of CD insertion,  $^{11}\text{C}_2\text{H}_3\text{D}$  and  $^{11}\text{C}_2\text{D}_4$ , are 29.2% and 23.0%, respectively, and the products of CH insertion,  $^{11}\text{C}_2\text{H}_4$  and  $^{11}\text{C}_2\text{HD}_3$ , are 25.3% and 19.8% of the total yield. The ratio of the sum of the products of CH insertion to the sum of the products of CD insertion (hereafter referred to as the CH/CD ratio) is 0.86, as shown in Table VII. On the other hand, the sum of the

products of insertion into a  $\text{CH}_3$  group, divided by the sum of the products of insertion into a  $\text{CD}_3$  group (hereafter referred to as the  $\text{CH}_3/\text{CD}_3$  ratio) is 1.27, according to Table VII. This pattern repeats itself so that, when the results of all ethanes and propanes are averaged, it is found that the products of CH insertion are less favored by a factor of 0.83 and products resulting from insertion into  $\text{CH}_3$  groups are more favored than insertion into  $\text{CD}_3$  groups by a factor of 1.41.

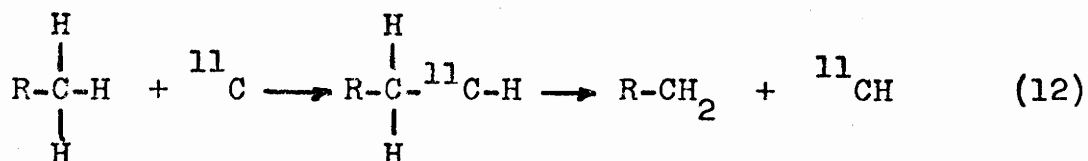
#### C. Insertion Into Methyl Group

The insertion isotope effect can be rationalized easily, since this reaction step requires scission of a C-H bond and is, therefore, bond energy dependent. The C-H bond is inserted into more easily because it is weaker than the comparable C-D bond by about 1.5 kcal/mol.<sup>75</sup> Chesick<sup>78</sup> has found a similar preference by methylene for insertion into the secondary C-H bonds of propane ( $k_{\text{H}}/k_{\text{D}} = 1.3$ ), and Ache, Christman and Wolf<sup>33</sup> have reported an isotope effect for carbon atom insertion ranging from 1.27 for aliphatic to 1.05 for aromatic carbon-hydrogen bonds.

#### D. Methyne Production

Closer inspection of the production of methyne indicates at least two possible routes. Methyne may form by direct abstraction of a hydrogen from a hydrocarbon or  $\text{H}_2$  by the approaching carbon atom. Since abstraction is

bond-energy dependent, this route would give a normal isotope effect, producing more  $^{11}\text{CH}$  than  $^{11}\text{CD}$ . A second possibility is that the carbon atom inserts into a C-H bond, forming a carbene intermediate, which decomposes to methyne and an unlabeled alkyl radical.



This carbene intermediate would be highly excited due to the excess translational energy brought by the carbon atom and could decompose in several different ways. Referring to the diagrams below, breakage of bonds a and c would lead to methyne formation, while bond rupture at b and d would not.



Although bond c may be somewhat weaker than a due to a secondary isotope effect, the major effect would be a considerable strengthening of d relative to b. Since we would expect a and c to break with almost equal frequency, and d to break with much less frequency than b, this path leads to formation of more  $^{11}\text{CD}$  than  $^{11}\text{CH}$ , the result we observe in alkanes. Therefore, although abstraction is expected to be an important pathway to methyne, the

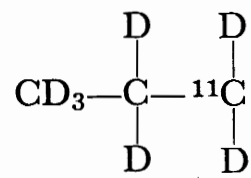
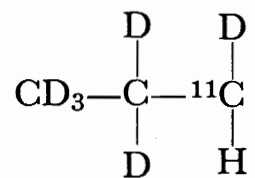


foregoing interpretation of the experimental data indicates that, at least in alkanes, the insertion-decomposition process is predominant.

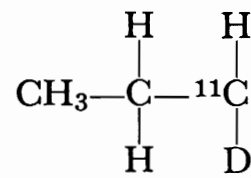
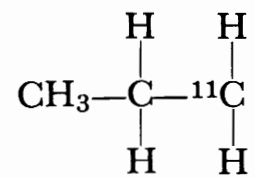
#### E. Decomposition of the Insertion Complex

The possibility of a decomposition isotope effect in the final step of the methyne mechanism must be considered. The  $^{11}\text{CH-}$  and  $^{11}\text{CD-}$  insertion complexes formed in the equimolar mixture of ethane/ethane- $\text{d}_6$  and in the specifically-deuterated ethane-1,1,1- $\text{d}_3$  are shown in Figures 30 and 31, respectively. In each case, C-C scission is required to lose a methyl group and form ethylene. The overall isotopic composition of the complexes formed in the case of  $\text{CH}_3\text{CD}_3$  (Figure 31) differs only slightly and not at the carbon atom at the center of action. Thus, one cannot expect any isotope effects in the decomposition of these complexes. The complexes formed following  $^{11}\text{CH-}$  or  $^{11}\text{CD-}$  insertion into  $\text{C}_2\text{H}_6$  or  $\text{C}_2\text{D}_6$  (Figure 30) have a considerably different isotopic composition; however, even here only small secondary isotope effects could be expected. The isotopic distributions of ethylenes in Table V are identical within experimental error for these two substrates, which shows clearly that isotope effects involved in the C-C bond breakage, if present, are small and well within the experimental error.

Insertion into  $C_2D_6$



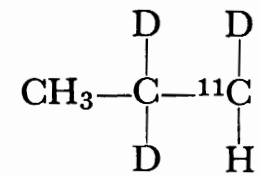
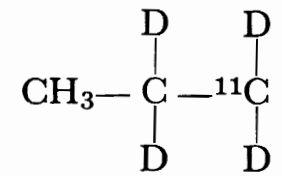
Insertion into  $C_2H_6$



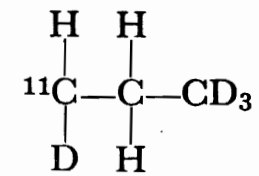
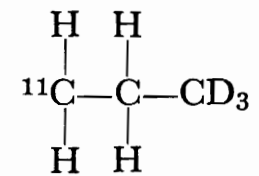
Insertion complexes in  $C_2D_6-C_2H_6$

FIGURE 30

Insertion into  $-\text{CD}_3$



Insertion into  $-\text{CH}_3$



Insertion complexes in  $\text{CH}_3\text{CD}_3$

FIGURE 31

F. Primary-to-Secondary Abstraction Ratio

We can calculate the relative likelihood of methyne formation from methyl and methylene groups of a hydrocarbon by examining the ethylene yields from  $\text{CH}_3\text{CD}_2\text{CH}_3$  and from  $\text{CD}_3\text{CH}_2\text{CD}_3$  shown in Table V. The only product of H-abstraction from  $\text{CH}_3\text{CD}_2\text{CH}_3$  is  $\text{C}_2\text{H}_4$  which must result from abstraction from a methyl group, just as  $\text{C}_2\text{H}_3\text{D}$  must result from abstraction from the methylene group. The same reasoning leads to the conclusion that  $\text{C}_2\text{D}_4$  is the product of abstraction from the methyl group of  $\text{CD}_3\text{CH}_2\text{CD}_3$  and  $\text{C}_2\text{HD}_3$  comes from abstraction from its methylene. We know that these yields have been altered by isotope effects, but we can cancel these effects by averaging the yields from methyl and from methylene groups from these two compounds. Therefore, the average yield from a methylene group is  $(32.0 + 26.8)/2 = 29.4\%$ . Similarly, the average yield from a methyl is  $(68.2 + 72.1)/2 = 70.2$ . The ratio of abstraction from a methyl to abstraction from a methylene is 1.00:0.84. You must divide by two to correct for the number of methyl groups. When the product ratios listed in Table VII for these two compounds and for  $\text{CH}_3\text{CH}_2\text{CD}_3$  are corrected using this ratio, they agree quite well with each other and with other propane ratios. The CH/CD ratio for the substrate  $\text{CH}_3\text{CH}_2\text{CD}_3$  can be corrected for this difference in ability to abstract primary and secondary hydrogens as follows

using ethylene percentages from Table V:

$$\frac{\text{CH}}{\text{CD}} = \frac{(34.0 + 26.1)}{(23.8 + 14.8)} = \frac{(1.0)}{(1.0 + 0.84)} = 0.84$$

This is the corrected ratio of  $^{11}\text{CH}$  to  $^{11}\text{CD}$  formation.

The ratio of primary abstraction to secondary abstraction, when calculated per bond, is 0.33:0.42 and shows the normal trend found in many radical reactions.<sup>79</sup>

### G. Xenon Moderator Experiments

The carbon atom has three low-lying electronic states which may play a role in recoil reactions. These are the  $^1\text{D}$  at 1.3 eV and  $^1\text{S}$  at 2.7 eV above the  $^3\text{P}$  ground state.<sup>80</sup> The present experiments were undertaken for the purpose of determining which electronic states are the precursors for the major products.

Newton and Blint<sup>81</sup> calculated the potential energy surfaces for the reaction of  $\text{C} + \text{H}_2$  for  $\text{C}(^3\text{P})$ ,  $\text{C}(^1\text{D})$  and  $\text{C}(^1\text{S})$ , and reached the following conclusions:

For energetic carbon atoms:

- 1) The potential energy surface for  $^1\text{S}$  reaction is purely repulsive. No reaction with this species.
- 2) The insertion complex in the case of  $^1\text{D}$  atoms would probably have a very short lifetime, leading to no reaction, or possibly decomposition to  $\text{CH} + \text{H}$ .
- 3) The large barrier for the case of  $^3\text{P}$  atoms might

allow temporary trapping of the  $\text{CH}_2$  complex.

- 4) Ground state methyne ( $2\Pi$ ) could arise from axial abstraction by energetic  $1D$  carbon atoms. Abstraction by energetic  $3P$  atoms could lead either to  $2\Pi'$  or  $4\Sigma^-$  methyne. The  $4\Sigma^-$  state would not be expected to insert into a C-H bond.

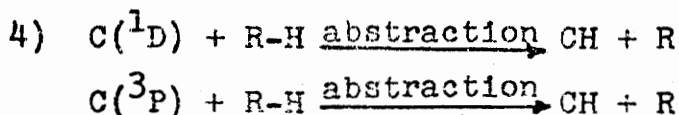
For near-thermal species:

- 5) The direct insertion complex would be inaccessible to  $3P$  atoms, and stabilization would become more likely for  $1D$  atoms.

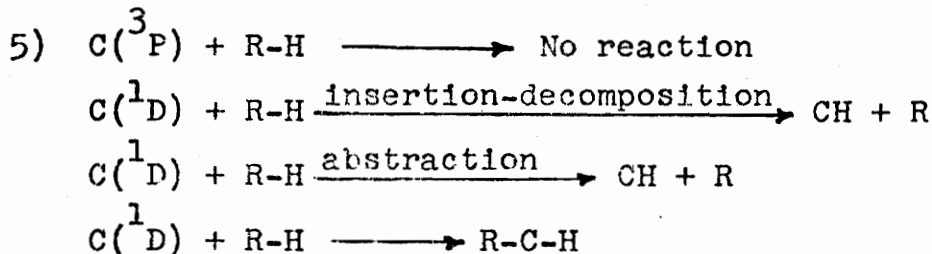
$\text{C} + \text{H}_2$  is a model for the system  $\text{C} + \text{RH}$ . A major difference is that attack from almost any direction is more hindered in the case of  $\text{RH}$ . Another important difference is the increased degrees of freedom in  $\text{RH}$  which would allow more energy dissipation in the insertion complex. The most likely result would be quantitative and not qualitative differences. Therefore, we can draw the following parallels:

For energetic carbon atoms:

- 1)  $\text{C}(^1S) + \text{R-H} \longrightarrow \text{No reaction}$
- 2)  $\text{C}(^1D) + \text{R-H} \xrightarrow{\text{Insertion-decomposition}} \text{CH} + \text{H}$   
 $\text{CH} + \text{R}'\text{-H} \longrightarrow \text{Ethylene}$
- 3)  $\text{C}(^3P) + \text{R-H} \longrightarrow \text{R-C-H}$   
 $\text{R-C-H} \longrightarrow \text{Acetylene}$



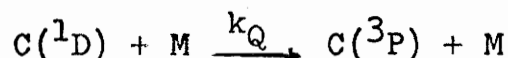
For near-thermal energies:



In summary, calculations predict that acetylene can be produced by high-energy  ${}^3\text{P}$  and near-thermal  ${}^1\text{D}$  carbon atoms. Ethylene can be produced by energetic  ${}^1\text{D}$  and  ${}^3\text{P}$  and by near-thermal  ${}^1\text{D}$  atoms. Thermal  ${}^3\text{P}$  carbons are responsible for carbon monoxide.

We can test these predictions by selectively removing high energy  ${}^1\text{D}$  atoms and observing the effect on the yield of ethylene. Conversion of  ${}^1\text{D}$  to  ${}^3\text{P}$  should cause the ratio of  ${}^{11}\text{C}_2\text{H}_2/{}^{11}\text{C}_2\text{H}_4$  to rise, and allow us to estimate the fractions of ethylene yield resulting from abstraction and from insertion-decomposition.

Husain and Kirsch<sup>1</sup> produced  $\text{C}({}^1\text{D})$  by flash photolysis of carbon suboxide and measured the second-order rate constants for collisional deactivation to the electronic ground state in the presence of various noble gases. They found xenon to be four orders of magnitude more efficient



than helium and three orders of magnitude more efficient than neon.

M	$k_Q$ (cc/molecule's)	# collisions/conversion
Xe	$1.1 \times 10^{-10}$	3
Kr	$9.4 \times 10^{-13}$	$2.7 \times 10^2$
Ar	$\lesssim 10^{-15}$	$> 2.5 \times 10^5$
Ne	$1.1 \times 10^{-15}$	$2.1 \times 10^5$
He	$< 3 \times 10^{-16}$	$> 1.1 \times 10^6$

The same workers have measured the rate of disappearance of  $C(^1D)$  in the presence of various hydrocarbons<sup>23</sup> and found  $k \approx 10^{-10}$ . Therefore, a significant fraction of the  $^1D$  carbons should, in the presence of xenon, be converted to  $C(^3P)$  before reaction with the substrate. The efficiencies of these same noble gases for energy degradation of the carbon atom are in the order:



This difference in order should prevent us from confusing energy moderator effects with spin conversion.

Figure 22 shows the experimental variation of product yields with increasing xenon concentration in ethane-4.5% oxygen mixtures. The hot products decrease as expected in the presence of an increasing fraction of "inert" gas molecules. The rapidly increasing carbon monoxide- $^{11}C$  yield is produced by near-thermal  $C(^3P)$  atom reactions with



oxygen scavenger.<sup>82</sup>

Comparison of product yield trends in xenon with those in helium<sup>2</sup> and neon<sup>64</sup> determined by other workers shows the effect of a spin converter in the system. Neon and helium should work primarily to change the energy spectrum of the hot carbons, and reaction should occur before appreciable conversion of C(<sup>1</sup>D) to the ground state.

The plot of acetylene-<sup>11</sup>C yield versus noble gas concentration in Figure 24 is ambiguous. The trends observed could be interpreted as a simple energy moderator effect, since the curves are in the expected order. Neon is the best energy moderator, but helium is nearly as good. And both are considerably better energy transfer in elastic collisions than is xenon. Therefore, acetylene yield should drop off faster in helium and neon than in xenon, and it does. But this is the same effect predicted for the conversion of <sup>1</sup>D to <sup>3</sup>P carbons by xenon. This would tend to offset the loss in C<sub>2</sub>H<sub>2</sub> due to energy degradation in xenon by an increased amount of hot C(<sup>3</sup>P) available for reaction, thus, keeping the acetylene yield high in xenon.

The trend of the ethylene-<sup>11</sup>C yield in the same three noble gases (Figure 23) presents a much clearer picture. Any inert gas would be expected to lower the ethylene yield since it is a hot product. Neon should do this better than

helium; and the experimental data show ethylene falling off faster with neon than with helium. However, xenon is much less efficient in energy transfer and should keep the ethylene yield high. We observe the opposite trend, with ethylene yield dropping off much faster in xenon than in helium and neon. This is the effect predicted if xenon is converting  $^1\text{D}$  to  $^3\text{P}$ , since methyne becomes less available for reaction to form ethylene.

The ratio of acetylene- $^{11}\text{C}$  to ethylene- $^{11}\text{C}$ , plotted versus noble gas concentration in Figure 26, shows this trend very clearly. Even though methyne (and, subsequently ethylene) can be formed by abstraction by  $\text{C}(^3\text{P})$ , this pathway appears to be of minimal importance, in view of the dramatic effect on ethylene yield by the xenon. The inflection points in the curves in the vicinity of 90% moderator may be indicative of the following circumstance: In helium and neon, a significant fraction of the  $^1\text{D}$  atoms should reach near thermal energies where some will be diverted from ethylene to acetylene production. This circumstance should cause a sharp rise in the acetylene/ethylene ratio. It must be pointed out, however, that confidence in the absolute yields of these products in mixtures containing 90% or more moderator is low, due to poor counting statistics. Conclusions based on the data in this region of high moderator should be made with this in mind.

The ratio of the sum of (carbon monoxide + acetylene) to the ethylene ratio is plotted in Figure 27. If  $^{11}\text{CO}$  is the thermal product of  $^3\text{P}$  and acetylene is its hot product, then

$$\frac{(\text{CO} + \text{C}_2\text{H}_2)}{(\text{C}_2\text{H}_4)} \approx \frac{\text{C}(^3\text{P})}{\text{C}(^1\text{D})}$$

This relationship is only approximate for two reasons. First, we have said that ethylene can be produced from methyne formed through abstraction reactions by both triplet and singlet carbon, as well as from methyne formed through decomposition of the  $^1\text{D}$  insertion complex. Second, not all products are accounted for by this equation. These three products account for only 75% of the gaseous activity in ethane. However, accepting the relationship as only an approximation, Figure 27 shows the ratio of triplet to singlet carbons in the system rising sharply in xenon, much faster than in helium and neon.

This discussion is pertinent to the interpretation of isotope effects found in alkyl chlorides.

#### H. Isotope Effects in Alkyl Chlorides

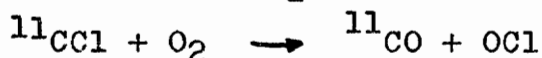
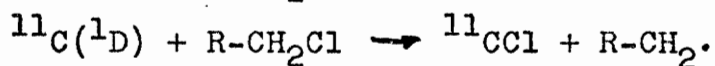
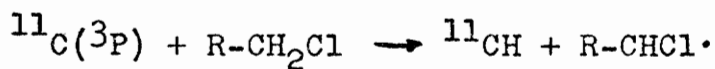
Table VI shows the distribution of isotopic ethylenes formed in an equimolar mixture of  $\text{C}_2\text{H}_5\text{Cl}$  and  $\text{C}_2\text{D}_5\text{Cl}$  containing 4.5% oxygen scavenger. The product ratios in Table VIII demonstrate the formation isotope effect for

methyne to be the inverse of that found in alkanes with production of  $^{11}\text{CH}$  being favored over  $^{11}\text{CD}$  by a factor of 1.1. Identical results were found in a  $n\text{-C}_4\text{H}_9\text{Cl}/n\text{-C}_4\text{D}_9\text{Cl}$  mixture and with a mixture of 14%  $\text{CCl}_4$ , 4.5%  $\text{O}_2$  and 81.5%  $\text{C}_2\text{H}_6/\text{C}_2\text{D}_6$ . The insertion isotope effect in these systems is in the same direction, and of approximately the same magnitude, as found in alkanes (i.e., insertion into  $\text{CH}_3$  is favored over insertion into  $\text{CD}_3$  by an average of 1.41). Absolute yields of ethylene are reduced dramatically in chloroalkanes, although, with increasing chain length, the ethylene yield approaches that in the equivalent alkane. For example,  $^{11}\text{C}_2\text{H}_4$  yield is 1% in  $\text{CH}_3\text{Cl}$ , 25% in  $\text{CH}_4$ , but 6% in  $\text{C}_4\text{H}_9\text{Cl}$  and 12% in  $\text{C}_4\text{H}_{10}$ .<sup>74</sup> But the ratio of  $^{11}\text{CH}$  products to  $^{11}\text{CD}$  products is independent of chain length. Moreover, the experiments with  $\text{CCl}_4$  and ethane indicate that the chlorine does not have to be on the molecule from which the methyne insertion complex is formed for the chlorine to cause this inversion in the ratio of products from  $\text{CH}$  and  $\text{CD}$ .

We can gain insight into the reactions of carbon atoms in alkyl chlorides by comparing them to the behavior of a more familiar carbene,  $\text{CH}_2$ , which also reacts in two different electronic states. Roth<sup>83-85</sup> and Setser<sup>86</sup> have shown that, when reacting with  $\text{CH}_2\text{Cl}_2$  and other chlorinated molecules, singlet methylene selectively

abstracts chlorine atoms, and triplet methylene abstracts hydrogen. They also found that the reaction of  $^1\text{CH}_2$  with chlorine is faster than the intersystem crossing to  $^3\text{CH}_2$ .

These facts suggest the following hypothesis. In alkanes, both singlet and triplet carbon atoms are present, and both contribute to the ethylene yield by abstraction of hydrogen to form methyne. However, in the presence of an alkyl chloride, some singlet carbon is diverted to form chloromethyne, which then further reacts with oxygen to

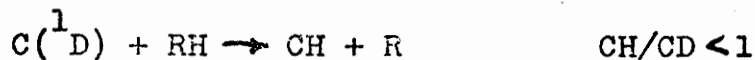


form carbon monoxide- $^{11}\text{C}$ . This diversion of a large fraction of methyne sharply reduces the ethylene- $^{11}\text{C}$  yield and contributes to the very high yield of carbon monoxide in these systems. The reaction of  $\text{C}(^3\text{P})$  is not influenced by the presence of chlorine in the medium. This explains why the acetylene yield in a typical alkyl chloride is identical with the acetylene yield in the analogous alkane.<sup>74</sup>

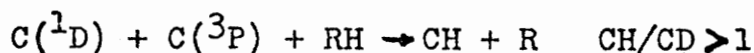
Now we can understand why the isotope effect apparently is inverted in alkyl chlorides. It has been demonstrated in this work how  $\text{C}(^1\text{D})$  may produce methyne with a ratio of  $\text{CH}/\text{CD} < 1$  by the insertion-decomposition mechanism. The

production of methyne by hydrogen abstraction would be expected to result in a ratio of  $CH/CD > 1$ . The overall isotope effect we observe in alkanes is the result of two competing reactions.

Insertion-decomposition pathway:



Abstraction pathway:



In alkyl chlorides  $C(^1D)$  atoms undergoing abstraction reactions will be diverted to form chloromethyne, and we see only the methyne formed by  $C(^3P)$  abstraction reactions with an overall ratio of  $CH/CD > 1$ . This suggests that the isotope effect associated with insertion-decomposition is much larger than that associated with abstraction. One other possibility is that the number of  $C(^1D)$  atoms present in alkanes is about three times the number of  $C(^3P)$  atoms. This is a crude approximation, based on the fractional reduction of ethylene yield in going from ethane (16%) to ethyl chloride (4.5%).

An attempt was made to alter the ratio of CH products to CD products in an ethane/ethane- $d_6$  mixture by addition of 50% xenon spin converter. Xenon should have depleted the singlet carbons, enhanced the concentration of triplet carbons, and increased the relative amount of methyne formed by abstraction. This should have increased the

ratio of CH/CD products. The results in Table VII show no noticeable effect. One possible reason for lack of effect is that not enough xenon was present to alter significantly the  $^3P/1D$  ratio.

### I. Relative Ethylene Yields in Hydrogen Mixtures

Various mixtures of hydrogen- $d_2$  with ethane, ethyl fluoride and ethyl chloride were irradiated and the isotopic ethylenes separated to determine the effect of various substituents on the ethylene distribution. Similarly, hydrogen was irradiated with ethane- $d_6$  and with neo-pentane- $d_{12}$ . Since ethylene- $^{13}C$  can be formed only from the carbon-containing component, only two isotopic ethylenes can result in each case. The variations in yield of these two products are plotted with respect to the collision fraction of hydrogen in the mixture in Figures 28 and 29.

The linear change of CH or CD product yield with increasing fraction of  $D_2$  in Figure 28 is to be expected. However, it is surprising that the slopes of these lines are identical for mixtures containing ethane, ethyl fluoride and ethyl chloride, since the absolute yields of ethylene in these systems vary from 4.5% in ethyl chloride to 16.3% in the ethane system (see Table X).

The curves do not cross exactly at 50% collision fraction  $H_2$  (or  $D_2$ ), but cross, instead, between 52 and

55%. Due to uncertainties in the data, and in the collision cross sections, it is not certain whether or not the point of crossing is significant. If real, it means that methyne formation from hydrogen is slightly less favored than formation from an alkane and alkyl halide. Furthermore, it clearly shows that methyne formation is not a function of the number of hydrogen atoms available in the hydrogen source.

#### J. Summary

We have demonstrated that methyne is the intermediate responsible for ethylene formation, and that two electronic species of carbon take part in the reactions in recoil systems. At high energies,  $C(^3P)$  is responsible for acetylene- $^{11}C$  production, whereas ethylene- $^{11}C$  is formed by both  $^1D$  and  $^3P$  carbons. At near-thermal energies,  $^3P$  carbons can no longer react with the substrate and are scavenged by oxygen. In this lower energy range,  $^1D$  carbon still can produce ethylene- $^{11}C$  and acetylene- $^{11}C$ . In alkanes the concentration of  $C(^1D)$  is approximately three times the concentration of  $^3P$  carbon atoms. Methyne can be formed both by direct abstraction of hydrogen by  $^1D$  and  $^3P$  carbons and by insertion of  $C(^1D)$  into the methyl C-H bond to form a complex which decomposes unimolecularly. In alkyl halides methyne is formed almost exclusively by abstraction.



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## VITA

Kathleen Taylor was born Kathleen Karen Carroll in Smithfield, Pennsylvania, on January 22, 1946. After attending the local public schools, she graduated from Albert Gallatin Senior High School in 1963. She pursued the study of chemistry at California State College in California, Pennsylvania, and graduated with honors in 1967, receiving the degree of Bachelor of Arts. After working briefly for the Petro-Tex Chemical Company in Akron, Ohio, she entered Virginia Polytechnic Institute in 1970, and began work in the research group of Professor Hans J. Ache. In that same year she met, and six months later she married, George Allan Taylor. Through the cooperation of Virginia Polytechnic Institute and of Brookhaven National Laboratory, she was able to continue research work in the group of Alfred P. Wolf in the chemistry department of Brookhaven. She completed the requirements for the degree of Doctor of Philosophy in Chemistry in May of 1974.

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REACTIONS OF ENERGETIC CARBON ATOMS PRODUCED BY  
 $^{12}\text{C}(\text{p},\text{pn})^{11}\text{C}$  IN ALKANES AND ALKYL CHLORIDES:  
MODERATOR EFFECTS AND DEUTERIUM ISOTOPE EFFECTS

by

Kathleen Karen Carroll Taylor

(ABSTRACT)

The reactions of energetic carbon atoms produced by the nuclear reaction  $^{12}\text{C}(\text{p},\text{pn})^{11}\text{C}$  in some specifically-deuterated ethanes and propanes were investigated. Evidence was put forth which supports the contention that ethylene- $^{11}\text{C}$  is produced via insertion of methyne into a methyl C-H bond of the alkane, followed by unimolecular decomposition. Two isotope effects were found to be operative in the production of ethylene in hydrocarbons. The average ratio of CH/CD produced in alkanes was found to be 0.83. The second isotope effect indicated that the ease of insertion into  $\text{CH}_3$  groups compared to insertion into  $\text{CD}_3$  groups is 1.41. A bond energy effect was also noted in these systems. Methyne is formed more easily from secondary than from primary hydrogens by a factor of 1.3.

The yields of major  $^{11}\text{C}$ -labeled products in xenon moderated ethane were compared to earlier data for ethane in neon and helium moderators. The results suggest that

ethylene- $^{11}\text{C}$  is primarily the product of the  $^1\text{D}$  electronic state of carbon and acetylene- $^{11}\text{C}$  is the product of the  $^3\text{P}$  state at high energies. At lower energies acetylene can no longer be formed by  $\text{C}(^3\text{P})$ , but can be produced by  $\text{C}(^1\text{D})$ , as can ethylene.

Experiments with alkyl chlorides provided evidence that methyne can be formed both by direct abstraction and by insertion of  $^1\text{D}$  carbon into a C-H bond, followed by decomposition of the intermediate to give methyne. In analogy to the selective reactions of singlet and triplet methylene, the data suggest that carbon  $^1\text{D}$  selectively abstracts chlorine, giving chloromethyne which subsequently is oxidized to carbon monoxide- $^{11}\text{C}$ . The overall effect is to divert  $^1\text{D}$  carbons from methyne production, sharply reducing the ethylene- $^{11}\text{C}$  yields in these substrates. A consequence of this diversion is that the residual ethylene is formed almost exclusively by abstraction of hydrogen by  $^3\text{P}$  carbon, thus altering the isotope effect for methyne production. The ratio of CH/CD which ultimately results in ethylene was found to be 1.1 in alkyl chlorides.