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Recoil reactions of atomic carbon in systems of simple oxygen containing organic molecules

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RECOIL REACTIONS OF ATOMIC CARBON IN SYSTEMS
OF SIMPLE OXYGEN CONTAINING ORGANIC MOLECULES

by

Gerard Francis Palino

A Dissertation Submitted to the
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INTRODUCTION

Atomic Recoil Chemistry

Hot atom chemistry is the study of the chemical reactions of atoms possessing kinetic and/or electronic energy in excess of their thermal or equilibrium values. The chemistry observed is usually significantly different from the thermally equilibrated species as a result of the excess energy brought into the system by the hot atom.

In a thermal reaction system, there exist only a limited number of reaction pathways. These pathways are threshold reactions or reactions involving transition states of low activation energy. As the energy brought into the system is increased, higher energy reaction pathways become successively available, their direction being determined by the internal energy of the activated complex and the rate of energy transfer to the surrounding medium.

Atomic recoil chemistry is that section of hot atom chemistry concerned with the reaction of kinetically energetic atoms produced as a result of a nuclear transformation. The nuclear event usually produces an atom with a very high kinetic energy (10^2 - 10^6 eV). The results of the primary interaction of this kinetically energetic atom are best classified as radiation chemistry. As the atom loses its energy by successive collisional encounters with the medium, it enters a region in which the interactions can be described as chemical in nature involving the recoiling atom and the molecule in a 'transition state' with definite lifetimes and pathways which produce molecular species containing the recoil atom. These secondary species may be stable molecules but more likely are highly excited molecules or molecular fragments which may be

radical in nature, undergoing chemical reactions which are dependent upon the chemical composition of their environment and upon the activated state in which they are produced. The initial reactive encounter can occur over the whole chemical energy range, from the thermal kinetic equilibrium value up to the maximum energy at which a transition state complex can be postulated. The final observed product spectrum may be thought of as resulting from the primary and secondary interactions of these atoms and molecular fragments with the medium under investigation.

It is the province of hot atom chemistry to study these interactions with the purpose of obtaining useful information that will aid in the eventual understanding of the interesting and relatively unexplored subject of high energy chemistry.

In using the nuclear technique to produce the recoil atoms one out of necessity chooses a system in which the product nucleus is radioactive. The activity serves to label the products and permits the application of sensitive radiochemical analytical techniques.

In this dissertation the recoil reactions of atomic carbon in condensed phase systems of methanol, ethanol, 1- and 2-propanol, diethyl ether, acetone, methyl acetate and methyl formate are discussed.

Historical Background

Recoil chemistry was born in the work of Szilard and Chalmers in 1934 (1). They bombarded ethyl iodide with fast neutrons causing the $^{127}\text{I}(n,\gamma)^{128}\text{I}$ reaction and they observed that a fraction of the radioactive iodine could be extracted into an aqueous phase and after reduction precipitated as silver iodide. In explanation, they postulated that the recoil energy imparted to the iodine atom during the (n,γ)

process was sufficient to break the C-I bond. Until this classic experiment, the product nucleus from the (n,γ) reaction with elements of $A > 30$ had been found to be inseparable from the target material (2). Amaldi, et al. (3) suggested that since the γ -recoil energy was sufficient to eject the active atom from its molecule, it was therefore probable that the residual activity in the organic phase was due to the ejected active atom entering another molecule. They also suggested that thermal neutrons should initiate similar results. These predictions were soon verified (4,5). Glueckauf and Fay (4) irradiated a number of alkyl halides with slow neutrons and observed evidence for organic synthesis. The radioactive halogen atom remaining in organic combination was found to be predominantly in the same chemical form as the irradiated halide but new chemical species were also produced. By dilution of bromoform with an inert solvent, carbon disulfide, they were also able to demonstrate that within experimental error, every halogen atom that captures a neutron is ejected from its molecule. This fact was also verified by Suess (6) in gas phase neutron irradiations of ethyl bromide. Barkas, et al. (7) using the (γ,n) process, obtained results qualitatively similar to those obtained from neutron bombardment of ethyl bromide and correctly concluded that the separation was not restricted to the (n,γ) process.

As a result of the availability of neutron sources, the favorable neutron capture cross sections, and the desirable chemical properties of the alkyl halides, a huge body of data has been accumulated on the recoil reactions in these systems. In an attempt to correlate these experimental results, a number of models have been proposed.

According to the "billiard-ball" model proposed by Libby (8,9), atoms with recoil energies of a few hundred electron volts interact and lose energy in the liquid and solid alkyl halides by momentum transfer during elastic collisions with single atoms. The collisions are similar in character to those which would occur in a loose assembly of nonbonded atoms. For head-on collisions with atoms of similar mass, most of the kinetic energy can be transferred to the struck atom. If the recoil atom is left with kinetic energy below a certain critical value necessary for escape from the collision site, bond formation with the molecular radical may result. If on the other hand, the collision is between atoms of unequal mass (e.g. between I^{128} and hydrogen) momentum considerations indicate that the residual velocity of the recoil atom would insure its escape from the collision site so that the probability of combination between the recoil atom and the molecular radical would be very low. This hypothesis would predict that all recoil atoms which re-enter organic combination must do so as the parent compound.

This model was extended by Friedman and Libby (10) in order to account for sizable yields of labeled organic compounds different from the parent molecule. In this modification, they proposed that a different type of energy transfer occurred when the recoil atom was reduced to energies near 10 eV. In this "epithermal region", the recoil atom collides inelastically with the molecule as a whole promoting molecular excitation and bond rupture. If the atom does not have sufficient residual energy to leave the solvent "cage" it will combine with these radicals producing a variety of molecular products.

A theoretical extension of Libby's elastic collisions hypothesis

was presented by Miller, et al. (11) in 1950. The theory was developed in terms of a model involving energy loss by elastic collisions, dissociation of solvent molecules by impact, and eventual reaction in a liquid "cage". Expressions were derived which related the fraction of the recoil atoms in a given molecular species to the composition and properties of the liquid. The predictions of this theory were in reasonable agreement with results already in the literature as well as with some of their own data (12). A very similar theoretical approach was presented by Capron and Oshima (13) in 1952.

In 1960, Estrup and Wolfgang (14) developed a model for the kinetics of hot atom reactions in the gas phase. The total probability that a hot atom will react before losing its kinetic energy was expressed in terms of the average collisional energy loss and the efficiency of the reaction upon collision. The model predicted the relative effect of inert moderating compounds and provided a measure of the relative energy at which various products were formed. This theory was tested (15) using experimental data on the effect of moderators upon the reactions of hot hydrogen with methane and the results were found to be in quantitative accord with the theory. This theory was later extended to binary systems of molecular reactants (16).

The reactions in the liquid and solid phases present a very different problem from those in the gas since the collisional phenomenon are quite complex and the role of the surrounding molecular debris may be of distinct influence. With these facts in mind and with increasing experimental evidence concerning the inadequacy of the "billiard ball collision-epithermal collision" hypothesis (17-19),

Willard (20) in 1953 proposed his "random fragmentation" model. This model assumes that the recoil atom inelastically interacts with the solvent molecules as a whole rather than by elastic collisions with individual atoms. These interactions result in random fragmentation and excitation of the medium in the vicinity of the energetic atom. When the energy of the recoil atom is reduced below that sufficient to rupture bonds, it will find itself adjacent to a pocket of radicals and inorganic atoms in high concentration. It may immediately react to form a stable compound, a "hot process", or it may enter a stable combination by a "thermal process" after diffusing into the medium. Such thermal reactions are vulnerable to competition from low concentrations of added radical scavengers (e.g. I₂, DPPH and olefins). The relative numbers and specific types of organic and inorganic fragments formed will then depend upon the chemical nature, crystal structure, and density of the medium and on the mass and possibly the energy of the recoil atom. This theory does not completely rule out "billiard-ball" type replacements but does reduce their significance. Although this theory successfully correlated a considerable fraction of the then present literature, definite evidence soon was forthcoming which completely altered the approach to atomic recoil chemistry. Hornig, Levey and Willard (18) in their now classic work observed gas phase organic synthesis for the recoil iodine atom, $\text{CH}_4 + {}^{128}\text{I} \longrightarrow \text{CH}_3 {}^{128}\text{I}$. The yield of $\text{CH}_3 {}^{128}\text{I}$ was as high as 50% and reaction was found to be a result of a kinetically energetic iodine atom. These results are inconsistent with Libby's "billiard-ball" hypothesis and in direct conflict with Willard's "random fragmentation" model.

Further studies have demonstrated the inadequacy of these models (21-23) and the trend in recent years has been away from the purely physical approach and towards a more unifying mechanistic approach that takes into account the chemical environment which the recoil atom encounters.

In recent years, a number of excellent reviews have appeared (20,24-35) which taken in their entirety provide a very complete picture of the past work and present status of hot atom chemistry.

Recoil Carbon Chemistry

Introduction

Significant progress in the study of the recoil reactions of atomic carbon has been made in recent years. This progress can be linked to two important advances. The first one has been the development of the gas chromatograph (36,37) and its application (38) to the separation of the products resulting from the hot atom reactions. The second which was made possible by the first was the increasing use of the short lived carbon-11 isotope. Carbon has two isotopes convenient for use in recoil studies, carbon-14 and carbon-11. Carbon-14 was discovered by Ruben and Kamen (39) in 1941 and is conveniently produced by the nuclear reaction, $^{14}\text{N}(n,p)^{14}\text{C}$. Because of the availability of neutron sources, the reactions of recoil carbon-14 were the first to be considered. The (n,p) reaction on ^{14}N produces a carbon atom with a recoil energy of about 42 keV.

The first recoil study involving carbon-14 was reported by Yankwich, et al. (40). They irradiated a variety of inorganic and

organic nitrogen containing compounds for two years with neutrons from the 60-inch Berkeley cyclotron. They interpreted their results in terms of carbon atom interactions and reaction with the solvent and molecular fragments and postulated possible reactive intermediates such as CH, CO, CN, and CH₂. Although the radiochemical yield of products was rather low, the overall results did encourage Yankwich to speculate as to the usefulness of hot atom chemistry in synthesizing carbon-14 labeled compounds. This last statement indicates the direction of a significant fraction of the early carbon-14 work (41-46). This area of recoil carbon chemistry has been thoroughly discussed in a recent review article by Wolf (26).

As an increasing amount of data became available, inquiries as to the location of the radioactive carbon in the product molecule (47-52) and to the mechanism for the product formation were made (53-56). The long half life of carbon-14, 5730 yr, coupled with the relatively low reaction cross section for its formation makes long irradiation periods necessary for the production of useful quantities of radio-carbon. As a result, the sample is exposed to a very high radiation field for long periods of time and radiation modifications of the primary products may result. This effect was observed by Yang and Wolf (57) in their study of the recoil reactions of carbon-14 in gaseous ammonia. Methane-¹⁴C accounted for nearly all of the radio-carbon produced but traces of methylamine-¹⁴C were also noted. In a later study of the same system using carbon-11 produced by the ¹⁴N(p,α)¹¹C reaction, Cacace and Wolf (58) showed that radiolytic reduction of the methylamine to methane occurred at doses greater

than 10^{-3} eV/molecule. The absorbed dose in the carbon-14 work was between 0.4 and 1.2 eV/molecule. As a consequence, the observed product spectrum was a result of extensive modification of the primary products and was not indicative of the actual reactions of the hot atoms.

All of the current mechanistic studies use carbon-11 as the recoil isotope. This isotope was discovered by Yost, Ridenour, and Shinohara (59) in 1935 but its first reported use in the hot atom field did not occur until 1953 (60). Because of its short half life (20.4 min), a rapid separation of the recoil products is required. This is conveniently accomplished in organic systems by using gas chromatography. The use of carbon-11 has significantly increased the latitude of the experimental variables. Irradiations can frequently be performed at any temperature with the compound in any phase. The radiation damage to the system is variable over wider limits and can be kept at a lower level than has been possible in the carbon-14 studies. Degradative studies to locate the position of the active carbon in the product molecule are very difficult in this system because the short half life requires a rapid separation, degradation, and counting procedure. In many cases this problem can be solved by using the carbon-14 system.

Carbon-11 can be produced by a variety of techniques, a number of which are: 1) $^{12}\text{C}(\gamma, n)^{11}\text{C}$ using >25 MeV bremsstrahlung; 2) $^{12}\text{C}(n, 2n)^{11}\text{C}$, using fast neutrons; 3) the $^{12}\text{C}(\text{Pt foil})^{11}\text{C}$ neutron stripping reaction; 4) $^{12}\text{C}(p, pn)^{11}\text{C}$, using 45 MeV protons; and 5) $^{14}\text{N}(p, \alpha)^{11}\text{C}$, using 8 MeV protons. A majority of these techniques are able to produce usable quantities of carbon-11 at radiation dose levels of 10^{-2} eV/molecule

or lower. Even at this low level, radiation modification of the system cannot be discounted.

Organic hydrocarbon systems

The C-H bond "insertion-decomposition" mechanism first proposed by MacKay and Wolfgang (61) to account for the formation of the observed large yields of acetylene in simple hydrocarbons, has had considerable success when applied to the mechanistic interpretation of the formation of other observed products. This mechanism postulates that a carbon atom can insert into a C-H bond of an organic molecule, e.g. C_nH_{2n+2} . The resultant adduct, $C_{n+1}H_{2n+2}$, which is definitely excited and not necessarily internally equilibrated, can fragment to a stable molecule like acetylene or into reactive intermediates (e.g. CH, CH₂, C₂H, C₂H₃, etc.). It may also stabilize or rearrange to form the corresponding C_{n+1} alkene, $C_{n+1}H_{2n+2}$. The pathways available to this excited adduct will depend upon its total energy and how this energy is distributed within the complex. It will also depend upon the rate of energy transfer to the surrounding medium and as a consequence, the phase of the system may be important in the determination of the overall product spectrum.

Acetylene has been observed to be a major product in all of the organic systems studied to date and a considerable effort has been made in recent years to elucidate the mechanism for its formation. Phase studies (32,62,63) have shown that the initial adduct formed in the reaction of carbon atoms with an alkane has a life time long in comparison with bond vibration frequency and can collisionally

deactivate. This suggested to Ache and Wolf (64) that the energy of this complex might be low enough that bond energy effects might change the "excitation-decomposition" sequence. This led them to a study of the bond energy effects on acetylene production in the alkyl halides and propane systems. They observed that 85% or more of the acetylene-¹¹C produced from the specifically deuterated hydrocarbons, CD₃CH₂CH₃, CH₃CD₂CH₃, and CD₃CH₂CD₃ or from the deuterated alkyl halides, CD₃CH₂X and CH₃CD₂X, is either isotopically pure C₂H₂ or C₂D₂. Since the deuterium label served as a probe for the point of attack of the hot atom, the results indicated that the reaction is mainly intramolecular and localized. Similar double labelling studies on other systems have confirmed these results (65,66). A regular increase was also noted in the proportion of the hot yield of acetylene from the -CH₂X group, where X is CF₃, F, Cl, Br, and I. This yield increase was found to be proportional to the decreasing C-C bond dissociation energy and the largest increase was observed from the -CH₂I group. These results were interpreted in support of the "excitation-decomposition" mechanism. In addition, Ache and Wolf presented evidence indicating a higher probability for acetylene production from the methyl group than from the methylene group, the ratio (C₂H₂)CH₃/(C₂H₂)CH₂ being = 1.9/group.

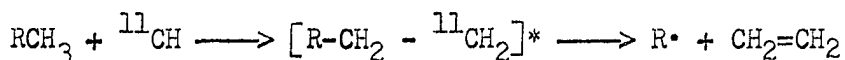
Dubrin, MacKay and Wolfgang (67) proposed that the triplet carbon atom, C(³P), was the primary precursor to acetylene in ethylene. They envisioned a rapid unimolecular reaction involving a spin conservation mechanism in which the triplet carbon atom inserted into either the C-H or C=C bond forming an excited adduct that could either decompose

to acetylene or other fragments or add to another ethylene molecule forming C_5 hydrocarbon products. These spin restrictions have been questioned by Wolf (32) on the basis that the rules for electronic transitions need not be strictly obeyed in an encounter of this sort since it involves a complex containing considerable excess energy which is partially a result of the conversion of translational energy into internal energy. Evidence for spin conservation in the reaction of thermal carbon atoms has been presented by Skell (68-72). These recent studies are of considerable interest and will be the topic of a later section of this introduction.

Carbon atom attack at the double bond in olefinic hydrocarbon was first postulated by MacKay, et. al. (73) in 1962. They envisioned the formation of a cyclopropylidene type intermediate which unless suitably substituted would rapidly collapse to a diene. Support for this hypothesis was obtained from degradative studies of the allene produced by the reaction of carbon atoms with ethylene (74). The results of this experiment indicated that the allene was predominantly center labelled (the ratio of center to end labelled allene was approximately 2:1 and independent of phase) and that both C-H and C=C insertion reactions were important. Double tracer studies using equal molar mixtures of C_2H_4 and C_2D_4 demonstrated that the allene contained all of the hydrogens of the attacked ethylene molecule and confirmed that allene is predominantly formed by the interaction of a carbon atom with a single ethylene molecule (75).

The possible role of the methyne intermediate (CH) in the carbon reaction scheme was first mentioned by MacKay and Wolfgang (61) and

was suggested by Rack and Voigt (76) as a possible alternative intermediate in the production of acetylene. The chemistry of this intermediate has been virtually unknown until recent years. In the carbon recoil systems, methyne can conceivably be formed by either the "insertion-decomposition" mechanism or by a hydrogen abstraction process. This intermediate is believed to exhibit insertion properties similar to that of the carbon atom and has been singled out as the major precursor to the ethylene-¹³C observed in saturated hydrocarbon systems (63). The yield of ethylene in these systems has been found to be directly proportional to the fraction of primary hydrogens. Negligible yields were observed in the C₃ to C₆ cyclic hydrocarbons. These results were interpreted in terms of the insertion of the methyne radical into a primary C-H bond followed by scission of the adjacent C-C bond (77).



Evidence for the formation and reaction of methyne in the H₂ - C₂H₄ system has recently been presented by MacKay, Nicholas, and Wolfgang (78). The methyne formed by the reaction of carbon atoms with hydrogen was observed to react with ethylene to give an allyl radical which reacted further to yield pentene-1.

Safrany, Reeves, and Harteck (79) observed the reaction of CH with ammonia in an acetylene-oxygen flame. They postulated that the methyne radical reacted with ammonia to form HCN, H₂ and H• and reported a rate constant of $6 \times 10^{10} \text{ mole}^{-1} \text{ cc sec}^{-1}$ for the reaction. Spectral evidence for CH from vacuum UV flash photolysis of methane was reported by Braun, McNesby and Bass (80). In this study, the rate constants for the reactions of methyne with CH₄, N₂ and H₂ were

determined. The methyne radical was observed to react with methane to form ethylene and a hydrogen atom with a rate constant of 1.5×10^{12} moles⁻¹ cc sec⁻¹. The reaction with hydrogen yielded the methyl radical but the products from the reaction with nitrogen were not determined. The rate constants were 6.2×10^{10} mole⁻¹ cc sec⁻¹ and 4.3×10^{10} mole⁻¹ cc sec⁻¹, respectively.

The participation of the methylene intermediate (CH_2) in these reactions has been inferred from the resultant product distribution of the C_{n+1} saturated alkanes in recoil studies of the saturated C_n alkane systems. Wolf (51) observed a statistical insertion of methylene into the C-H bonds of pentane to give labelled hexanes and a similar statistical insertion in toluene to give ethyl benzene and labelled xylenes. The results were in agreement with the indiscriminate reaction of methylene first observed by Doering, et al. (81) in photolysis studies of diazomethane in liquid n-pentane and 2,3-dimethylbutane and are consistent with the postulated methylene insertion reaction (82). MacKay and Wolfgang (61) observed that the relative yields of the butanes produced in the gaseous propane system were in agreement with the expected gas phase insertion ratios (83). Additional support was obtained by Stoecklin and Wolf (63) in their study of the gaseous, liquid and solid propane systems. Recent results in this laboratory have confirmed this statistical distribution for a number of C_5 hydrocarbons (84,85).

The gas phase reactions of methylene are known to be more discriminate (86) and chemical evidence has been obtained which indicates that methylene may react in more than one spin state (87).

In the reactions of photolytically produced methylene with isopentane vapor, Carr (88) has shown that triplet CH_2 abstracts hydrogen and singlet methylene inserts into C-H bonds with about the same reactivity and that the abstraction reaction is much more selective than the insertion reaction. The abstraction selectivity is in the order tert > sec > prim in the ratio 8.9:1.5:1 and the insertion selectivity is in the same order but with a ratio, 1.5:1.3:1. The observed selectivity for gas phase methylene was noted to be somewhat greater than in the liquid and was consistent with earlier findings (81,89). Methylene has also been shown to add to the C=C bond with the formation of cyclopropanes (81). Spin conservation is observed for these additions (90) and the selectivity of addition over insertion is found to be energy dependent (91).

Hydrogen abstraction by triplet methylene or the insertion decomposition reaction by singlet methylene will produce methyl radicals ($\cdot\text{CH}_3$). Evidence for methyl radical production in recoil carbon systems was first presented by Schuler (92). He observed a 3.3% yield of methyl iodide- ^{11}C in the iodine scavenged cyclohexane system. In a more recent study in the same system, Clark and Voigt (93) observed a 3.0% reduction of the methane yield upon addition of scavenger quantities of iodine. These results indicated that the iodine had reacted with $^{11}\text{CH}_3$ radicals which otherwise would have abstracted or picked up hydrogen to form methane, although methyl radical reaction with radiation produced radicals was not ruled out. Evidence for reactions of $^{11}\text{CH}_3$ radicals with other radicals was first presented by Jewett (85) who observed that the yield of CH_3I was significantly

greater than the reduction of methane in the iodine scavenged C₅ hydrocarbon systems. A similar trend was observed by the author in the methanol and ethanol systems.

Since methane is the last product to be produced in the reaction sequence in hydrocarbon systems, its yield may be considered as a mirror of the overall reactivity of the system.

Other systems

The early investigations in recoil carbon chemistry were carried out in inorganic systems.

Rowland and Libby (60) observed the products produced as a result of the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in solid and liquid CO₂. Carbon monoxide- ^{11}C and carbon dioxide- ^{11}C were the only products formed in significant yields. In the liquid sample 95-100% of the radiocarbon was in the form of CO. In the solid phase approximately equal fractions of each product were observed. It was suggested that the solid phase system would confine the radicals generated along the recoil path long enough for them to recombine, while in the liquid where the caging effect is less pronounced, the carbon could diffuse out of the recoil track into a region of higher reaction probability with carbon dioxide molecules. Similar results were obtained for crystalline sodium bicarbonate and for an aqueous sodium bicarbonate solution. These last results were in conflict with the work of Edwards and McCallum (94), who studied both the CaCO₃ and NaHCO₃ systems. They observed very little carbon monoxide but did find significant yields of carbon dioxide, oxalic acid, glyoxylic acid and glycolic acid. They attributed the disagree-

ment in results to the fact that Rowland and Libby had used sulfuric acid to liberate the gases and as a consequence considerable decomposition of the acids had occurred. Further studies in similar systems indicated that the relative proportions of the radicals formed by carbon-11 were independent of the nature of the cation present and of the crystal structure (95). Crystal annealing effects were also observed. McCallum and Edwards (96) have also reported recoil carbon data for the solid sodium formate system.

Dubrin, et al. (97) and MacKay, et al. (98) reported results for the reaction of recoil carbon-11 with a number of π -bonded inorganic molecules. Carbon monoxide-¹¹C was the only significant product to result from carbon reactions with O₂, CO, CO₂ and SO₂. Carbon monoxide-¹¹C was still the only product in liquid oxygen where there is no three-body restriction on CO₂ formation. With N₂, N₂O and NO, both ¹¹CO and ¹¹CN were observed as major products. With NO₂, ¹¹CO is again the major product. These results were interpreted in terms of an "end-on" attack at the oxygen or nitrogen atom which is in direct contrast to the "sideways π -complex" mode demonstrated for ethylene. Molecular orbital arguments were also invoked in support of this proposal. Using neon to moderate the energy of the recoil carbon atom, they were able to demonstrate that these reactions would occur with both hot and thermalized carbon atoms. The endoergic reaction in which carbon-11 reacts with N₂ to form ¹¹CN was the only exception.

Moll and Thompson (99), using photochemical decomposition of matrix-isolated carbon suboxide at 4.2°K as a source of carbon atoms, observed a number of the radical intermediates in the reactions of

carbon atoms with N_2 , H_2 and D_2 . Their attempts to form methylene in spectroscopically observable quantities were unsuccessful but definite evidence for the NCN and CNN radical intermediates was observed. Contrary to earlier predictions (97,98) these results do indicate a possible " π -bond" insertion mechanism in nitrogen.

Recoil carbon has also been shown to react with N_2-O_2 mixtures to produce >90% yields of carbon monoxide- ^{11}C . The significance of this result in reference to the natural radiocarbon cycle has recently been discussed (100,101).

The radiation modification of the primary reaction products in the recoil carbon-gaseous ammonia system has previously been mentioned. MacKay et al. (98) studied the ammonia system and observed very little product activity. They attributed this result to the trapping of the primary products (possibly HCN) on the reaction vessel walls. When the sample was exposed to a very high radiation dose, $^{11}CH_4$ was observed as the major product. These results were in agreement with earlier work by Yang and Wolf (57). The most definitive study of this system has recently been presented by Cacace and Wolf (102). The observed reaction products were methane, methylamine, and methylenimine. Methylenimine and part of the methylamine were a result of reactions with kinetically energetic carbon atoms but most of the methane resulted from a thermal process. The radiolytic reduction of methylenimine and methylamine to methane was demonstrated and no evidence for the formation of HCN or any derivative thereof was found. Competition studies with equimolar mixtures of ammonia and propane indicated a relatively low efficiency for the carbon atom

reaction with ammonia. For the pure system, irradiated at low conversion in the solid and liquid phases, methylamine and methane were observed in yields of 74% and 8%, respectively. These results are nearly identical to those found by Yankwich and Vaughan (44) in the carbon-14 recoil study in crystalline ammonium bromide and may indicate a possible parallelism between the reactions in both systems.

Cacace, Stoecklin and Wolf (103) examined the reactions of carbon-11 in methylamine. The results were in general agreement with what is known about the reactions of energetic carbon atoms with alkanes and ammonia. Acetonitrile, the only hot product observed (e.g. yield was independent of phase and scavenger) was proposed to be formed by decomposition of an excited ethyleneimine molecule since the activity was found to be equally distributed between the two carbon atoms. From the comparison of the acetylene and ethylene yields in the methylamine and ethane systems, it appears that the C-H bonds are much more reactive towards insertion reactions than are the N-H bonds. This selectivity is not apparent for the methylene insertion reaction since the ratio of the yields of dimethylamine and ethylamine in the scavenged condensed phase system appear to be in the ratio of what one should expect by indiscriminant methylene insertion reactions into the C-H and N-H bonds.

Carbon recoil reactions in the acetamide system have been reported (48,51,104). Wolf et al. (48) have reported data on degradative studies of a number of product molecules. In all cases, considerable divergence from what one would expect from statistical insertion or replacement was observed. Similar results were obtained by

Diehm (104) who has made a much more comprehensive study of the product distribution. Dose studies were performed on a number of products, and significant radiation damage effects were shown to persist down to 10^{-3} eV/molecule or less. The acetamide molecule had a relative replacement probability for the carbonyl and methyl carbon atoms of about 1.9:1. These results indicate to this author that participation of the carbonyl group via the formation of a possible cyclic intermediate may be responsible for the mixing and replacement ratios reported by both Diehm and Wolf. In any case, further study of this system or of similar systems will be required before an adequate interpretation of the data can be made.

Ache and Wolf (66,105) recently reported results bearing on their study of carbon atom reactions in N_2 - H_2 and N_2 -hydrocarbon systems. In the N_2 - H_2 system, HCN and CH_4 were the only products observed. In the N_2 -alkane systems, HCN (<50% of the total ^{11}C) was the only nitrogen containing compound observed in addition to the usual spectrum characteristic of carbon atom-alkane interactions. The $H^{11}CN$ was shown to be a product of a hot atom reaction in agreement with previously reported results (97,98). The addition of oxygen decreased the HCN yield owing to the competing reaction by oxygen for the hot carbon atoms. From the kinetic treatment of the data, the following hot atom reaction cross section ratios were obtained; $\sigma_{CO(hot)}/\sigma_{HCN(hot)} \approx 9$, $\sigma_{HCN(hot)}/\sigma_{C_2H_2(hot)} \approx 0.22$ and $\sigma_{C_2H_2(hot)}/\sigma_{C_2H_2(hot)}$ from $C_3H_8/\sigma_{C_2H_2(hot)}$ from $C_2H_6 = 1.31$. The last ratio is nearly identical to what one would predict on the basis of a statistical insertion decomposition reaction.

Mackay and Wolfgang (23) have reported some data for ethylene oxide. Significant yields of both acetylene- ^{11}C and carbon monoxide- ^{11}C were observed. Carbon monoxide was postulated to have resulted from an attack by a carbon atom at the oxygen unshared electron pairs with subsequent electronic rearrangement to form ethylene and carbon monoxide- ^{11}C .

Investigations have also been performed on the methanol system (52,106). The early work by Schrodt and Libby (106) cannot be considered meaningful by present day standards since it involved a reactor irradiation of a mixed system of aniline and methanol and the product distribution was obtained by fractional distillation. Oae, Redvanly, and Wolf (52) have reported some of the results they have obtained in the $\text{NH}_3\text{-CH}_3\text{OH}$ system. The yields of the $\text{C}_1\text{-C}_5$ alcohols were tabulated and degradative studies on the products ethanol and n-propanol were reported. Since some of their results have direct bearing on the current investigation, this work will be discussed later in greater detail.

Thermal Carbon Chemistry

Information relating to the reactions of thermal carbon atoms would be of considerable help in interpreting the results of recoil carbon studies. In recent years, such information has become available.

Stief and De Carlo (107) produced atomic carbon by photolysis of carbon suboxide and observed that in reactions with methane, both acetylene and ethylene were produced. The carbon atom was visualized as reacting with methane to form an excited C_2H_4 intermediate that could either collisionally deactivate to ethylene or lose hydrogen to form acetylene.

The reactions of carbon atoms produced by a carbon arc have been extensively studied by Skell and his co-workers (68-72, 108-110). In their experiments the carbon vapor was deposited on an inert paraffin surface at -196°C giving as major constituents of the deposit, C_1 and C_3 with small amounts of C_2 . Evidence for the reactions of carbon atoms in various states of electronic excitation was obtained by varying the timing of depositions and introduction of the reactant. The half-lives for the electronic transition $\text{C}(^1\text{S}) \longrightarrow \text{C}(^1\text{D})$ and $\text{C}(^1\text{D}) \longrightarrow \text{C}(^3\text{P})$ were estimated at 2 and 15 seconds, respectively (69).

In reactions with olefins, $\text{C}(^3\text{P})$ displays its reactivity through its filled and unfilled orbitals rather than through its half filled orbitals and reacts with conservation of spin angular momentum to form a triplet cyclopropylidene. The cyclopropylidene then reacts with another olefinic molecule to form a spiropentane by a non-stereospecific step. The $\text{C}(^1\text{D})$ is observed to react with olefins by two stereospecific addition steps to form spiropentanes. The initial cyclopropylidene adduct formed by olefin reaction with $\text{C}(^1\text{S})$ rapidly rearranges to an allene before addition of the second olefin can occur (72).

The $\text{C}(^1\text{S})$ has also been shown to undergo insertion reactions with the C-H bonds in saturated hydrocarbons. No isomerization to the C_{n+1} alkene was observed but intra- and intermolecular C-H insertion by the product carbene was noted. No evidence for C-H insertion by $\text{C}(^3\text{P})$ or $\text{C}(^1\text{D})$ was obtained.

In reactions with chlorinated hydrocarbons, C-Cl insertion by $\text{C}(^1\text{S})$ and $\text{C}(^1\text{D})$ was noted (109). The $\text{C}(^1\text{D})$ adduct preferentially rearranged to the corresponding alkene by methyl, chlorine atom or

hydrogen atom shift. The $C(^1S)$ adduct underwent intra- and inter-molecular C-H or C-Cl reinsertion reactions to form cyclic and build-up products.

Evidence for carbon atom reactions with hydroxyl, epoxy, alkoxy, and carbonyl functional groups has recently been obtained (68,110,111). Deoxygenation with formation of carbon monoxide was observed for acetone, methyl ethyl ketone, cyclopentanone, propylene oxide, diethyl ether and tetrahydrofuran. At the present time, it appears probable that $C(^1D)$ and $C(^1S)$ are the major reactants. No deoxygenation was observed to occur with simple alcohols and water but the alcohols do react with $C(^3P)$ to form dialkoxymethanes. Sprung, Winstein, and Libby (112) have used a similar technique to study the reactions of deposited carbon with benzene. Cycloheptatriene and toluene were the only products identified and evidence for the formation of a large fraction of high boiling polymeric material was presented.

Although the reactions of vapor-deposited carbon occurred in the solid phase at -196°C and may involve intermediate complexes acting as carbon donors, qualitative similarities have been noted between this system and recoil carbon. Little or no acetylene or ethylene was produced in the carbon vapor studies and that which was observed was shown to have resulted from a C_2 precursor (111). In the recoil carbon system, acetylene is a major product and is believed to be a result of the "insertion-decomposition" mechanism previously discussed.

The reactions of the primary adduct will depend upon its internal energy and spin state and upon the character and phase of the surrounding molecules. The effects of these factors have been exten-

sively investigated by Wolfgang and his co-workers for the ethylene (67,113-115) and 2-butene (116) systems. In a dilute solution of these reagents in a solid xenon matrix where thermalization of the carbon atom and de-excitation of the adduct are both efficient, the yields of the fragmentation products (e.g. C_2H_2 , C_2H_4 , etc.) were substantially reduced. Evidence was found to indicate that some of the cyclic adducts in the 2-butene system survive sufficiently long to react with a second 2-butene molecule to form spiro compounds. These results are in qualitative agreement with the carbon vapor studies on the same system.

At the present time, it is very difficult to assess the significance of the carbon vapor studies in relation to the reactive properties one might expect from thermal carbon atoms produced in gaseous or condensed phase systems at or near ambient temperatures.

Purpose of Investigation

As is evidenced from this brief review, considerable progress has been made in the understanding of the mechanisms of the gas phase reactions of atomic carbon in simple hydrocarbon and inorganic systems. In recent years, these mechanisms have been applied to the condensed phase reactions of larger hydrocarbon molecules with considerable success. No information is as yet available concerning the reactions of atomic carbon with molecules containing the carbonyl, hydroxyl or alkoxy functional groups.

It is the purpose of this present investigation to:

1. Obtain information relating to the overall reaction mech-

anism for atomic carbon in low molecular weight alcohol systems,

2. Obtain information concerning the structural dependence of the fragmentation modes for a number of target molecules containing carbonyl, hydroxyl and alkoxy functional groups,

3. Determine the yields of the observed products on an absolute basis,

4. Assess the significance and magnitude of the radiation damage in these systems, and

5. Determine whether insertion reactions similar to those postulated for C-H bonds in alkanes and N-H bonds in amines can also take place on O-H bonds, and if so, to compare the reactivities of the C-H and O-H bonds towards these insertion reactions.

The degree to which any of these objectives have been satisfied will be discussed in later sections of this dissertation.

EXPERIMENTAL

Reagents, Purification, and Sample Preparation

Reagents

Pertinent data concerning the source and initial purity of the reagents used in this study appears in Table 1.

Table 1. Reagent source and purity data

Compound	Source and Description	Purity (mole percent)
Methanol	Fisher Scientific Company Fisher Certified Reagent (A-936)	99.9+
Ethanol	Commercial Solvents Corporation Rossville Gold Shield Alcohol	99.9+
1-Propanol	Fisher Scientific Company Fisher Certified Reagent (A-414)	not stated
2-Propanol	Fisher Scientific Company Fisher Certified Reagent (A-432)	99+
Methyl Formate	Eastman Organic Chemicals Spectro Grade (S 1227)	not stated
Methyl Acetate	Matheson Coleman & Bell Chromatoquality Reagent (CQ 2409)	99.9
Acetone	Matheson Coleman & Bell Chromatoquality Reagent (CQ 2953)	99
Diethyl Ether	Baker & Adamson Reagent Grade Code 1700	not stated
Isopentane	Phillips Petroleum Company Research Grade	99.99

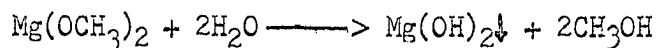
Iodine and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were used as radical scavengers. The iodine, sublimed, 'Baker Analyzed' reagent, had a stated purity of 100.0 percent. The DPPH was obtained from Eastman Organic Chemical and used without further purification. The gases used as carriers and for product identification were all of research grade and were obtained from the Matheson Company. The other chemicals were obtained from a number of commercial sources and since these materials were only used as carriers or for product identification, they were considered to be sufficiently pure.

Purification

All of the materials studied, with the exception of the isopentane, were subjected to further purification. Because of the primary consideration in this study, the overall product spectrum in the alcohol systems, these materials were extensively purified. Traces of aldehydes and ketones, normally found in alcohols, were removed by a procedure similar to that outlined by Baxendale and Mellows (117). In this procedure, 400-ml of the alcohol were refluxed with 2-g of 2,4-dinitrophenylhydrazine and 1-ml of concentrated H_2SO_4 for a period of 12 hours. The material was then rectified with retention of the central 200-ml fraction. A procedure outlined by Morton and Mark (118) and designed to accomplish similar results, proved to be unsuccessful when traces of furfural employed in the purification procedure were found in the ultraviolet spectrum of the rectified methanol.

The alcohols were then treated to remove traces of water. The technique used for methanol was different from that employed in the

other alcohol systems. The methanol was dried by a procedure outlined by Fieser (119). In this procedure, water is removed by reaction with magnesium methoxide. The reaction being:



Since the magnesium hydroxide is insoluble in methanol, the reaction proceeds to completion. In this procedure 2-g of Mg (J.T. Baker, purified) were dissolved in 200-ml of methanol. The mixture was then refluxed for 3-6 hours and rectified with the retention of the second 50-ml fraction. The collected fraction was then manually transferred to the vacuum line for degassing and sample preparation. This process reduced the water content of methanol to below 0.05%.

The other alcohols and acetone were dried using the same apparatus but with a substantially modified distillation column, pictured in detail in Figure 1.

The ability of molecular sieves to remove moisture from a variety of gases has been known for many years and recently increasing use has been made of them for the drying of organic liquids (120). In this apparatus, Molecular Sieve 4A (Linde Co., Division of Union Carbide) was used as the drying agent, the principle employed being similar to that of a Soxhlet extractor. The water in the organic liquid, which has some vapor pressure over the solution is swept up with the organic solvent through the fractionating column. The vapors are then condensed and passed down through the bed of molecular sieve finally returning to the vaporization flask via the side flow tube. By refluxing the solution for several hours, the water content of these solvents can be substantially reduced. Using a similar

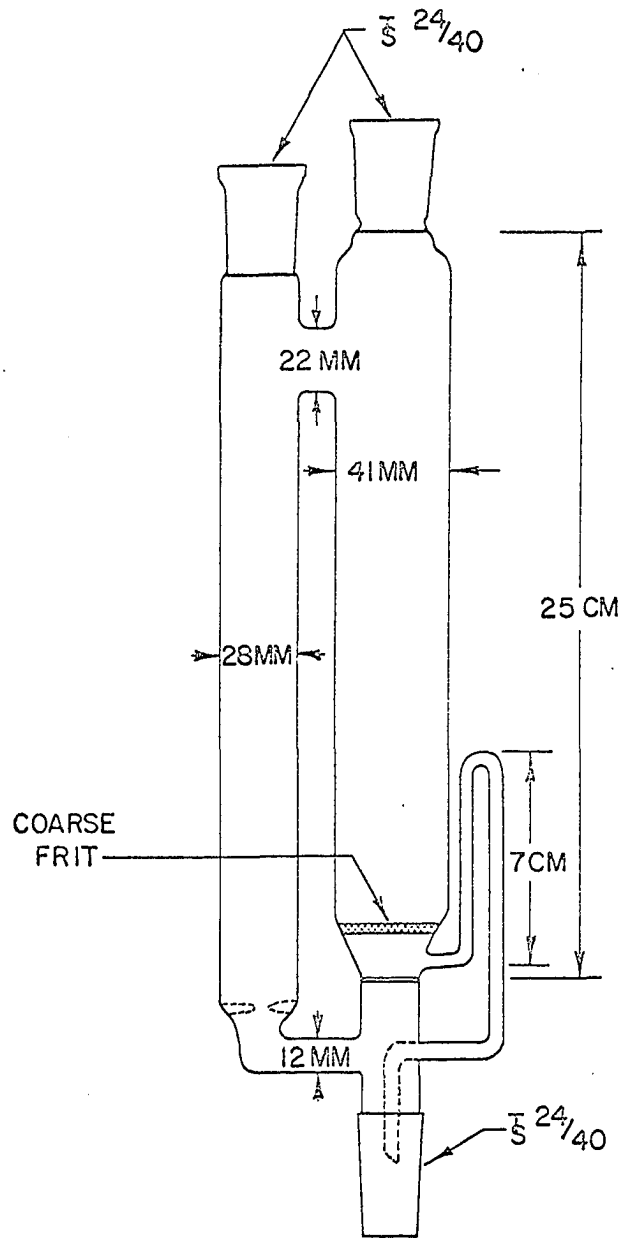


Figure 1. Molecular sieve reflux extractor

technique, Arthur, et al. (121) demonstrated that the concentration of water in 2-propanol and 1-butanol could be reduced below the detection limit of the Karl Fisher technique ($\approx 0.0005\%$). Hersh (120), using a considerably less efficient molecular sieve drying process, reduced the water content of ethanol, 1-propanol and acetone to about 10 p.p.m. Methanol, possibly because of its small molecular size, is not efficiently dried using the molecular sieve technique.

A 200-ml sample of ethanol, 1-propanol, 2-propanol or acetone was refluxed in this apparatus for 12 hours and then fractionated with retention of the second 50-ml fraction. This fraction was manually transferred to the vacuum line for degassing and sample preparation.

Diethyl ether, acetone, methyl formate, and methyl acetate were subjected to only a minor purification involving a simple fractionation step. Usually 250-ml of the material were refluxed for several hours before fractionation and only the central 100-ml retained for the drying step. The acetone was dried by the molecular sieve procedure outlined for the alcohols. The other solvents were dried using non-indicating Drierite in the vaporization flask of the distillation apparatus. The ability of Drierite to efficiently reduce the water content of many organic solvents has recently been discussed by Hammond (122). After refluxing for several hours, the solvent was rectified with collection of the central 30-40 ml fraction. This fraction was then transferred to the vacuum line for degassing and sample preparation. Before the drying step, the complete distillation system was flushed for several hours with dry air and was protected from atmospheric moisture during the refluxing and distillation

steps by a combination Drierite - molecular sieve drying tube. The sample purity was checked with the gas chromatograph using a sensitive thermal conductivity scale setting. In all systems, the results indicated an absence of detectable impurities.

Sample preparation

The unscavenged samples were usually prepared by a vacuum distillation technique. The apparatus is shown in Figure 2. The dried solvent was placed on the reservoir side of the system and frozen with liquid nitrogen. The stopcock above the reservoir was then opened and the space above the frozen solvent evacuated to a pressure of about one micron. The stop cock was closed, the liquid nitrogen removed, and the solvent allowed to melt. This procedure was repeated at least three times or until the vacuum gauge indicated an absence of dissolved gases. The sample bulblet, see Figure 2, was fabricated from Pyrex and had a diameter of 8.6 ± 0.1 mm. The bottom of these bulblets were slightly flattened to increase the sample activation during irradiation. The bulblet was mounted on the sample side of the distillation apparatus and evacuated. The stopcock to the vacuum line was closed and the two stopcocks above the reservoir and the sample were opened. The distillation was effected by cooling the sample bulblet with a dry ice-acetone mixture. The stopcock to the reservoir was closed and the sample was frozen in liquid nitrogen. The vacuum line stopcock was opened, the space above the bulblet evacuated, and the sample was sealed.

The scavenged samples were prepared by a pipeting technique.

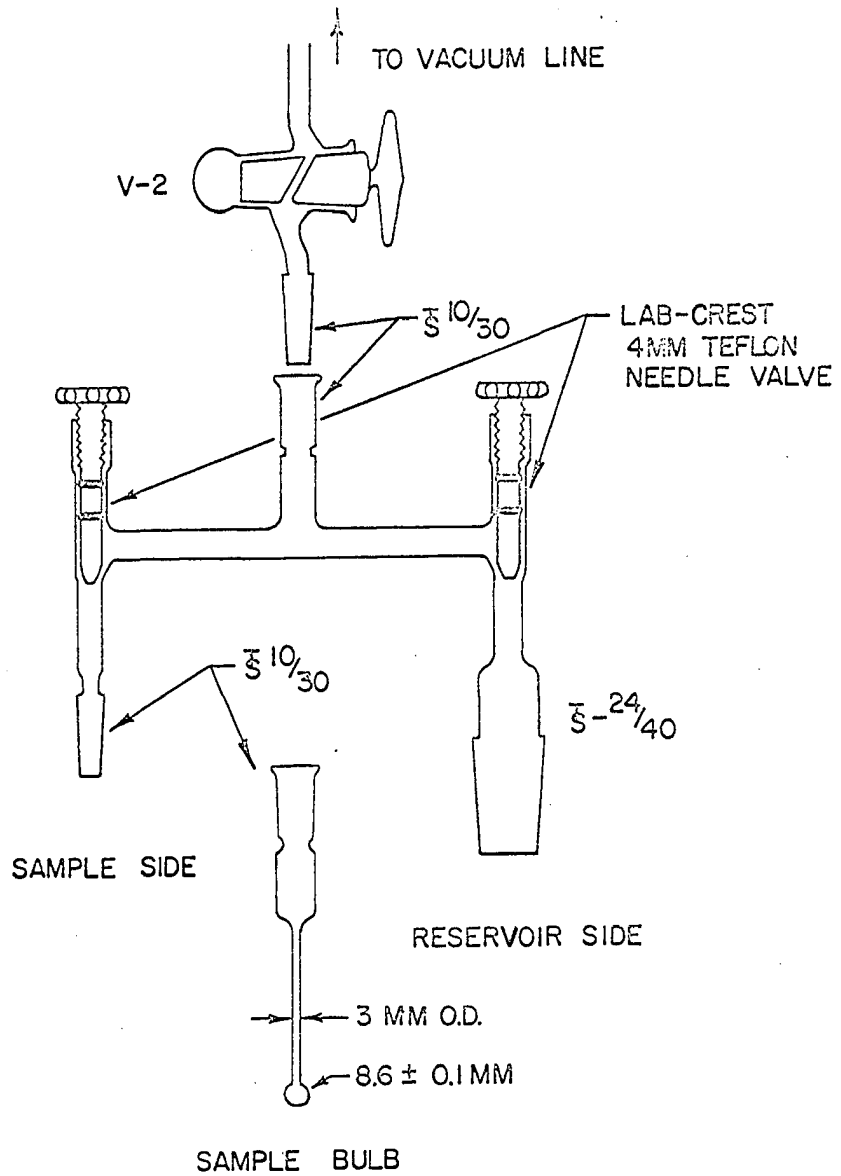


Figure 2. Vacuum distillation apparatus and sample bulb

The scavenged solutions were made by weighing the iodine or DPPH to the nearest 0.1 mg and dissolving it in a known volume of the vacuum distilled solvent. The samples were prepared by pipeting this mixture into the sample bulblets. These samples were vacuum degassed by the freeze-thaw technique and sealed. The iodine was observed to be completely soluble in all of the solvents over the range of iodine scavenger concentrations studied. In the acetone system iodine was observed to react, and only a few runs performed immediately after sample preparation gave results indicative of the scavenged systems. DPPH was found to be relatively insoluble in methanol; a solution prepared to 1×10^{-3} mole fraction still contained some undissolved DPPH.

The isopentane was used without further purification, the samples being prepared by the pipeting technique.

Experimental Apparatus

The separations of the radioactive products were performed on an F&M Research Chromatograph, Model-810, DR-12. This instrument has been modified to facilitate the analysis required in this research. A description of the major modifications has been outlined by Jewett (85) and consequently only a brief discussion of these alterations is presented.

The instrument is commercially equipped with both a gas sampling valve and syringe injection port. To facilitate the on-column injection of a large sample, a sample breaker was installed between the syringe injection port and the column connection. The breaker was insulated from the oven and heated with a 250 watt heater controlled by one of

the chromatograph electronic circuits. The injection configuration allowed the simultaneous operation of the three injection systems as well as independent operation of each. This condition is useful when gaseous or liquid carriers are added for column reactivity studies or for product identification.

The chromatograph is equipped with dual columns and dual thermal conductivity and hydrogen flame detectors. The hydrogen flame detection system was disconnected and one of the columns bypassed directly to the reference side of the thermal conductivity cell. The other column, to which the injection system is connected, was used for the product separations. A description of the columns and the column materials used in this study will be presented later.

The detection system for the radioactive effluent, shown in Figure 3, consisted of a 3.0 x 3.0 inch NaI(Tl) side-hole crystal (Isotope, Inc.). The effluent from the chromatograph was directed through this 5/8 inch hole by a 8-mm quartz tube wound with iron resistance wire. The wound tube was coated with Sauereisen to insure intimate contact between the wire and the glass and to prevent shorting of the electrical circuit. This tube could be heated by application of voltage from a variable transformer. The crystal which is very sensitive to thermal shock was protected by a silvered air condenser placed between the heated counting tube and the crystal wall. With this configuration, the counting tube could be safely heated to 160°C. The crystal and photomultiplier are incased in a 1.25 inch cylindrical lead shield and surrounded by a 2 inch thick lead cave. This was done to reduce the level of the background radiation.

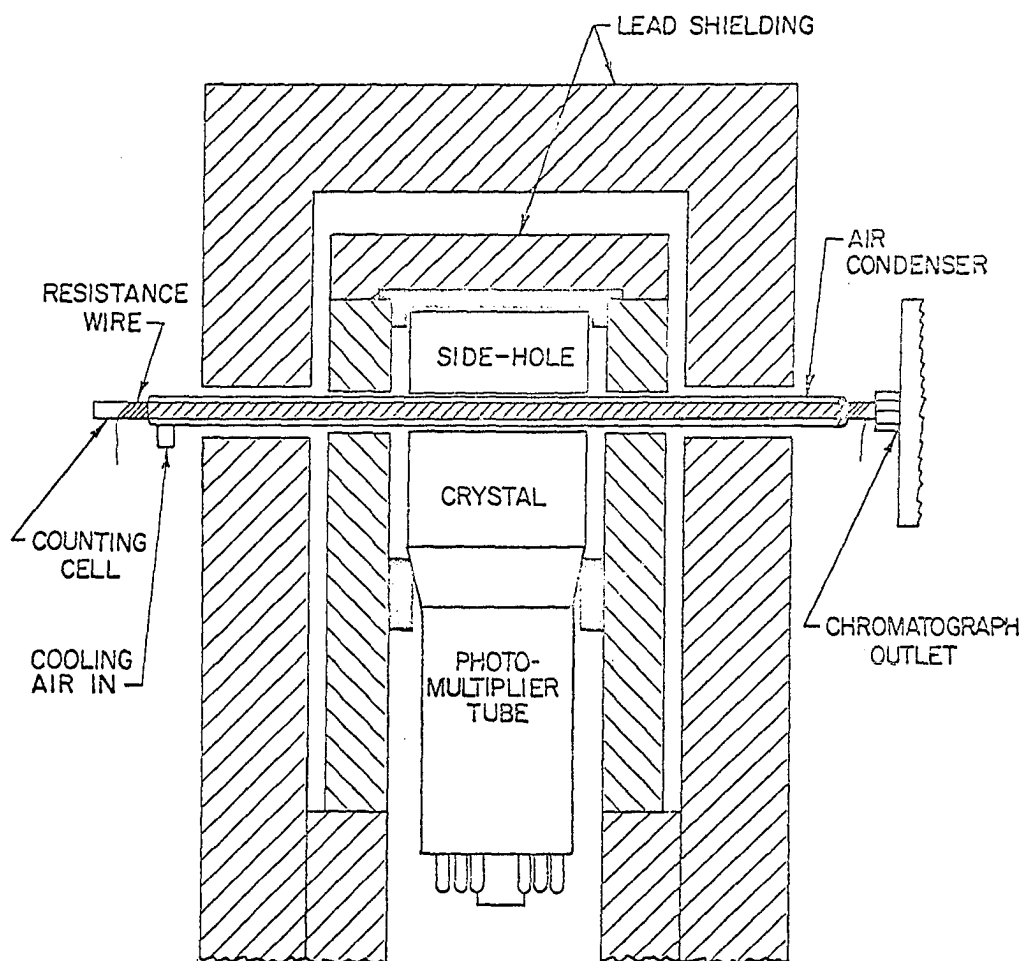


Figure 3. Diagram of radioactive effluent detector system

The output of the photomultiplier is connected to a Hewlett-Packard Model 5201 L Scaler-Timer Pulse Height Analyzer. This system permits the continuous recording of the counts accumulated in consecutive time intervals. In this study these are 5.0 and 10.0 seconds. This analyzer was set to accept pulses only in the region of 0.4 to 1.2 MeV, in order to include the positron 0.511 MeV annihilation radiation and the 1.022 MeV sum peak. By using the analyzer in this mode, a reduction in background and a substantial increase in the signal to noise ratio were achieved.

Other equipment, see Figure 4, included a Hewlett-Packard Model 5551A High Voltage Supply, a Hewlett-Packard Model 562A Digital Recorder and a RIDL Model 35-9 Rate Meter. The digital recorder prints out the recorded activity accumulated by the analyzer during each preset time interval. The information transfer from the scaler to the printer is very rapid, 3×10^{-3} seconds, and assures negligible count losses during the transfer operation. The output from the analyzer is used in conjunction with the rate meter to drive one of the pens on the Honeywell Electronik 16 Two-Pen Strip Chart Recorder. The other pen is connected to the output of the thermal conductivity cell control module. The thermal conductivity unit was used to determine the retention times for known compounds injected into the chromatograph and to facilitate the identification of unknown radioactive products by carrier techniques. The latter procedure is required since in a typical irradiation only about 10^{-16} mole of any one product is produced.

The activity induced in the sample during bombardment was measured

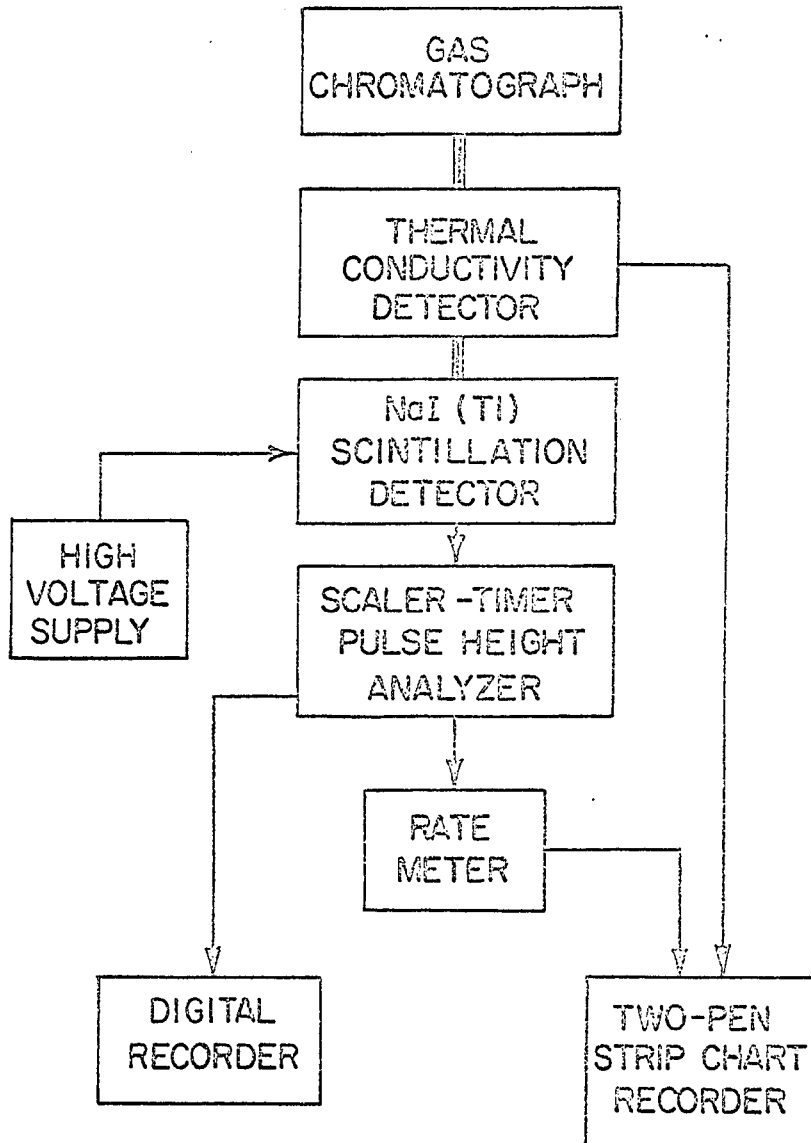


Figure 4. Block diagram of analysis system

on a monitor counter which was a 2.5 x 2.5 cm NaI(Tl) crystal connected to a Nuclear Chicago Model 186 Scaler. The crystal was shielded with lead to reduce background. The samples were counted under conditions of constant geometry at a time after irradiation sufficient to insure negligible contribution from interfering activity (vide infra). The measured activity was used in product yield calculations and as a monitor of the dose and dose rate to which the sample was exposed (vide infra).

The columns used to effect the product separations were fabricated from 8 mm Pyrex tubing and ranged in length from 6 to 35 feet. The solid supports were obtained from the F & M Scientific Division of Hewlett-Packard and from Analabs, Inc. The materials used for the solid-gas phase chromatography were obtained from Matheson Coleman & Bell and the Fisher Scientific Company. The liquid phases were purchased from F & M Scientific Division of Hewlett-Packard, K & K Laboratories, Inc., Eastman Organic Chemicals, and Carbide and Carbon Chemicals Corporation. The columns were prepared by dissolving a known amount of the liquid phase in a suitable solvent, mixing it with an appropriate amount of solid support, and evaporating the solvent using a flash evaporator. A listing of the columns used in this study along with the source of the preparation materials appears in the Appendix.

The early part of this study was performed using less sophisticated chromatographic and detection equipment. A description of the basic equipment has been presented by De Vries and Voigt (123). This equipment was extensively modified for use in this investigation.

The major modifications included a radical redesign of the sample injection, detection and data read-out systems. The data read-out system is identical to that outlined in a recent thesis by Matkovich (124). A variety of detectors were employed. Initially the detection system was similar to that outlined by De Vries and Voigt (123) and was considered satisfactory for gaseous product analysis. The higher boiling products required a heated detection system and use was made of a flow-through proportional counter. The proportional counter was found to be much more efficient than the NaI(Tl) crystal in the detection of the carbon-11 activity but suffered from fluctuations in sensitivity. The experimental problems encountered in the attempt to stabilize the proportional counter soon outweighed the efficiency advantage and use of the system was discontinued. The latter part of the work with the older chromatograph was performed using the 3 inch NaI(Tl) crystal outlined previously. The results obtained in all systems were identical and indicated that the formula developed by Wolfgang and Rowland (125) to correlate the observed counts under an elution peak to the activity in the peak for a flow proportional counter was also applicable in the NaI(Tl) flow systems.

Calculation of Product Yields

In a typical experiment, the sample-containing bulblet was irradiated for a predetermined time and returned to the laboratory for product analysis. After a period of time sufficient to allow a major fraction of the interfering activity to decay, the activity in the sample blub was monitored. The product activity was then

analyzed using the gas chromatograph to perform the product separations. The chromatograph effluent was monitored by the flow detection system discussed previously. The output of the detection system was recorded simultaneously on both a strip chart and a digital recorder. Each radioactive product produces a nearly Gaussian peak on the strip chart recorder as it passes through the detection system. The effluent is then vented into a hood via a soap-film flow meter. The flow rate is normally monitored during the peak elution.

An expression relating the activity in the peak to the total number of counts observed under a peak has been given by Wolfgang and Rowland (125),

$$A = (C-b) (f.r.)/V$$

where

A = activity in peak (counts/min),

C = total counts observed under peak,

b = background counts under peak,

f.r. = flow rate (ml/min), and

V = sensitive volume of counting chamber (ml).

This expression was developed for a flow proportional counter but has been found to be applicable for the detection systems used in this investigation.

The yield of any product is equal to the product's activity divided by the total sample activity and may be expressed by the following relationship.

$$\text{Yield (\%)} = \frac{(C-b)(e^{-\lambda_1 t_p})(f.r.)}{(M.A.)(e^{-\lambda_1 t_m})(c.f.)} \quad (1)$$

where

λ_1 = decay constant for carbon-11,

t_p = time after bombardment that product activity is measured,

M.A. = activity of sample as measured by the monitor counter,

t_m = time after bombardment that sample activity is monitored, and

c.f. = calibration factor relating the two detection systems.

The calibration factor incorporates the proportionality constants relating to the efficiency of each detection system and also takes into account the sensitive volume of the flow system. The determination of the calibration factor is the subject of a later section.

Interpretation and Representation of Data

The identification of the products in the alcohol systems proved to be a significant part of this investigation. Since only about 10^{-16} mole of any one product is produced during an irradiation, identification could only be achieved by comparison of retention times during carrier addition experiments. Most of the products were verified on two or more columns. A small number of the higher boiling products in both methanol and ethanol were only identified by retention on one column. These identifications seemed reasonable in the light of the expected chemistry. Only those unknown products whose yields were determined and are useful in experimental data interpretation are reported.

In the analysis of the data, the product yields were plotted as a function of dose. The results which appeared to be linear were analyzed with the computer by the method of least squares. For those distributions for which a linear line could not be justified, a curve through the data points was drawn by visual inspection.

In most cases the data are reported to three significant figures and the reported error represents the standard deviation of an individual determination. In the few cases where the curves were not linear and had to be extrapolated to the dose region reported, the yield was reported to the nearest tenth of a percent and an approximation sign placed in front of the value. In other cases where data were insufficient to justify calculating a standard deviation of the value was just reported to the nearest tenth of a percent without indicating the error.

A summary of the experimental results will be presented in the Results and Discussion Section. The graphical representation of the product dose dependencies are not presented because of their limited value and voluminous nature.

RESULTS AND DISCUSSION

Absolute Yield Calibration

The knowledge of the absolute radiochemical product yield is of value when interpreting experimental data. It allows the comparison of data between laboratories and may be of aid in the future development of a quantitative mechanistic theory of recoil carbon chemistry. It is also useful in accessing the magnitude and significance of the unobserved or unidentified products, the knowledge of which may be very helpful in the analysis of experimental results.

If the absolute radiochemical yield of any one product is known for one compound, the calibration factor of the detection system can be calculated by using a rearranged form of Equation 1.

$$\text{c.f.} = \frac{(\text{C-b})(e^{\lambda_1 t_p})(\text{f.r.})}{(\text{M.A.})(e^{\lambda_1 t_m})(\text{Yield } (\%))}$$

Knowledge of the calibration factor allows the calculation of the absolute yields of products in other systems.

In this laboratory, a number of attempts have been made in recent years to determine the calibration factor and the corresponding absolute product yields.

Clark (126) has previously determined an absolute radiochemical yield of 17.8% for acetylene in methylcyclopentane. In a later study, Jewett (85) reported a value of 16.4% for the same determination. He also determined a value of 21.7% for the acetylene yield in isopentane, a yield which appeared to be independent of dose. This value was used for calibrating the detection system in early experiments of the current work.

As further experimental data became available, it was apparent that this factor was not correct for the system at present, since when it was used the total product yield in the methanol system was over 100%. Also evidence was obtained that the acetylene yield was dependent in dose. Hence, it was decided to redetermine the calibration factor and to determine the acetylene yield dose dependence in isopentane.

A diagram of the essential features of the experimental equipment is presented in Figure 5.

The general outline of the experiment follows. A sample bulblet filled with isopentane was irradiated at the synchrotron. After the usual waiting period, the carbon-11 activity in the sample bulb was monitored. The sample was introduced into the sample breaker, heated above its boiling point, and broken. The vaporized sample was swept into the CuO combustion furnace where it was burned to carbon dioxide and water. The carbon dioxide passed through the chromatograph column to the flow detection system where its activity was measured. The activity in the elution peak was recorded in 30 second intervals and the flow rate was measured throughout the experiment.

The expansion chamber and packed chromatograph column were used only to allow the system sufficient time to equilibrate before the active carbon dioxide reached the counting tube. Unless this was done, the pressure surge during the initial combustion was of such a magnitude that extreme flow rate fluctuations occurred during the early periods of carbon dioxide elution.

To verify that complete combustion had occurred, weighed inactive samples of the n-octane were combusted in the same apparatus. After

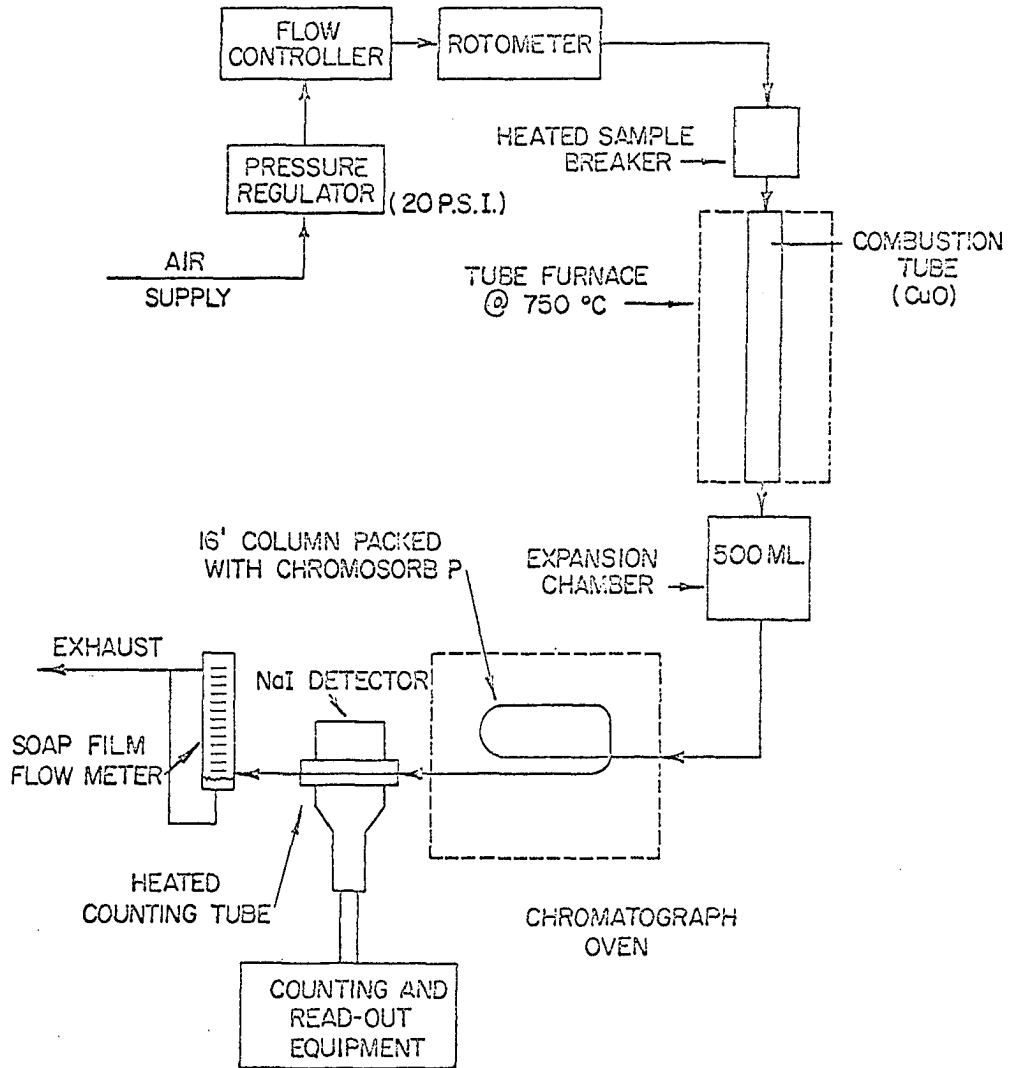


Figure 5. Experimental arrangement for the combustion determination of the equipment calibration factor in absolute product yield studies

removing the water, the carbon dioxide produced was absorbed on Ascarite and complete recovery was obtained.

The resultant radiochromatogram consisted of a broad distribution with an extended tail. To obtain the calibration factor the peak was broken up into 30 second intervals and integrated by the computer using the following equation,

$$\text{c.f.} = \frac{\sum_{i=1}^n (C_i - b_i)(e^{-\lambda_1 t_i})(f.r.)_i}{(\text{M.A.})(e^{-\lambda_1 t_m})(100)}$$

The experimental results appear in Table 2.

Table 2. Results of combustion determination of equipment calibration factor

Sample Designation	Calibration Factor
CB2	2.760
CB3	2.764
CB4	2.783
CB6	2.773
CB7	2.763
CB8	2.807
	Average 2.775 $\sigma = \pm 0.018$

The calibration factor is a function of the individual detection system and requires redetermination if any modification of the equipment occurs. Because of the extensive equipment setup required to do this type of experiment, it became necessary to use the measured calibration factor immediately to determine the absolute product yields for a number of the products in isopentane. By doing so, the yield values could be used as a secondary standard in the redetermination of the calibration factor.

A summary of the results of these experiments appears in Table 3.

Table 3. Yields of radioactive products as a result of the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in isopentane, unscavenged dose dependence

Product	Yield, Percent	
	a	b
CH_4	5.30 ± 0.3	5.61 ± 0.3
C_2H_6	1.45 ± 0.17	1.70 ± 0.17
C_2H_4	10.1 ± 0.2	10.1 ± 0.4
C_2H_2	17.3 ± 0.2	16.4 ± 0.4
Total	34.2 ± 0.2	33.8 ± 0.4

Dose (eV/molecule) a - 0.020, b - 0.080

Since this system has been previously studied by Jewett (85), no interpretation of the mechanisms for product formation will be presented. The only important new result is the definite evidence for

dose dependence of the acetylene yield.

Dose and Dose Rate Calculations

In integrated dose rate at the probe position in the electron synchrotron has been estimated previously (127) as approximately 10^{19} eV/g min from the observed disappearance of iodine in a 2,2-dimethylbutane solution. Clark and Voigt (93) determined the radiation dose rate by two methods, Fricke and cobalt glass dosimetry, and obtained similar results. They reported a value of approximately 3×10^{19} eV/g min for a beam of "average" intensity. These determinations were made at an electron energy of 47 MeV. Since in this work an electron energy of 70 MeV was used and the dose values reported by previous investigators (93,127) could not be correlated to the dose monitor used in this study, the integrated dose rate was redetermined and the measured values correlated to the dose rate monitor, \bar{N}_T/t_b .

The use of the higher energy beam resulted in a substantial increase in the number of photons of sufficient energy to cause the reaction, allowing a shorter bombardment period for the production of similar quantities of carbon-11. A disadvantage is that the dose rate may also increase as a result of the increased efficiency of bremsstrahlung production at the higher electron energy. Clark and Voigt (93) stated that their experimental results at 47 and 70 MeV were identical. This may indicate that the dose rate per carbon-11 produced does not change substantially in the region from 47-70 MeV or that the systems investigated were relatively insensitive to dose or dose rate changes.

The number of radioactive carbon-11 nuclei, N_1 , at any time, t , after the end of an irradiation can be expressed by the following relationship

$$N_1 = \frac{P_1}{\lambda_1} (1 - e^{-\lambda_1 t_b}) e^{-\lambda_1 t} \quad (2)$$

where P_1 = rate of production of carbon-11 nuclei by the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction,
 λ_1 = decay constant of carbon-11, and
 t_b = duration of bombardment.

The dose delivered to the sample during such a bombardment is proportional to the total number of nuclei transformed.

$$\text{Dose} = kP_1 t_b \quad (3)$$

By substitution of Equation 2 into Equation 3, the dose may be expressed by

$$\text{Dose} = \frac{kN_1 \lambda_1 e^{\lambda_1 t} t_b}{(1 - e^{-\lambda_1 t_b})}$$

The carbon-11 activity in the sample, A_1 , is given by $A_1 = k' \lambda_1 N_1$.

The dose may be expressed as

$$\text{Dose} = \frac{kA_1 e^{\lambda_1 t} t_b}{k'(1 - e^{-\lambda_1 t_b})}$$

In the various systems investigated, the carbon atom densities, ρ_c , in carbon atoms per cm^3 , varied from 1.49 to 2.46×10^{22} . Since the observed activity is directly dependent upon the number of nuclei in the beam path, the proportionality constant, k/k' , depends on the system and can be replaced by k''/ρ_c for a more universal expression.

The dose may then be expressed as;

$$\text{Dose} = k'' \bar{N}_T \quad (4)$$

where \bar{N}_T is defined by

$$\bar{N}_T = \frac{A_1 e^{\lambda_1 t_b}}{(1 - e^{-\lambda_1 t_b})} \times 10^{17} \rho_c \quad (5)$$

and the dose rate by

$$\text{Dose Rate} = k'' (\bar{N}_T / t_b)$$

The previously developed arguments are based on the assumption that the activity observed is a result of a single nuclear reaction, $^{12}\text{C}(\gamma, n)^{11}\text{C}$. In the systems studied, this is not realized since other nuclear reactions contribute to the observed sample activity. A brief study was undertaken to estimate the significance of their contribution. The reactions that contribute are two photonuclear reactions on oxygen-16, $^{16}\text{O}(\gamma, n)^{15}\text{O}$ and $^{16}\text{O}(\gamma, t)^{13}\text{N}$, which produce interfering nuclides with half lives of 2.07 and 9.96 minutes, respectively, and the $^{16}\text{O}(\gamma, \alpha n)^{11}\text{C}$ reaction which adds a small amount to the ^{11}C produced from carbon. Like ^{11}C , ^{15}O , and ^{13}N are positron emitters. Since the activity monitor is based upon the positron activity of the sample, discrimination by the detection system is impossible.

If we consider first the activity induced in the liquid sample, the error encountered by using the observed sample activity as a dose monitor may be evaluated. The relationship of the total sample activity, A_T , to that produced by the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction, A_1 , may be expressed by the following equation.

$$A_T/A_1 = 1.00 + \frac{f_o}{f_c} \left[\frac{P_1'}{P_1} + \frac{P_2(1-e^{-\lambda_2 t_b})e^{-\lambda_2 t}}{P_1(1-e^{-\lambda_1 t_b})e^{-\lambda_1 t}} + \frac{P_3(1-e^{-\lambda_3 t_b})e^{-\lambda_3 t}}{P_1(1-e^{-\lambda_1 t_b})e^{-\lambda_1 t}} \right]$$

where P_1' is the production rate of the reaction $^{16}_0(\gamma, \alpha n)^{11}_6\text{C}$, P_2 and λ_2 and P_3 and λ_3 are the production rates and decay constants of $^{15}_6\text{C}$ and $^{13}_7\text{N}$, respectively, and f_o/f_c is the atomic ratio of oxygen to carbon in the irradiated compound.

The values for the ratios of production of the various isotopes were determined by analysis of the decay spectra of synchrotron irradiated H_2O , H_3BO_3 , Li_2CO_3 and $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CO}_2\text{H}$. SMASH, a decay resolution computer program, developed by Korthoven and Carlson (128) was used to evaluate the relative contributions of the induced activities. From these results, the production ratios were determined to be; $P_1'/P_1 = 0.026 \pm 0.006$, $P_2/P_1 = 1.0 \pm 0.2$, and $P_3/P_1 = 0.013 \pm 0.003$.

Calculated values for the ratio A_T/A_1 for samples irradiated for 4.00 minutes and counted 23.5 minutes after bombardment are given in Table 4. These data indicate that the induced activity from the photonuclear reactions on oxygen-16 results in a relatively minor contribution to the total activity, the error being most significant for methanol and methyl formate and least significant for diethyl ether.

The error resulting from the activity induced by photonuclear reactions in the glass of the sample bulb are not easy to evaluate.

Table 4. A_T/A_1 values^a

System	A_T/A_1
Methanol, Methyl Formate	1.042
Ethanol	1.021
1- and 2-Propanol, Acetone	1.014
Methyl Acetate	1.028
Diethyl Ether	1.010

^a4.0 minute bombardment, activity monitored 23.5 minutes after end of bombardment.

Although the attempt was made to fabricate the bulbs with identical shapes, variations in diameter, concentricity, wall thickness, and bottom flattening did occur and as a result, the proportion of the activity that was contributed by the glass could vary considerably between runs. From computer analysis of the decay of the activity produced during a four minute bombardment of isopentane, the activity in the glass was estimated to contribute about 2% to the total activity when measured at the usual monitoring time. From this result, the errors in the other systems were estimated to range from 2-4% with the maximum error again occurring in methanol where the carbon atom density is the least. From these results, it was concluded that the total activity induced in the sample could be used as a dose and dose rate monitor.

The evaluation of the proportionality constant, k'' , in Equation 4 was accomplished using cobalt glass dosimetry which makes use of the

darkening of glass by radiation. Kreidl and Blair (129-131) described a form of cobalt glass useful in high-level dosimetry. This glass (F-0620) is available commercially in the form of 15 x 6 mm rectangular plates, 1.5 mm in thickness, from Bausch and Lomb Optical Company. It is useful over a range in dose from 5×10^3 to 10^6 rads and in dose rate from 5×10^3 to 5×10^{10} rads/min (132). The dose range can be extended to 10^7 rads with reduced precision but no information is available on extending the upper limit of the range in dose rate. Samples of the cobalt glass were exposed for varying times to the cobalt-60 source of the I.S.U. Veterinary Medical Research Institute and the subsequent optical density changes were measured at 500 m μ with a Beckman Model DU Spectrophotometer. The changes in optical density were plotted versus the dose as determined by the Fricke dosimeter.¹ A dose range of 8×10^4 to 2×10^6 rads was covered and the shape of the resultant curve was in agreement with published results (130,131). Sample bulbs filled with methanol, ethanol, methyl formate, isopentane and benzene were irradiated simultaneously with samples of cobalt glass at the synchrotron. The dose was determined from the change in optical density of the glass and a value for \bar{N}_T was calculated from the observed ^{11}C activity (Equation 5). The results of these experiments appear in Table 5.

In the methyl formate and alcohol systems, the contribution to the total activity produced by the photonuclear reactions on oxygen is

¹Dr. Joseph Picken, Jr., Veterinary Medical Research Institute, Iowa State University of Science and Technology, Ames, Iowa. Calibration of cobalt-60 source by Fricke dosimetry. Private Communication. 1967.

Table 5. Results of cobalt glass dosimetry: relation of dose to \bar{N}_T

System	Dose / \bar{N}_T (rads)	Number of Determinations
Methanol	$7.18 \pm 0.46 \times 10^5$	7
Ethanol	$6.89 \pm 0.38 \times 10^5$	6
Iospentane	$8.36 \pm 0.13 \times 10^5$	3
Benzene	$8.60 \pm 0.34 \times 10^5$	3
Methyl Formate	7.46×10^5	1

reflected in the lower values of the Dose / \bar{N}_T ratio. Since the precise evaluation of these sources of errors is difficult, as outlined earlier, and since the precision of the measurements on these systems is believed to be much better than the absolute accuracy, the average of this ratio for all systems is probably the best relation available. Hence, in all of the calculations involving the effect of dose on the yields, the value $(7.70 \pm 0.75) \times 10^5$ rads / \bar{N}_T was used for k'' . Equation 4 then becomes

$$\text{Dose (eV/gm)} = (4.8 \pm 0.5) \times 10^{19} \bar{N}_T$$

For a five minute irradiation of methanol with a beam of average intensity, representative values for \bar{N}_T and dose (in eV/molecule) are 5.0 and 1.3×10^{-2} , respectively.

The instantaneous dose rate in these systems, is considerably higher. The electron synchrotron is a pulsed machine with a cycle time of 1.7×10^{-2} seconds and pulse duration time of approximately 4×10^{-8} seconds. The carbon-11 is produced only during the pulse and as a consequence finds itself in a radiation field considerably more intense

than would be indicated by the integrated dose and dose rate values. De Vries and Voigt (123) estimated the thermalization time for a 1.0 MeV carbon-11 at about 10^{-9} seconds. Thus it is very likely that all of the carbon-11 produced in one burst has reacted before the next burst occurs.

Very little information is available concerning the time dependence of the radical concentration during and after the electron burst.

Sutton and Rotblat (133) estimated the minimum lifetime of radicals produced during such a burst at 5×10^{-7} second with an upper lifetime limit of 2.5×10^{-3} second. It is then very possible that the radical concentration remains relatively high during the thermalization time for the carbon-11 but does drop to zero before the next burst occurs.

In any study of the product yield dose rate or dose dependence, one would ideally like to fix the total dose delivered to the sample and vary the dose rate or at constant dose rate vary the total dose. The electron synchrotron used in this study has neither capability at this time. The approach has been to study the dose dependence of the product yields while keeping the dose rate as constant as possible. The value of the dose rate is usually relatively constant during any one bombardment but may vary between bombardments. Although it is apparent from the analysis of the data that the total dose is the dominant factor, the dose rate dependence may be somewhat reflected in the experimental scatter of the dose dependent products.

Production of Atomic Carbon

Free atoms of ^{11}C are produced by the nuclear reaction, $^{12}\text{C}(\gamma, n)^{11}\text{C}$, using the bremsstrahlung beam from a General Electric Model M 70 MeV

electron synchrotron operating at a maximum energy of 70 MeV. The sample bulb is mounted at the end of a specially constructed Synthane sample holder and positioned within the acceleration chamber of the synchrotron. The probe arrangement and sample positioning have been illustrated by De Vries and Voigt (123). The irradiation periods ranged from two to twenty minutes, their duration depending upon the operational characteristics of the synchrotron and the requirements of the experiment. The instrumental techniques employed for these irradiations have been discussed by Hammer and Bureau (134-136).

Using the techniques of least structure analysis of the yield curves, Cook, et al. (137) have measured the photoneutron cross section for the production of carbon-11 from the reaction threshold, 18.7 MeV, to 65 MeV. The giant resonance was resolved into a predominantly triplet structure with peaks at 22.1, 22.75, and 23.6 MeV.

Neglecting the momentum brought into the system by the incoming photon, the recoil energy imparted to the carbon atom as a result of the nuclear reaction can be calculated from the following expression:

$$E_r = (E_\gamma + Q) \frac{m_n}{m_{^{11}\text{C}} + m_n}$$

where

- E_r = ^{11}C recoil energy,
- E_γ = energy of photon,
- Q = energy of reaction (eg. -18.7 MeV),
- m_n = mass of neutron and
- $m_{^{11}\text{C}}$ = mass of ^{11}C .

The absorption of a 22.1 MeV photon would impart a recoil energy of 0.28 MeV to the carbon-11. The absorption of higher energy photons

would correspondingly produce recoiling carbon of higher energy. Since the photoneutron cross section decreases rapidly above 28 MeV as does the intensity of the bremsstrahlung beam, the fraction of carbon-11 atoms produced with recoil energies in excess of 1 MeV is small. The average recoil energy will be on the order of 0.5 MeV.

Energy Loss Mechanisms - Charge and Spin State Upon Reaction

The impulse imparted to the carbon atom as a result of the nuclear reaction is of such a large magnitude and short duration when compared with bond energies and vibrational frequencies that the atom is ejected like a projectile from the vicinity of the parent molecule. This atom is initially charged but rapidly achieves electronic equilibrium with the medium by successive charge transfer collisions. As a general rule, those electrons whose Bohr orbital velocities are less than the velocity of the recoiling atom are expected to be lost. Since the recoil velocity of a 0.5 MeV carbon-11 atom is approximately 3×10^8 cm/sec and the Bohr orbital velocity of the least bound electron as calculated from the first ionization potential is about 2×10^8 cm/sec, it is expected that this electron will be lost and that the recoiling carbon atom will be at least singly charged. Harvey (138) has presented an approximate formula for calculating the charge of a recoiling atom. The value obtained from this calculation is in agreement with that predicted above.

For velocities greater than about 2×10^8 cm/sec the recoiling ion loses energy mainly by electronic excitation and ionization of the stopping medium. As the velocity decreases to the order of the

velocity of the valence electrons of the stopping material, the mechanism of energy loss essentially becomes one of elastic and inelastic collisions (i.e. without causing ionization) between the recoil ion or atom and the atoms of the stopping material.

The range of a recoiling ion is very roughly proportional to its initial energy. De Vries and Voigt (123) using equations developed by Bohr (139) have calculated a range of approximately 8×10^{-4} cm for a 1.0 MeV carbon-11 atom in a number of condensed phase systems.

Definite information concerning the final charge or electronic excitation of the recoil species when it reaches the region of chemical reactivity (<50 eV) is lacking. Atomic carbon has a 3P ground state and two low lying electronic excited states, 1D and 1S , which are 1.3 and 2.7 eV, respectively, above the ground state (140). The application of Massey's near-adiabatic hypothesis (141) to obtain information concerning the final charge and electronic state of the recoil carbon has lead Wolfgang (34) and Mesich (84) to predict that the carbon atom reaches the region of chemical interest as a neutral species in one of its lower lying electronic states (3P , 1D , or 1S). A similar calculation performed upon the systems under current investigation confirm their findings but as of the present time there appears to be no definite chemical evidence to either contradict or support these predictions.

Introduction to Experimental Results

In interpreting the recoil carbon data, one must consider how the accompanying radiation field affects the final observed product

distribution. Radiolysis of the target material will produce radicals and molecular species that may be reactive towards the recoil products or their thermal radical intermediates. A number of experimental techniques are available that may be useful in assessing the significance of these effects.

One of these techniques involves the study of the product distribution as a function of total dose. The establishing of relationships between dose dependent products may be useful in the interpretation of reaction mechanisms.

The other technique is the addition of radical scavengers to the system. Two commonly used radical scavengers in liquid systems are iodine and DPPH. If the concentration of the scavenger is low, it will not interfere with hot reaction processes but will scavenge the thermal radical intermediates. The scavenger also has the effect of reducing the concentration of radiation produced radicals and as a consequence, radiation modification of the products is substantially reduced.

Considerable care must be taken in the interpretation of the effects of radical scavengers. Their use will generally give information on which products are a result of thermal processes and may also help to indicate those products resulting from hot atom processes. Different scavengers may give different results under identical radiation conditions since they may vary considerably in their effectiveness to react with particular radicals. In some very favorable cases this specificity can be exploited. To do this requires some knowledge of the relative rate constants of radical-scavenger reactions and this knowledge is not usually available. Another difficulty arises

if the products resulting from radical scavenging are themselves reactive towards the solvent. In this case, a number of unexpected products may be observed.

Another very important tool in the understanding of the radiation effects is the knowledge of the radiation chemistry of the system studied. The writer is very fortunate in this respect since in recent years a considerable amount of literature has been published on this subject. This knowledge will generally yield a reasonably accurate picture of the expected reactive radical or ion distribution which may be useful in the understanding of some of the reaction sequences.

In this investigation, a study has been made of the distribution of all observable products in methanol and ethanol as a function of total dose in both the scavenged and unscavenged systems. In methanol, both iodine and DPPH were used as radical scavengers although only a limited amount of data was obtained in the DPPH scavenged system. A study was also performed on the effects of the iodine scavenger concentration on the yields of C_1 and C_2 products in diethyl ether. A limited amount of similar data has also been obtained for methanol.

The yields of the fragmentation products and the dependence of these yields on dose and scavenger were also determined in the systems; 1-propanol, 2-propanol, acetone, methyl acetate, methyl formate and diethyl ether.

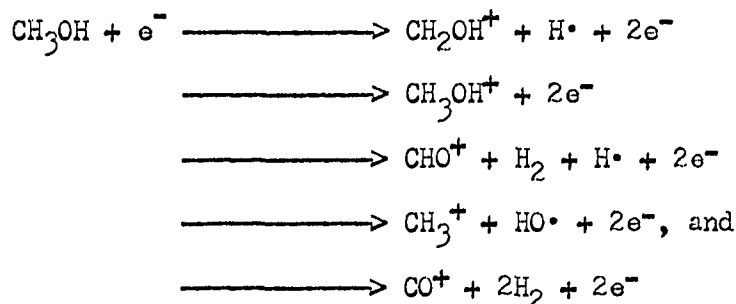
Recoil Chemistry of Atomic Carbon in Methanol

Radiation chemistry of methanol

As a background to the interpretation of the methanol-carbon-11 recoil data, a brief description of the radiation chemistry of this

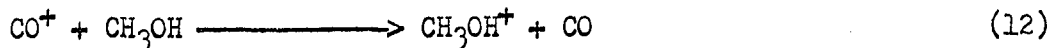
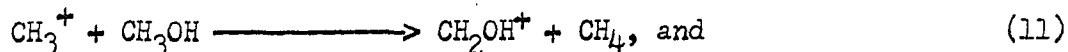
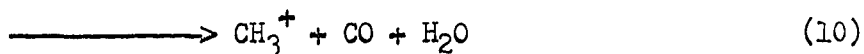
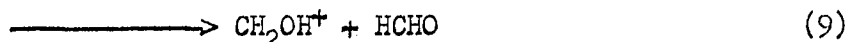
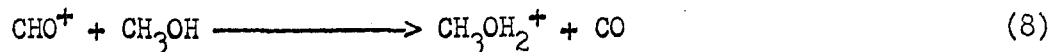
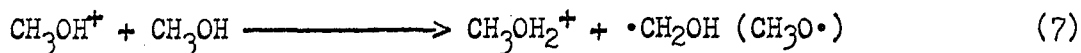
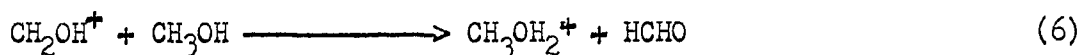
system will be presented.

An indication of the ions most likely to be of concern can be obtained from the mass spectrum of electron bombarded methanol vapor (142). The most important ions and their relative abundances are: CH_2OH^+ (100), CH_3OH^+ (68), CHO^+ (52), CH_3^+ (23), and CO^+ (15). These are produced by the following reactions:



In the liquid, the relative yields of CH_2OH^+ and CH_3OH^+ are expected to be higher because the solvent cage effect will reduce the loss of H_2 from CH_2OH^+ and the losses of $\text{HO}\cdot$ and 2H_2 from CH_3OH^+ (143).

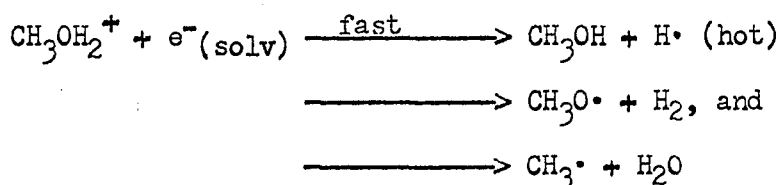
These ions can participate in ion-molecule reactions, the most probable being (143);



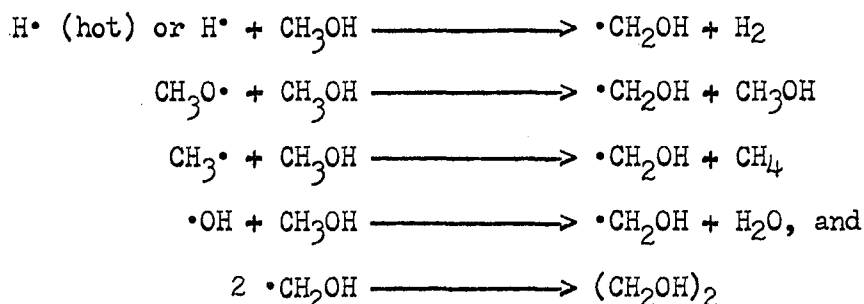
Theard and Burton (144) studied reaction 7 by accelerating partially deuterated methanol molecules in a mass spectrometer. Their results indicated that in the condensed system $\text{CH}_3\text{O}\cdot$ should be the

avored product. Evidence for the production of the methoxy radical has also been obtained by Ekstrom and Garnett (145) in their study of the radiolysis of a binary mixture of methanol and benzene. Wilmenius and Lindholm (143) found that reactions 8, 9, and 10 occurred with about equal probability.

The CH_3OH_2^+ can be neutralized by reaction with solvated electrons. The expected reactions are (117);

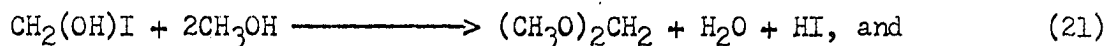
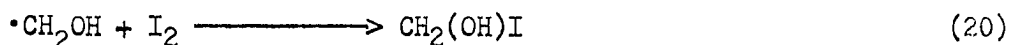
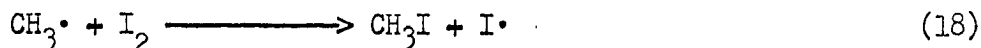
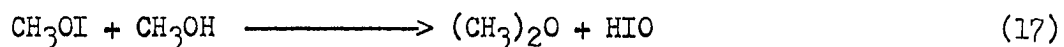
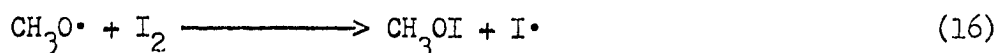
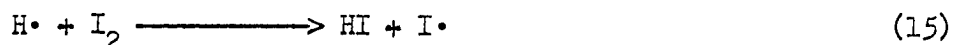
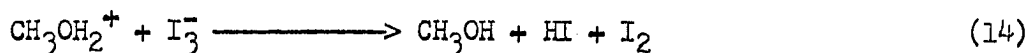
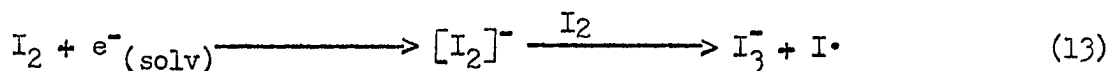


The overall results of these reactions are the production of radicals and molecular products. The radicals may then undergo a number of radical-molecule reactions, the most probable ones being:



In the iodine scavenged system, this reaction sequence is substantially modified. Meshitsuka and Burton (146) have studied the radiolysis of the iodine scavenged methanol system. The changes in the radiolysis product yields were attributed to the scavenging of both radicals and solvated electrons by iodine. Thomas, et al. (147) have recently determined a rate constant of $5 \times 10^{10} \text{ M}^{-1}\text{sec}^{-1}$ for the reaction of I_2 with a hydrated electron. The rate constant in methanol is not expected to be significantly different. The I_2

will be more than competitive with CH_3OH_2^+ for the solvated electron because of its much higher concentration ($\sim 10^{-3}\text{M}$) and the very high rate constant for the reaction. The ion-molecule reactions (Equations 6-12) should not be significantly different in the scavenged systems since most of these reactions occur rapidly within the spur.



Iodine atoms may also react directly with the radicals. The decomposition of the transient species $[\text{I}_2]^-$ to I_3^- and $\text{I}\cdot$ is only speculative and is based upon the observation of Grossweiner and Matheson (148) of the reaction, $2\text{I}_2^- \longrightarrow \text{I}_3^- + \text{I}^-$.

From this brief introduction, it is evident that in the unscavenged system the radicals $\cdot\text{CH}_2\text{OH}$, $\cdot\text{H}$, and $e^-(\text{solv})$ may play a role in the observed recoil carbon chemistry. The other radicals and the CH_3OH_2^+ molecular ion will only have a minor effect. Experimental support for this conclusion will be presented.

In the iodine scavenged methanol system, the contributions of these radicals and molecular ions are substantially reduced due to the

reactions represented by Equations 13-22. The iodine also reacts with the thermal radicals containing carbon-11 to produce iodides and intermediates which undergo further reactions with the solvent. (e.g. Equations 17 and 21).

No information is available concerning the effect of DPPH on methanol radiolysis although some inferences can be made by the analysis of the carbon-11 recoil data.

Recoil carbon chemistry in methanol

From Table 6, it can be seen that the recoil carbon-11 atom stabilizes in a variety of products and that the yields of some of these products are dose dependent. This product spectrum can be reasonably well explained on the basis of the insertion reactions of C, CH, and CH₂ and the reactions of the products or radical intermediates with the radiation produced radicals or added scavengers. In attempting to account for these data a large number of possible reaction paths of carbon atoms with methanol were considered. Most of these proved to be inconsistent with some of the data and were discarded. This discussion will be restricted to those mechanisms that appear to be in reasonable accord with these results and those of other related studies. A brief outline of these mechanisms is presented in Figures 6-8. These figures are not intended to represent all the possible reaction pathways, but only to serve as a general guideline for the discussion.

Carbon atom reactions The initial insertion of the recoil carbon-11 atom into the C-H and O-H bonds of methanol will produce

Table 6. Yields of radioactive products as a result of the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in methanol

Product	Yields, Percent ^a			
	Unscavenged		$X_{I_2} = 1.01 \times 10^{-3}$	
	a	b	a	b
Carbon Monoxide	15.6 ± 1.9	9.5 ± 1.6	24.2 ± 0.3	24.9 ± 0.3
Carbon Dioxide	-	-	0.21 ± 0.03	0.13 ± 0.03
Methane	3.97 ± 0.2	3.97 ± 0.2	2.47 ± 0.09	2.66 ± 0.09
Ethane	0.91 ± 0.15	1.07 ± 0.15	0.60 ± 0.11	0.80 ± 0.11
Ethylene	9.84 ± 0.4	9.89 ± 0.4	8.44 ± 0.3	9.07 ± 0.3
Acetylene	14.9 ± 0.6	13.8 ± 0.9	15.4 ± 0.7	16.1 ± 0.7
Propylene	0.41 ± 0.03	0.27 ± 0.03	0.41 ± 0.05	0.25 ± 0.05
Dimethyl Ether	4.64 ± 0.14	4.51 ± 0.2	4.08 ± 0.2	4.12 ± 0.2
Methyl Ethyl Ether	0.45 ± 0.03	0.50 ± 0.03	0.37 ± 0.07	0.41 ± 0.07
Methyl Vinyl Ether	0.39 ± 0.04	0.30 ± 0.04	0.42 ± 0.3	0.47 ± 0.3
Dimethoxymethane	4.53 ± 0.2	4.08 ± 0.2	9.5 ± 0.4	10.6 ± 0.2
1,1-Dimethoxyethane	-	-	3.54 ± 0.8	2.53 ± 0.8
Acetaldehyde	~ 3.9	0.85 ± 0.2	-	t
Methyl Formate	t	t	0.65 ± 0.09	0.60 ± 0.09
Methyl Acetate	3.57 ± 0.13	3.05 ± 0.13	-	-
Ethanol	8.29 ± 0.6	8.88 ± 0.6	4.97 ± 0.3	5.66 ± 0.3
1-Propanol	1.47 ± 0.2	1.78 ± 0.2	0.39 ± 0.09	0.33 ± 0.09
Allyl Alcohol	1.87 ± 0.2	1.76 ± 0.2	1.05 ± 0.13	1.21 ± 0.13

^aYield in percent of total ^{11}C produced.

Table 6. (Continued)

Product	Yields, Percent ^a		$X_{I_2} = 1.01 \times 10^{-3}$	
	Unscavenged		a	b
	a	b	a	b
2-Methoxyethanol	3.68±0.4	3.28±0.4	0.99±0.13	1.33±0.13
Ethanediol	0.95±0.2	1.11±0.2	-	-
1,2-Propanediol	5.73±0.05	8.50±1.7	-	-
1,3-Propanediol	1.14±0.4	1.32±0.4	-	-
Methyl Iodide	-	-	3.38±0.2	3.72±0.2
Vinyl Iodide	-	-	2.10±0.09	2.67±0.09
Unknown	~ 4.0	1.15±0.3	-	-
Unknown	-	-	9.3	5.3
	90.2	79.6	92.5	92.8

Dose (eV/molecule) a-0.009, b-0.036

the excited adducts B and C (see Figure 6). These adducts may fragment or may collisionally deactivate to the carbene. Rearrangement processes are not excluded and will be discussed later.

An indication of the expected chemistry of these carbenes may be obtained from the recent studies of the reactions of dimethoxycarbene by Hoffmann and Haeuser (149). In this study they observed that in a methanol solution, dimethoxycarbene reacted to form methyl orthoformate.

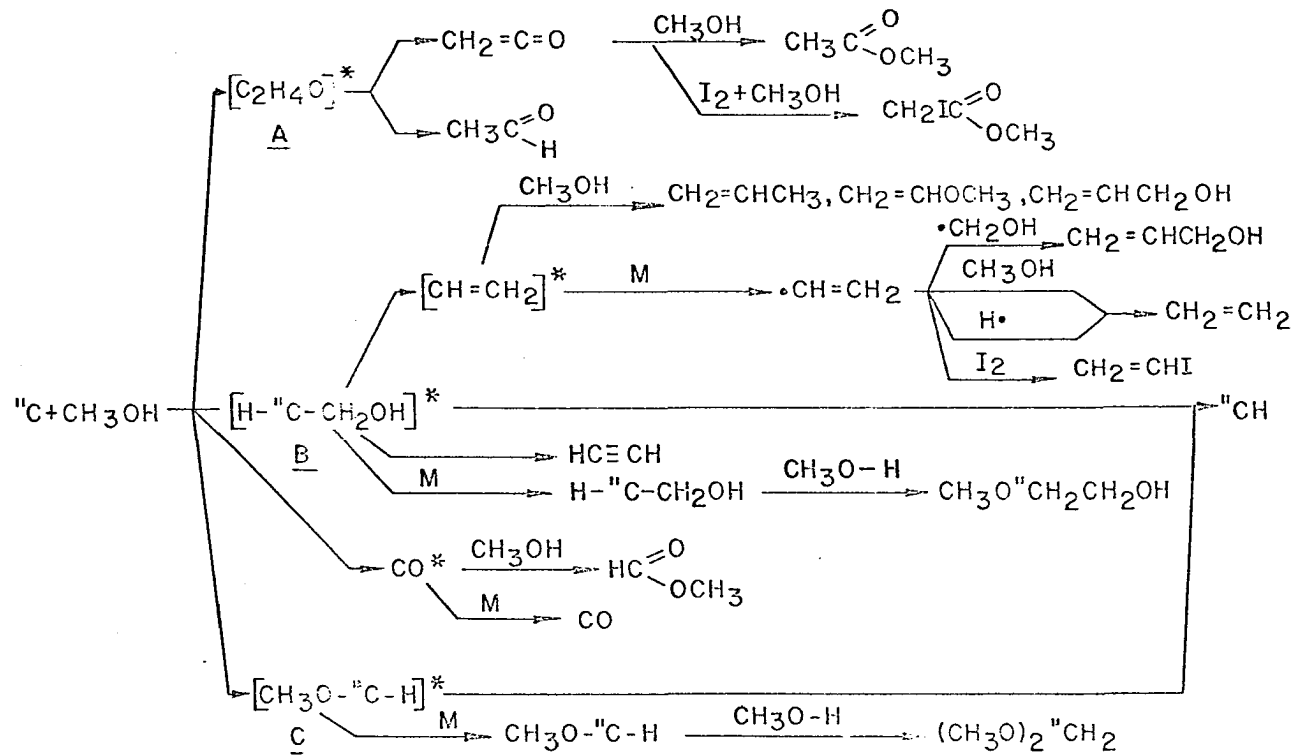


Figure 6. Chemistry of recoil carbon in methanol, reactions of ^{11}C .

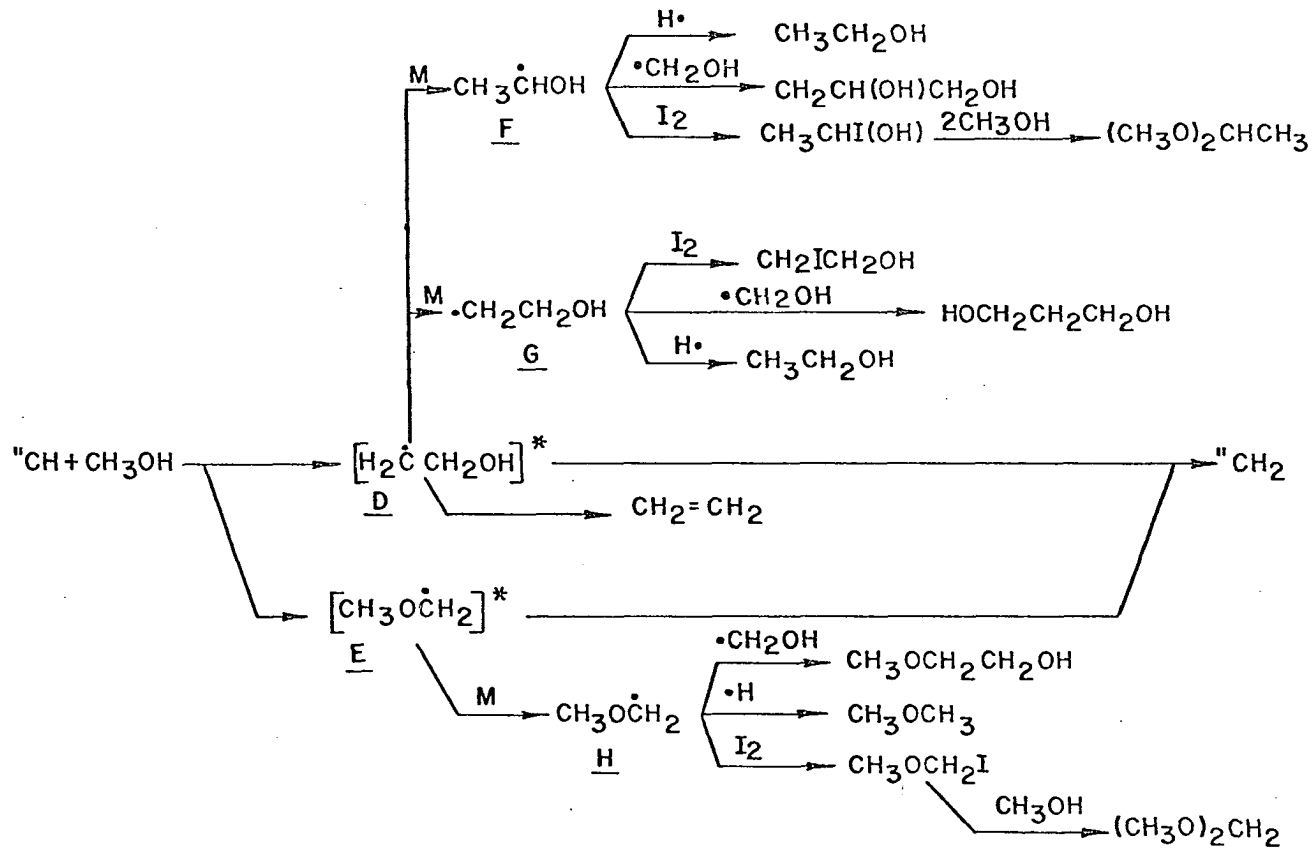


Figure 7. Chemistry of recoil carbon in methanol, reactions of ${}^{11}\text{CH}$

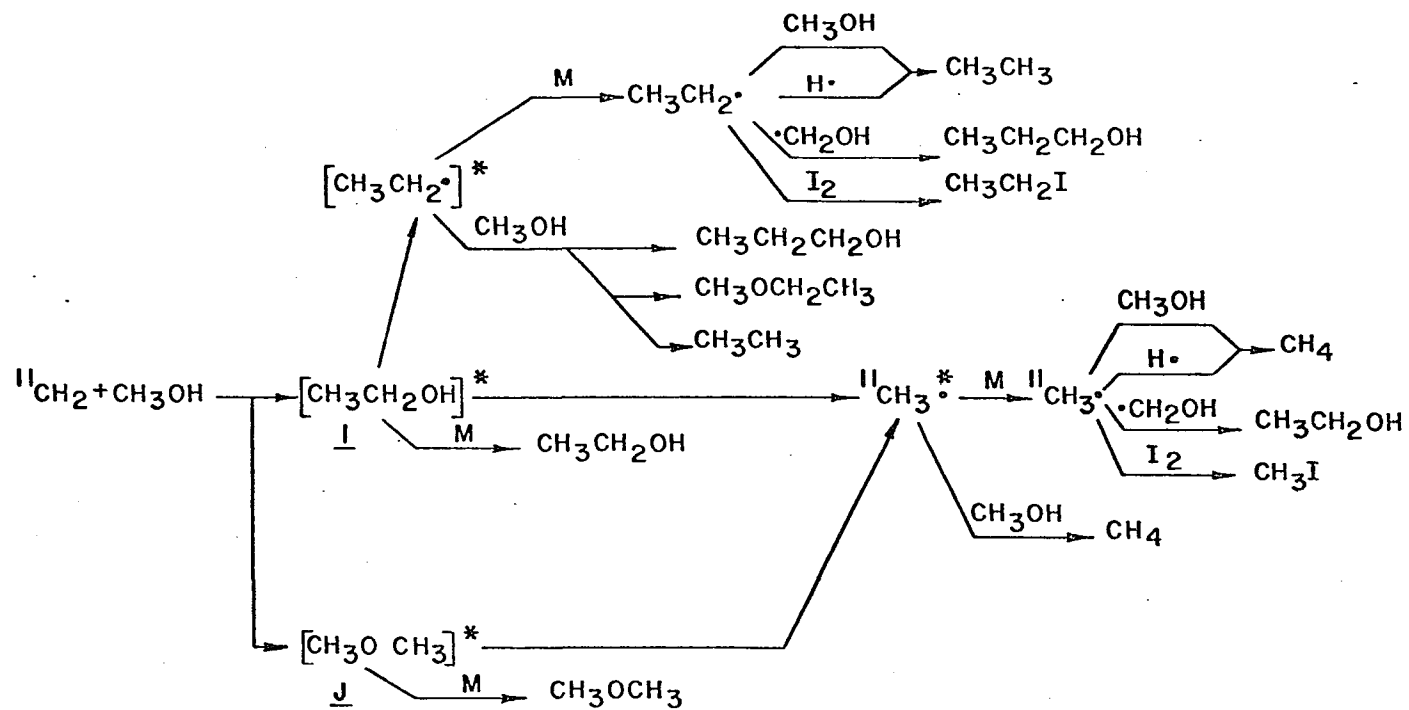
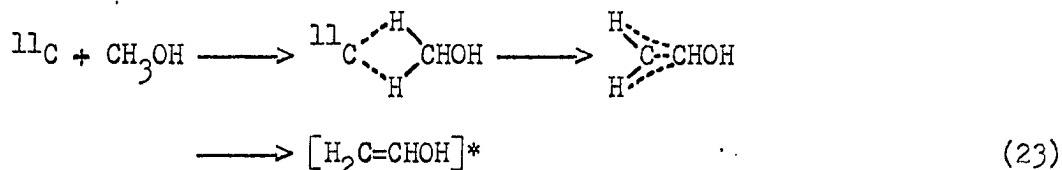


Figure 8. Chemistry of recoil carbon in methanol, reactions of $^{11}\text{CH}_2$ and $^{11}\text{CH}_3$

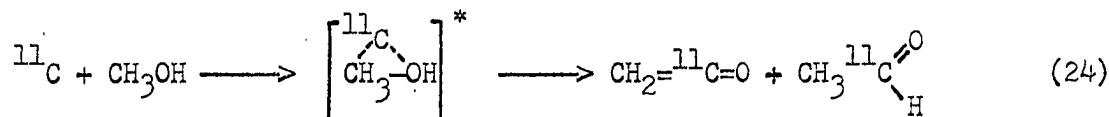
No evidence for products consistent with insertion into the C-H or C-O bond was obtained. Tracer studies by Franzen and Fikentscher (150) have shown that methylene will not insert into the C-O bond of diethyl ether. Evidence in support of the relative inertness of the C-O bond has also been obtained by Oae, Redvanly, and Wolf (52) from recoil carbon-14 studies in methanol. The production of ethanol ^{-14}C could conceivably result from the insertion of labelled methylene (see Figure 8) into either the C-O or C-H bond. Degradative studies on the ethanol showed that 95.1% of the carbon-14 activity to be in the methyl group and indicated a distinct preference for C-H bond insertion. In the reactions of vapor deposited carbon with methanol only one product, dimethoxymethane, was observed (68,110,111). If dimethoxymethane is produced by a double insertion mechanism, these results indicate that the thermal carbon atom has a distinct preference for O-H insertion as has also the resultant methoxycarbene. On the basis of these data and upon the basis of the analysis of the results in this study, the insertion of C, CH, CH₂ and other carbenes into the C-O bond does not presently appear to be a major mechanistic pathway. These results also tend to indicate a preference for O-H bond insertion by the substituted methylenes. For this reason we have considered only the reinsertion reaction of the collisionally deactivated carbenes, B and C, into the O-H bond of methanol to form 2-methoxyethanol- ^{11}C and dimethoxymethane- ^{11}C , respectively.

The formation of ketene and acetaldehyde via excited adduct A is only speculation. Both of these products could conceivably result from the fragmentation and deexcitation of B especially if B

is formed by the pathway outlined below.



This sequence has been proposed by Wolf (32) as a possible alternative to methyne insertion-decomposition or the methyne abstraction reaction for the formation of methylene. It may also be a possible alternative to ethylene formation in saturated hydrocarbons. This point will be discussed later in further detail. One can only speculate as to the nature of adduct A. An attack of the carbon atom on the C-O bond may result in an excited intermediate that will decay to acetaldehyde or ketene.



A similar intermediate to the formation of acetonitrile- ^{11}C in methylamine has been proposed by Cacace, et al. (103).

Up to this time we have assumed that methyl acetate (the product of the reaction of ketene with methanol) and acetaldehyde have the same precursor. This may not be so. Degradative studies on both acetaldehyde and methyl acetate should provide some interesting clues to help unravel this problem. If the distribution of carbon-11 in the methyl and carbonyl groups are similar for each product one may argue for a common precursor. If specific labelling is found, then a possible differentiation between B and the intermediate in Equation 24 may be possible. In either case degradative studies would help.

Both intermediates B and C may fragment to ^{11}CH . Methyne- ^{11}C may also result from a hydrogen abstraction process, but at the present time there appears to be no way to distinguish between these two paths.

The excited complex B may also fragment to acetylene or to an excited vinyl radical. These predictions are consistent with the "insertion-decomposition" mechanism first proposed by MacKay and Wolfgang (61) and discussed in detail in the introduction. Within experimental error, the acetylene- ^{11}C yield is independent of dose and added scavenger. The scavenger independence is in agreement with a rapid unimolecular decomposition reaction not involving a radical intermediate.

The excited vinyl radical may undergo rapid radical-molecule reactions with the solvent to form propylene- ^{11}C , methylvinyl ether- ^{11}C and allyl alcohol- ^{11}C . The apparent scavenger independence of the yields of propylene- ^{11}C and methylvinyl ether- ^{11}C rules out a scavengable radical intermediate in their production and supports the postulate of a rapid reaction of an excited C_2 fragment with the solvent. The choice of the vinyl radical as the product precursor is based upon the simplicity of the reaction. In each case, the reaction involves only one leaving group, H^\bullet or $\bullet\text{OH}$. With other less saturated C_2 fragments, extensive rearrangements are required and the possibility of radical intermediates exists. This of course does not rule such fragments out completely. In any case, the yields of these products are very low and the mechanism for their production a minor one.

The collisionally deactivated vinyl radical can react with the

radiation produced radicals or abstract hydrogen from methanol. Since the ethylene- ^{11}C yield does not change substantially upon addition of iodine scavenger, the abstraction and hydrogen radical reactions are not the major mechanisms for ethylene production.

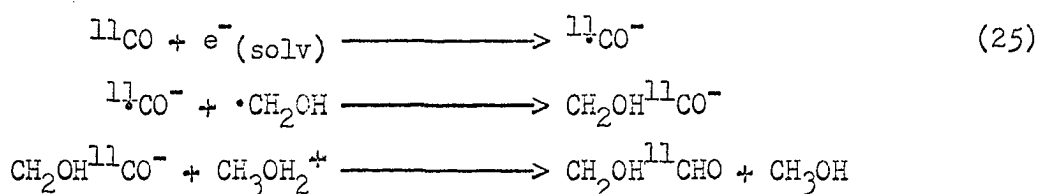
In the iodine scavenged system, the vinyl radical will react preferentially with iodine to form vinyl iodide- ^{11}C . The addition of scavenger reduces the yield of allyl alcohol- ^{11}C substantially. Within experimental error, the yield of vinyl iodide- ^{11}C (+2.1%) is exactly compensated for by the reduction in the ethylene- ^{11}C (-1.4%) and allyl alcohol- ^{11}C (-0.8%) and lends support for the reaction sequence presented.

Carbon monoxide- ^{11}C is produced in a substantial yield and the mechanism for its production is of primary concern in this study. For this reason, the carbon monoxide- ^{11}C yield for a number of systems has been systematically investigated. A summary of this investigation along with some of the conclusions that have been made will be the topic of a later section. The present discussion will be limited to the chemistry observed in methanol.

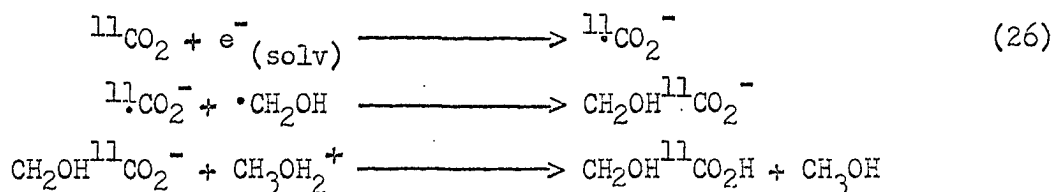
In the unscavenged system, the yield of ^{11}CO is found to be highly dose dependent as are the yields of acetaldehyde- ^{11}C and 1,2-propanediol- ^{11}C . Carbon dioxide- ^{11}C also fits into this group for reasons that will become apparent during this discussion. Since these dose dependencies are believed to result from a common precursor these four products will be discussed together. The common precursor is believed to be the solvated electron. Hart, et al. (151,152)

have reported the rate constants for the reactions of hydrated electrons with CO, CO₂ and CH₃C(=O)H to be approximately 10⁹, 7.7x10⁹, and 5.4x10⁹ M⁻¹ sec⁻¹, respectively. These rate constants are not expected to be significantly different for the solvated electron in methanol.

From the investigations of Holian, et al. (153) of the reactions of hydrated electrons with carbon monoxide in a 10⁻¹ M methanol solution, a reasonable prediction as to the expected reactions in pure methanol may be made. The following reactions are believed to occur;



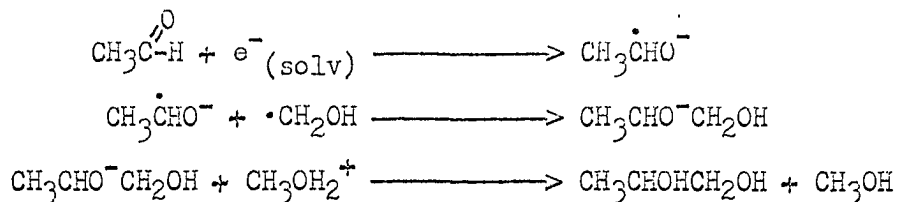
The reaction sequence expected for carbon dioxide-¹¹C is (154);



The products expected from these reactions, glycolaldehyde and glycolic acid cannot be determined under the conditions involved in this experiment so that direct evidence is not available to confirm these reaction sequences.

Indirect evidence is available which tends to support this reasoning. The addition of scavenger quantities of iodine is expected to efficiently remove the solvated electrons ($k_{\text{e}^- + \text{I}_2} = 5.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ (147)) so that reactions 25 and 26 will not occur. In the scavenged system, the yields of both ¹¹CO and ¹¹CO₂ are shown to undergo substantial increases. The lack of ¹¹CO₂ in non-scavenged methanol can then be attributed to the scavenging reactions by the solvated electrons.

Further support for these proposals may be obtained from the analysis of the acetaldehyde reaction sequences. The expected reactions are;



The determination of the product from this sequence of reactions, 1,2-propanediol, shows that a definite relationship exists between the yields of these two products. Within experimental error, the decrease in acetaldehyde- ^{11}C (-3.0%) is compensated for by the increase in the yield of 1,2-propanediol- ^{11}C (+2.8%). Additional support for this inter-relationship was obtained from the results of an experiment in which carrier quantities of acetaldehyde were added to the methanol sample before irradiation. The carrier acetaldehyde served to protect the acetaldehyde- ^{11}C from reduction. The yield of acetaldehyde- ^{11}C was up by >5.7% while that of 1,2-propanediol- ^{11}C was reduced by a corresponding amount (6.0%). These results tend to confirm the explanations proposed to account for the dose dependencies observed for the four products, ^{11}CO , $^{11}\text{CO}_2$, acetaldehyde- ^{11}C and 1,2-propanediol- ^{11}C .

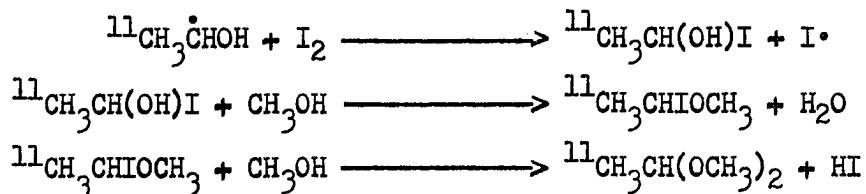
In the low dose system, the addition of iodine scavenger reduces the yields of acetaldehyde- ^{11}C and 1,2-propanediol- ^{11}C to zero. An unknown product appears with a yield slightly less than the corresponding reduction of acetaldehyde- ^{11}C and 1,2-propanediol- ^{11}C . This product is believed to result from the reactions of acetaldehyde or its precursor with iodine, possibly under the influence of the irradiation field. This hypothesis may be tested by addition of carrier quantities of

acetaldehyde to the methanol solution along with scavenger quantities of iodine tagged with iodine-131. If this reaction proposal is correct, one would expect to observe a radioactive iodine containing product with identical retention times as the unknown. Since macroscopic quantities may be produced, a chemical analysis of the product may be possible.

The fact that the yield of the unknown product is less than the reduction in yield of acetaldehyde- ^{11}C and 1,2-propanediol- ^{11}C may be just experimental error or may indicate that other reaction pathways are possible for the production of 1,2-propanediol- ^{11}C (see Figure 7),



Upon the addition of iodine scavenger, the following sequence of reactions is expected to occur (155,156);



The product, 1,1-dimethoxyethane- ^{11}C is also observed in the DPPH scavenged system and a similar sequence of reactions can be postulated.

In the DPPH scavenged methanol system acetaldehyde- ^{11}C and methyl acetate- ^{11}C are observed in yields similar to those in the unscavenged system. These facts are consistent with the hypothesis of a non-radical precursor for these products. Ketene- ^{11}C will not react with DPPH whereas in the iodine scavenged system, the reaction to form methyl iodoacetate in Figure 6 may be expected to occur. The fact that the acetylene- ^{11}C and carbon monoxide- ^{11}C yields are higher (see Table 7) in the DPPH scavenged system may indicate that DPPH is an

Table 7. Scavenger dependence of gaseous product yields in methanol

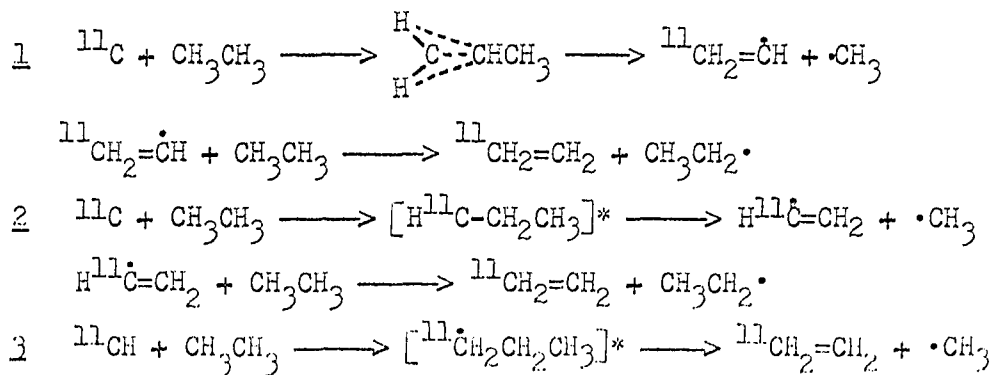
Product X(Scavenger)	CO	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
0.00	15.0±1.9	3.97±0.2	0.92±0.15	9.85±0.4	14.9±0.6
1.01x10 ⁻³ (I ₂)	24.2±0.3	2.48±0.09	0.61±0.11	8.46±0.3	15.4±0.7
2.26x10 ⁻³ (I ₂)	23.6±0.8	2.08±0.17	0.50±0.06	7.23±0.2	14.5±0.4
Saturated (DPPH)	25.4±0.5	3.02±0.2	0.90±0.05	9.66±0.4	16.1±0.4

Dose (eV/molecule) - 0.010

efficient solvated electron and hydrogen atom scavenger.

Reaction of the methyne radical Insertion of the methyne-¹¹C radical into both the C-H and O-H bonds is expected. The resultant excited adducts may collisionally deactivate or fragment to methylene-¹¹C and ethylene-¹¹C (see Figure 7).

The production of ethylene-¹¹C has been discussed in the introduction. Although the methyne radical appears to be the logical precursor, definite experimental evidence is lacking. Double tracer studies do allow some conclusions to be made. Dubrin, et al. (75) irradiated equal molar mixtures of C₂H₆ - C₂D₆ and observed that the deuterated ethylene-¹¹C's (C₂H₄, C₂H₃D, C₂HD₃, C₂D₄) were produced in equal amounts. These results are consistent with three possible mechanisms for production of ethylene.



From scavenger experiments in a number of systems, it appears that if mechanisms 1 or 2 are valid, the vinyl radical is very excited and reacts rapidly with the substrate before it can deactivate and be scavenged. It is more likely that mechanism 3 is the primary path for ethylene production and that the observed scavengeable ethylene results from mechanisms 1 or 2.

It is very difficult to distinguish between mechanisms 1 and 2. Some indication of the importance of the attack steps may be obtained from the study of the propylene- ${}^{11}\text{C}$ produced during irradiations of ethane (75). In this study, equal molar mixtures of C_2H_6 and C_2D_6 were irradiated. The results of the analysis indicated that extensive mixing of one hydrogen had occurred ($\text{C}_3\text{H}_6/\text{C}_3\text{H}_5\text{D} = \text{C}_3\text{D}_6/\text{C}_3\text{D}_5\text{H} \approx 1.3$). If deexcitation of the intermediate in mechanism 1 to propylene occurred as the primary pathway for propylene production, this mixing should not be observed. If these results are also valid in the methanol system, then the mechanism outlined as a possibility in Equation 23 may be only of minor importance and the cyclic excited intermediate (Equation 24) the primary pathway.

The possibility of fragmentation of the excited adducts to

methylene-¹¹C has previously been discussed. Methylene-¹¹C may also result from hydrogen abstraction reactions or from decomposition of the transition state proposed in Equation 23. At the present time the experimental evidence require to make this differentiation is lacking.

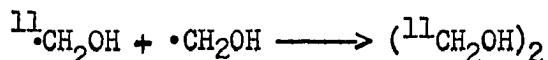
Deexcitation of D (Figure 7) may produce two types of ethanol-¹¹C radicals; the more stable one being the radical with the α -hydrogen removed. Both of these radicals are unable to abstract hydrogen from the solvent and consequently stabilize as products by the radical-radical reactions shown in Figure 7. The reactions of F have already been discussed. The reaction of G with the methanol radical to produce 1,3-propanediol-¹¹C is the major mechanism for production of this product. The possibility of double insertion into the C-H bonds by carbon-11 is excluded on the basis of the disappearance of this product in an iodine or DPPH scavenged solutions.

The production of 2-iodoethanol-¹¹C, in an I₂ scavenged system could not be verified. Various attempts to elute this product were unsuccessful, possibly as a result of its thermal instability (157).

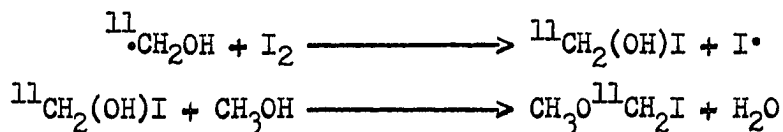
The CH₃OCH₂• radical, H in Figure 7 is unable to abstract hydrogen from the solvent and will form stable products by radical-radical reactions. A major fraction of the 2-methoxyethanol-¹¹C is believed to be formed in this manner. The unscavenged fraction may have resulted from the double insertion reaction proposed earlier and shown in Figure 6. In the iodine scavenged system, this radical will undergo the reactions shown. The instability of the α -iodoethers has already been pointed out. This is believed to be the major reaction which causes the rather substantial increase in the yield of dimethoxymethane-¹¹C in the iodine

scavenged system. This increase is not observed in the DPPH scavenged system possibly because the $\text{CH}_3\text{OCH}_2\text{DPPH-}^{11}\text{C}$ adduct is less labile than the iodoether.

Another pathway to dimethoxymethane- ^{11}C exists in the iodine scavenged system. The small yield of ethanediol- ^{11}C is believed to result from the following reaction;



The mechanism for the production of the methyl alcohol- ^{11}C radical is not as yet understood. The addition of iodine scavenger reduces the yield of ethanediol- ^{11}C to zero. The reaction sequence is believed to be the following;



The iodo ether is expected to react as shown in Figure 7 to form dimethoxymethane- ^{11}C .

The increased yield of dimethoxymethane- ^{11}C (+5.0%) is within experimental error of the decrease in the sum of dimethyl ether- ^{11}C (-0.6%), 2-methoxyethanol- ^{11}C (-2.7%), and ethanediol- ^{11}C (-1.0%).

Reactions of the methylene radical Methylene- ^{11}C can react by insertion into either the O-H or C-H bonds of methanol (see Figure 8). The excited adducts, I and J, can fragment or collisionally deactivate to the stable molecules, ethanol- ^{11}C and diethyl ether- ^{11}C , respectively. The formation of methylethyl ether- ^{11}C is believed to be the result of the reaction of an excited ethyl- ^{11}C radical with the solvent. The yield of this product is independent of the addition of scavenger and indicates that the production process does not involve thermally equilibrated

radicals. The unscavenged 1-propanol-¹¹C and ethane-¹¹C may be a result of a similar sequence of reactions involving a hot ethyl-¹¹C radical reaction with the solvent.

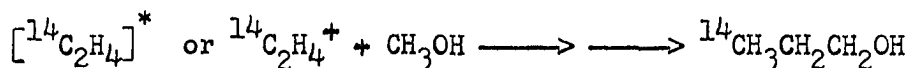
The thermal ethyl-¹¹C radical can pick up or abstract hydrogen from the solvent to form ethane-¹¹C. It may also react with the methanol radical to form 1-propanol-¹¹C although as will be explained later this mechanism is not believed to be important.

Evidence in support of a C₂ entity participation in this last reaction has been presented by Oae, et al. (52). Degradative studies of the 1-propanol-¹⁴C produced during reactor irradiations of a methanol-ammonia solution indicated that 98% of the activity was located in the 2 and 3 positions. The distribution is shown below;

CH ₃	CH ₂	CH ₂ OH
42.1%	55.8%	2.1%

Their assumption that labelled ethylene might be the reactive intermediate was tested by irradiation of a mixture of ethylene-¹⁴C and methanol (no ammonia present) under the same reactor conditions as were used for the recoil experiment. They observed that 41.5% of the ethylene-¹⁴C reacted with methanol to form labelled propanol and that the distribution of activity was equally divided between the 2 and 3 positions. They proposed the following mechanisms to account for these results.





These proposals appear to be reasonable. The absence of detectable quantities of ethyl iodide- ^{11}C in this investigation indicates that the major source of ethyl- ^{11}C radicals is not via the fragmentation of I since this process would not be expected to depend upon the presence of scavenger.

On the basis of the yields of ethanol- ^{11}C and dimethyl ether- ^{11}C in the scavenged system, an estimation of the relative insertion-stabilization probabilities of the methylene- ^{11}C radical into the O-H and C-H bonds of methanol can be made. The scavenged system was chosen in order to reduce the contribution to the product yields by the radical reactions (see Figure 8). The ratio of the O-H and C-H insertion-stabilization probability, on a per bond basis, is 2.5 and indicates that either the O-H bond in methanol is much more reactive than is the C-H bond or that the O-H insertion adduct stabilizes more readily than does the C-H insertion adduct. A combination of both of these factors is also possible. A higher reactivity of the O-H bond would be in agreement with the previously discussed higher O-H insertion probabilities observed for the substituted carbenes.

Reactions of the methyl radicals The reactions of methyl- ^{11}C radical are illustrated in Figure 8. In the unscavenged system, the methyl radical can abstract hydrogen from the solvent or react with the radiation produced radicals. The addition of iodine scavenger reduces the yield of both ethanol- ^{11}C (-3.3%) and methane- ^{11}C (-1.5%) and is consistent with the proposed reaction scheme. The fact that the yield of methyl iodide- ^{11}C is less than this reduction confirms that other

radical reaction pathways are available for ethanol production (e.g. radicals F and G). In fact, from these results one can estimate that about 1.4% of the ethanol in the unscavenged system results from the radical reactions of F and G.

The unscavenged methane- ^{11}C may result from hydrogen abstraction reactions by excited or energetic methyl- ^{11}C radicals.

Recoil Chemistry of Atomic Carbon in Ethanol

The results of the recoil carbon-11 studies in ethanol are presented in Table 8. As was observed in the methanol system, the recoiling carbon atom stabilizes in a large variety of products. The product spectrum is much more complex than that for methanol and the number of unidentified or possibly identified products has increased sharply. This increased product complexity is due to the increasing number of possible reaction paths. In this system, a complete description of the reaction mechanisms will not be attempted, for much of it would of necessity be a repeat of that presented in the previous section for methanol. Instead, the discussion will be restricted to those aspects which are unique to ethanol or which lend support to the proposals presented for methanol.

The radiolysis of ethanol is very similar in its main features to that of methanol (158). The radicals, $\text{CH}_3\dot{\text{C}}\text{HOH}$ and $\text{H}\cdot$ play a dominant role in the production of the major radiolysis products. The reaction sequence is as follows;

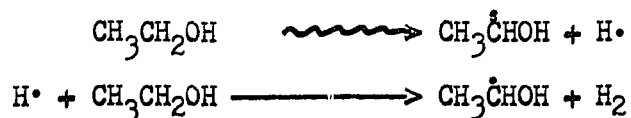


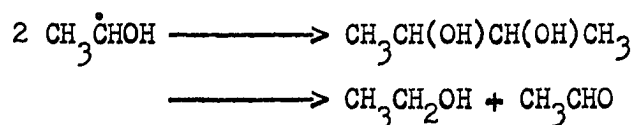
Table 8. Yields of radioactive products as a result of the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in ethanol

Product	Yields, Percent ^a			
	Unscavenged		$X_{I,2} = 9.7 \times 10^{-3}$	
	a	b	a	b
Carbon Monoxide	14.5 ± 0.4	14.6 ± 0.4	16.9 ± 0.6	17.6 ± 0.6
Methane	4.25 ± 0.2	4.38 ± 0.2	2.74 ± 0.08	2.61 ± 0.08
Ethane	1.04 ± 0.08	0.91 ± 0.08	0.57 ± 0.03	0.81 ± 0.03
Ethylene	7.76 ± 0.4	6.27 ± 0.4	7.18 ± 0.12	7.40 ± 0.12
Acetylene	12.8 ± 0.4	10.6 ± 0.4	13.8 ± 0.3	13.7 ± 0.3
Propane	0.40 ± 0.05	0.38 ± 0.05	0.26 ± 0.01	0.24 ± 0.01
Propylene	3.84 ± 0.15	3.55 ± 0.15	3.48 ± 0.10	3.54 ± 0.10
Allene	0.80 ± 0.10	0.70 ± 0.10	0.72 ± 0.10	0.46 ± 0.10
Propyne	2.82 ± 0.16	2.75 ± 0.16	2.99 ± 0.14	2.84 ± 0.14
Methyl Ethyl Ether	2.86 ± 0.15	2.84 ± 0.15	2.50 ± 0.18	2.77 ± 0.18
Methyl Vinyl Ether	0.39 ± 0.05	0.33 ± 0.05	~0.3	
Diethyl Ether	0.51 ± 0.10	0.43 ± 0.10	0.33 ± 0.08	0.28 ± 0.08
Diethoxymethane	2.04 ± 0.17	2.07 ± 0.17	6.67 ± 0.5	7.26 ± 0.5
1,1-Diethoxyethane and/or Ethyl Propionate	-	-	1.70 ± 0.8	4.92 ± 0.4
Acetaldehyde	2.48 ± 0.4	2.50 ± 0.4	-	0.52 ± 0.2
Propionaldehyde	1.23 ± 0.4	1.11 ± 0.4	-	t
(Ethyl Formate)?	t	t	1.34 ± 0.3	0.75 ± 0.3

^aYields in percent of total ^{11}C produced

Table 8. (Continued)

Product	Yields, Percent ^a			
	Unscavenged		$X_{I_2} = 9.7 \times 10^{-3}$	
	a	b	a	b
Ethyl Acetate	1.89±0.10	1.77±0.10	-	0.8
Acetone	2.39±0.3	2.63±0.3	2.87±0.2	3.06±0.2
2-Propanol	5.76±0.2	5.08±0.2	3.01±0.17	3.02±0.17
1-Propanol	4.54±0.08	5.01±0.08	4.01±0.09	3.76±0.09
Allyl Alcohol	5.0 ±0.3	3.5 ±0.3	4.41±0.40	3.93±0.40
2-Propyne-1-ol	1.25±0.2	0.91±0.2	1.22±0.04	1.28±0.04
1-Butanol	0.95±0.13	0.86±0.13	0.48±0.05	0.39±0.05
2-Butanol	1.88±1.0	2.22±1.0	0.53±0.16	0.60±0.16
1-Butene-3-ol	2.33±0.4	2.56±0.4	0.60±0.04	0.58±0.04
1-Pentanol	0.64±0.08	0.47±0.08	t	t
3-Ethoxy-1-Propanol	0.75±0.14	0.51±0.14	-	-
CH ₃ I	-	-	3.29±0.2	3.41±0.2
CH ₂ I ₂	-	-	~0.7	
Total	85.1	78.9	82.6	87.2
Dose (eV/molecule)	a - 0.010, b - 0.050			



The addition of iodine scavenger is expected to greatly reduce the radical concentration of H• and CH₃ĊHOH.

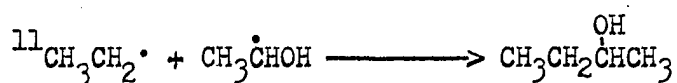
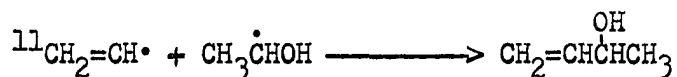
One of the most important differences between this system and the methanol system is the dose independence of both the carbon monoxide-¹¹C and acetaldehyde-¹¹C yield. The difference may be a result of the high G value for the radiolytic production of acetaldehyde (e.g. G = 3.14) (159). The acetaldehyde which is produced in macroscopic quantities by radiolysis will, as a result of its high rate constant for reaction with solvated electrons (152), act as an efficient electron scavenger. Another possible reason for the apparent absence of solvated electrons has been discussed by Hayon and Weiss (159). In their paper, they indicated that the positive and negative polarons (e.g. $\text{CH}_3\text{CH}_2\text{OH}^+$ and the solvated electron) may not be as stable as those produced in water or methanol because of the lower solvent polarity and the polarons greater structural complexity. Whatever the actual reason is, it is apparent from the ethanol data that effects attributed to the solvated electrons in the methanol system were not observed in ethanol.

The yields of both ethylene-¹¹C and acetylene-¹¹C show a definite dose dependence as do the yields of a number of the unsaturated products in this system. This dose dependence very likely arises as a result of reduction by radiolytically produced hydrogen atoms or radicals. The resultant radical can stabilize in a variety of products by further radical reactions which accounts for the inability to establish a direct relationship between any of the dose dependent products.

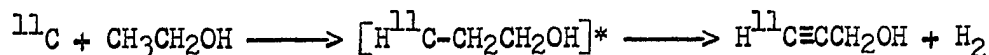
The product diethoxymethane-¹¹C is expected to arise from the double insertion reaction proposed for the production of dimethoxymethane-¹¹C in methanol. The yield of the double insertion product is

substantially lower in the ethanol system reflecting the greater number of reaction possibilities. In the iodine scavenged system, the yield of diethoxymethane- ^{11}C undergoes a large increase which is believed to result from the reaction of the iodomethylethyl ether- ^{11}C with the solvent. A quantitative yield comparison such as that presented for methanol cannot be made in this system because the expected loss in yield of the complementary product (1-ethoxy-2-propanol- ^{11}C) cannot be verified.

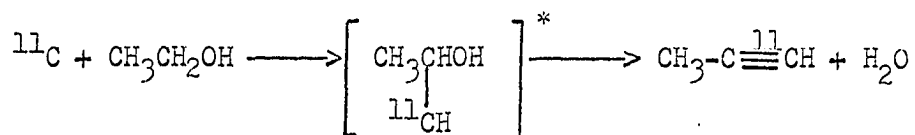
The products 2-butanol- ^{11}C and 1-butene-3-ol- ^{11}C bear a similar relationship to the products 1-propanol- ^{11}C and allyl alcohol- ^{11}C in the methanol system. Both products are believed to be results of the reactions of tagged C_2 entities with the radiation produced ethanol radicals. The following reactions are offered as possibilities.



The scavenger independence of the yield of 2-propyne-1-ol- ^{11}C is indicative of a reaction which does not involve a radical intermediate. A possible reaction pathway to this product involves the stabilization by loss of hydrogen of an excited carbon- 11 insertion adduct.

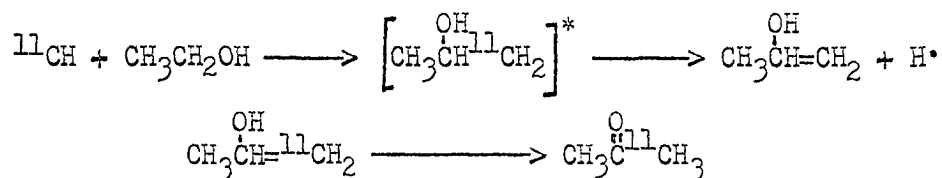


Degradative studies to locate the position of the active carbon atom may provide support for this mechanism. A similar mechanism involving insertion into the α -hydrogen of ethanol may result in the formation of propyne- ^{11}C .



An excited propyne- ^{11}C can readily isomerize to allene- ^{11}C . The relative scavenger independence of the yields of these products is consistent with this rapid unimolecular decomposition and isomerization step. The ratio of propyne- ^{11}C to allene- ^{11}C is independent of scavenger and further supports the possibility of this isomerization process.

The production of acetone- ^{11}C may involve the insertion of a methyne- ^{11}C radical into the α -hydrogen of ethanol. The resultant adduct can stabilize by loss of a hydrogen atom to acetone- ^{11}C .



The scavenger dependence of the yield of 2-propanol- ^{11}C is similar to that of ethanol- ^{11}C in the methanol system. In both cases, part of the reduction is believed to result from the scavenging of methyl- ^{11}C radicals which in the absence of scavenger would have reacted with the radiation produced alcohol radical.



The yield of methyl iodide- ^{11}C (+3.3%) is again less than the loss of methane- ^{11}C (-1.5%) and 2-propanol- ^{11}C (-2.8%) indicating that other possible radical pathways exist for the production of 2-propanol- ^{11}C . The unscavenged methane- ^{11}C may result from abstraction reactions by hot methyl- ^{11}C radicals.

From the comparison of the yield of 1-propanol- ^{11}C and 2-propanol- ^{11}C

to that of methylethyl ether- ^{11}C in the scavenged ethanol system, an estimate of the C-H and O-H insertion-stabilization probability can be obtained. This ratio, on a per bond basis, is $\text{O-H/C-H} \approx 1.8$.

Although this ratio is lower than that obtained by a similar argument in methanol, it does support the general hypothesis of the greater reactivity of the O-H bond.

Structural Dependence of the C_1 and C_2 Product Yields

One of the objectives of this study was to obtain information bearing on the structural dependence of the fragmentation modes for a number of target molecules containing the carbonyl, hydroxyl and alkoxy functional groups. For this purpose, the dose and scavenger dependence of the yields of carbon monoxide- ^{11}C , methane- ^{11}C , ethane- ^{11}C , ethylene- ^{11}C and acetylene- ^{11}C were determined in the following group of compounds; methanol, ethanol, 1-propanol, 2-propanol, acetone, diethyl ether, methyl formate and methyl acetate. The results of these studies are summarized in Tables 6-16.

The reported results for the iodine scavenged acetone system (Table 11) represent only one determination. As mentioned in the experimental section, iodine was observed to react with acetone. This reaction is relatively slow and only became apparent days after the samples were prepared. The reported determination was performed within hours of the sample preparation and the results are believed to be representative of the scavenged system.

For diethyl ether (Table 14) and methyl formate (Table 13) dose studies in the scavenged systems were not performed. Since a majority of the previous data for the other scavenged systems indicated

Table 9. Yields of radioactive products as a result of the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in 1-propanol

Product	Yield, Percent			
	Unscavenged		$X_{I_2} = 1.03 \times 10^{-3}$	
	a	b	a	b
CO	11.3 ± 0.5	9.57 ± 0.5	12.7 ± 0.2	12.7 ± 0.2
CH ₄	4.62 ± 0.2	4.94 ± 0.2	2.76 ± 0.11	3.17 ± 0.11
C ₂ H ₆	0.63 ± 0.09	0.79 ± 0.09	0.48 ± 0.02	0.49 ± 0.02
C ₂ H ₄	5.30 ± 0.2	4.40 ± 0.2	4.87 ± 0.08	5.28 ± 0.08
C ₂ H ₂	12.1 ± 0.2	9.31 ± 0.15	12.9 ± 0.2	13.2 ± 0.2
Total	33.9 ± 0.6	29.0 ± 0.6	33.7 ± 0.3	34.8 ± 0.3

Dose (eV/molecule) a - 0.010, b - 0.070

Table 10. Yields of radioactive products as a result of the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in 2-propanol

Product	Yield, Percent			
	Unscavenged		$X_{\text{I}_2} = 9.7 \times 10^{-4}$	
	a	b	a	b
CO	14.6 ± 0.4	14.1 ± 0.4	14.5 ± 0.2	14.9 ± 0.2
CH ₄	4.91 ± 0.2	4.88 ± 0.2	2.45 ± 0.05	2.58 ± 0.05
C ₂ H ₆	1.69 ± 0.17	1.55 ± 0.17	1.11 ± 0.07	1.20 ± 0.07
C ₂ H ₄	9.94 ± 0.4	5.09 ± 0.4	9.74 ± 0.2	10.40 ± 0.2
C ₂ H ₂	14.4 ± 0.8	6.62 ± 0.8	16.1 ± 0.2	16.8 ± 0.2
Total	45.5 ± 1.0	32.3 ± 1.0	43.8 ± 0.4	45.8 ± 0.4

Dose (eV/Molecule) a - 0.010, b - 0.070

Table 11. Yields of radioactive products as a result of the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in acetone

Product	Yield, Percent		
	Unscavenged	$X_{I_2} = 9.97 \times 10^{-4}$	
	a	b	c
CO	30.2 ± 0.5	28.9 ± 0.5	30.7
CH ₄	1.37 ± 0.12	1.76 ± 0.12	0.5
C ₂ H ₆	1.52 ± 0.16	1.84 ± 0.16	0.9
C ₂ H ₄	12.2 ± 0.6	8.9 ± 0.6	9.9
C ₂ H ₂	20.5 ± 0.5	17.9 ± 0.5	21.4
Total	65.8 ± 0.9	59.3 ± 0.9	63.4

Dose (eV/molecule) a - 0.010, b - 0.070, c - 0.0073 (one determination)

Table 12. Yields of radioactive products as a result of the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in methyl acetate

Product	Unscavenged		Yield, Percent $X_{I_2} = 9.86 \times 10^{-4}$	
	a	b	a	b
CO	37.1 ± 0.6	33.5 ± 0.6	40.6 ± 1.0	41.6 ± 1.0
CH ₄	1.36 ± 0.11	1.29 ± 0.11	0.72 ± 0.04	0.63 ± 0.04
C ₂ H ₆	1.62 ± 0.07	1.71 ± 0.07	0.82 ± 0.13	0.83 ± 0.13
C ₂ H ₄	7.64 ± 0.17	6.10 ± 0.17	7.71 ± 0.3	8.04 ± 0.3
C ₂ H ₂	16.3 ± 0.6	13.9 ± 0.6	19.8 ± 0.6	20.5 ± 0.6
Total	64.0 ± 0.9	56.5 ± 0.9	69.7 ± 1.2	71.6 ± 1.2
Dose (eV/molecule) a - 0.020, b - 0.080				

Table 13. Yields of radioactive products as a result of the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in methyl formate

Product	Yield, Percent		$X_{I_2} = 1.00 \times 10^{-3}$
	Unscavenged		
	a	b	a
CO	48.6 \pm 0.8	40.9 \pm 0.8	54.4 \pm 0.2
CH ₄	1.90 \pm 0.2	2.03 \pm 0.2	1.17 \pm 0.16
C ₂ H ₆	1.29 \pm 0.18	1.71 \pm 0.18	0.72 \pm 0.09
C ₂ H ₄	5.73 \pm 0.3	4.80 \pm 0.3	5.14 \pm 0.2
C ₂ H ₂	13.8 \pm 0.5	11.6 \pm 0.5	15.9 \pm 0.4
Total	71.3 \pm 1.0	61.0 \pm 1.0	77.4 \pm 0.5

Dose (eV/molecule) a - 0.018, b - 0.070

Table 14. Yields of radioactive products as a result of the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in diethyl ether

Product	Yield, Percent		$X_{\text{I}_2} = 9.36 \times 10^{-4}$
	Unscavenged a	b	
CO	9.38 ± 0.3	9.45 ± 0.3	9.40 ± 0.10
CH ₄	4.33 ± 0.13	4.84 ± 0.13	2.24 ± 0.07
C ₂ H ₆	0.86 ± 0.11	0.94 ± 0.11	0.61 ± 0.07
C ₂ H ₄	8.35 ± 0.16	8.27 ± 0.16	7.65 ± 0.3
C ₂ H ₂	16.9 ± 0.3	16.4 ± 0.3	17.4 ± 0.6
Total	39.8 ± 0.5	39.9 ± 0.5	37.3 ± 0.7

Dose (eV/molecule) a - 0.020, b - 0.080

Table 15. Gaseous product yield dependence upon iodine scavenger concentration in the diethyl ether system^a

$X_{\text{I}_2} =$	Product	Yield, Percent				
		CO	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
0.00		9.38	4.33	0.86	8.35	16.88
1.6×10^{-4}		8.93	2.91	0.81	7.90	17.29
4.4×10^{-4}		9.23	2.51	0.67	7.92	17.69
9.4×10^{-4}		9.41	2.24	0.61	7.65	17.41
9.6×10^{-3}		9.87	1.59	0.45	7.07	16.78

^aAverage Dose (eV/molecule) = 2×10^{-2}

Table 16. Summary of gaseous products in iodine scavenged systems^a

Target Molecule	Yield of Products, Percent ^b				
	CO	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
Methanol	24.5 ±0.3	2.55±0.09	0.68±0.11	8.67±0.3	15.7±0.7
Ethanol	17.0 ±0.6	2.70±0.08	0.63±0.03	7.23±0.12	13.7±0.3
1-Propanol	12.7 ±0.2	2.83±0.11	0.48±0.02	4.94±0.08	13.0±0.2
2-Propanol	14.5 ±0.2	2.48±0.05	1.12±0.07	9.85±0.2	16.2±0.3
Acetone	30.7	0.5	0.9	9.9	21.4
Methyl Acetate	40.6 ±1.0	0.72±0.04	0.82±0.13	7.71±0.3	19.8±0.6
Methyl Formate	54.4 ±0.2	1.17±0.16	0.72±0.09	5.14±0.2	15.9±0.4
Diethyl Ether	9.40±0.1	2.24±0.07	0.61±0.07	7.65±0.3	17.4±0.6

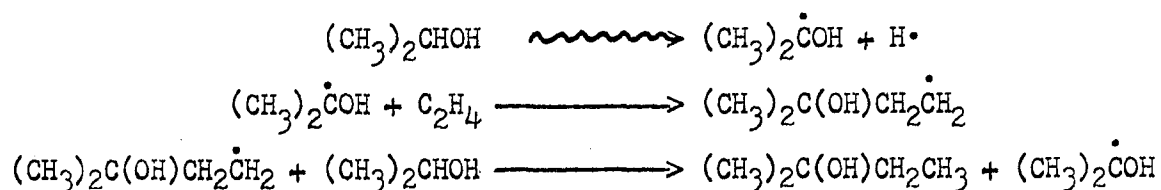
^aX_{I₂} ≈ 1x10⁻³

^bYields calculated at dose ≈ 2x10⁻² eV/molecule except for acetone where the listed values are a result of one low dose run, 7x10⁻³ eV/molecule.

only a minor dose dependence of these products, the average value for a number of low dose runs was used to represent the data.

In most of these systems, the yields of the C_1 and C_2 products were dose dependent. This dose dependence is believed to result from reactions of the product molecules with radiation produced radicals, although, in most cases, the radicals participating in these reactions have not been identified.

A radiation produced reaction common to alcohols is the loss of the α -hydrogen atom to give $R_1R_2\dot{C}OH$. The observed radiolysis product resulting from the production of this radical is the α -glycol $R_1R_2C(OH)C(OH)R_1R_2$. Indications of the possible reactions responsible for the dose dependence of the yields of ethylene- ^{11}C and acetylene- ^{11}C in the alcohols may be obtained from studies of the addition reactions of 2-propanol to ethylene under the influence of a radiation field (160,161). For ethylene dissolved in liquid 2-propanol, Hirota and Hatada (160) postulate the following sequence of reactions;



Under the conditions of their study, a G value of 120 for the production of 2-methyl-2-butanol was measured. The high G value indicated that a chain mechanism was responsible for the production of the tertiary alcohol. Similar results and interpretation were presented by Kurihara and Hotta (161) for the gas phase system. This sequence of reactions may be responsible for the large dose dependence of ethylene- ^{11}C in 2-propanol (Table 10) although reduction by hydrogen atoms or

other radiation produced radicals cannot be excluded. Support for this proposal may be obtained if a definite relationship can be established between the loss of ethylene- ^{11}C and the production of 2-methyl-2-butanol- ^{11}C . A similar sequence of reactions with production of 2-methyl-3-butene-2-ol- ^{11}C can be postulated to account for the loss of acetylene- ^{11}C in 2-propanol. Similar reactions may also account for the dose dependence of acetylene and ethylene in the other alcohol systems. However, in methanol and ethanol where the dose dependence of the complimentary products were measured, the experimental error was such that this proposal could not be verified for these systems.

The dose dependence of ethylene- ^{11}C and acetylene- ^{11}C in acetone (Table 11) may result from their reaction with $\text{H}\cdot$, $\cdot\text{CH}_3$ or $\cdot\text{CH}_2\text{COCH}_3$ followed by a subsequent hydrogen abstraction from the acetone.

For the esters, methyl formate and methyl acetate, the dose dependence of the ethylene- ^{11}C and acetylene- ^{11}C may also be attributed to reactions with the radicals produced by the radiation field. The radiation chemistry of methyl acetate has been studied by Ausloos and Trumbore (162) and by Hummel (163). The complete radiolysis mechanism is not available for methyl acetate but the radiolysis results can be explained on the basis of known radical reactions and the assumption that every bond in the molecule with the exception of the $\text{C}=\text{O}$ bond is broken (158). The acetyl radical is a primary product from this dissociation and has been shown by Hirota, et al. (164) to undergo similar chain reactions with ethylene as presented earlier for the radical $\text{CH}_2\dot{\text{C}}(\text{OH})\text{CH}_3$. This may be the major radical reaction accounting for the dose dependence of ethylene- ^{11}C and possibly acetylene- ^{11}C in

methyl acetate. The formyl radical is expected to be produced in the radiolysis of methyl formate and may undergo similar reactions. The dose dependence observed for ^{11}CO could possibly result from the reactions of the acetyl and formyl radicals with the ^{11}CO , although no evidence is currently available to support this hypothesis.

In the diethyl ether system, $^{11}\text{CH}_4$ was the only product that exhibited a yield dose dependence. This indicated that either the radicals produced by the radiation field are relatively unreactive towards these molecular products or the diethyl ether contained trace impurities (possibly peroxides) which acted as scavengers for the radiation produced radicals. No definite distinction can be made between these alternatives but the characteristic induction period representative of trace scavenger impurities was not observed. The increasing yield of $^{11}\text{CH}_4$ with increasing dose may result from decomposition of larger radioactive products by the radiation field.

In all of the iodine scavenged systems, the acetylene- ^{11}C yield is higher than in the unscavenged systems when irradiated under similar dose conditions which indicates that acetylene- ^{11}C reacts to some extent with the radiation produced radicals to produce build-up products. As discussed earlier, one of the major purposes of adding a radical scavenger is to reduce the concentration of the radicals produced by the radiation field. The other effect of the scavenger is to intercept some of the thermal radical intermediates to a specific product. The fact that the acetylene- ^{11}C yields are higher in the scavenged systems indicates that the part of the acetylene which is produced by way of a scavengeable radical intermediate is small in comparison to the yield

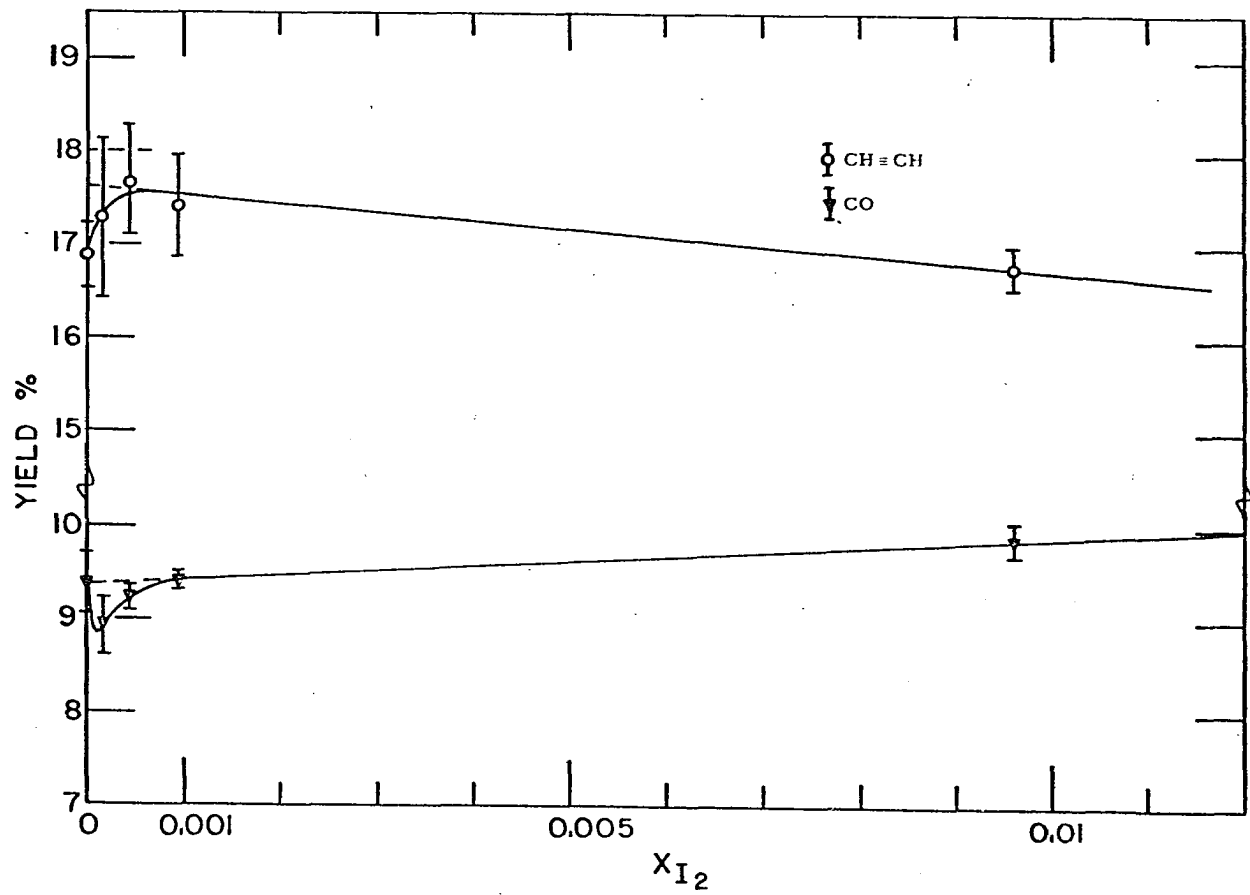


Figure 9. Iodine scavenger dependence of product yields in diethyl ether, dose 2×10^{-2} eV/molecule

intermediate has been obtained from gas phase studies of specifically deuterated hydrocarbon molecules (63,65). The results obtained in this study are consistent with the previously discussed mechanism for acetylene- ^{11}C production involving a rapid unimolecular decomposition of the carbon atom C-H insertion adduct.

The ethylene- ^{11}C yields in most of the systems studied show a significant decrease upon addition of scavenger quantities of iodine which indicates that some of the ethylene is produced by way of a radical intermediate. Evidence for the vinyl radical as the intermediate in the production of part of the ethylene has been presented in the discussion of the methanol data. It is clear, however, that the major fraction of the ethylene yield results from insertion of ^{11}CH into a primary C-H bond followed by rapid unimolecular decomposition. Support for this hypothesis was obtained from the data for the iodine scavenged 1- and 2-propanol systems where the ethylene- ^{11}C yield was found to be directly proportional to the number of primary C-H bonds in the molecule (Table 16). The scavenged system was chosen for this comparison in order to reduce the significance of the radical reactions and the effect of the radiation field. Further evidence that part of the yield of ethylene- ^{11}C , at least in the diethyl ether system, is a result of a scavengable radical intermediate is presented in Table 15 and illustrated in Figure 10. The yield of ethylene decreases with increasing iodine scavenger concentration; the initial rapid decrease is indicative of the scavenging of a thermal radical. The further decrease at high scavenger concentrations may result from competition reactions for excited vinyl- ^{11}C radicals within the solvent cage.

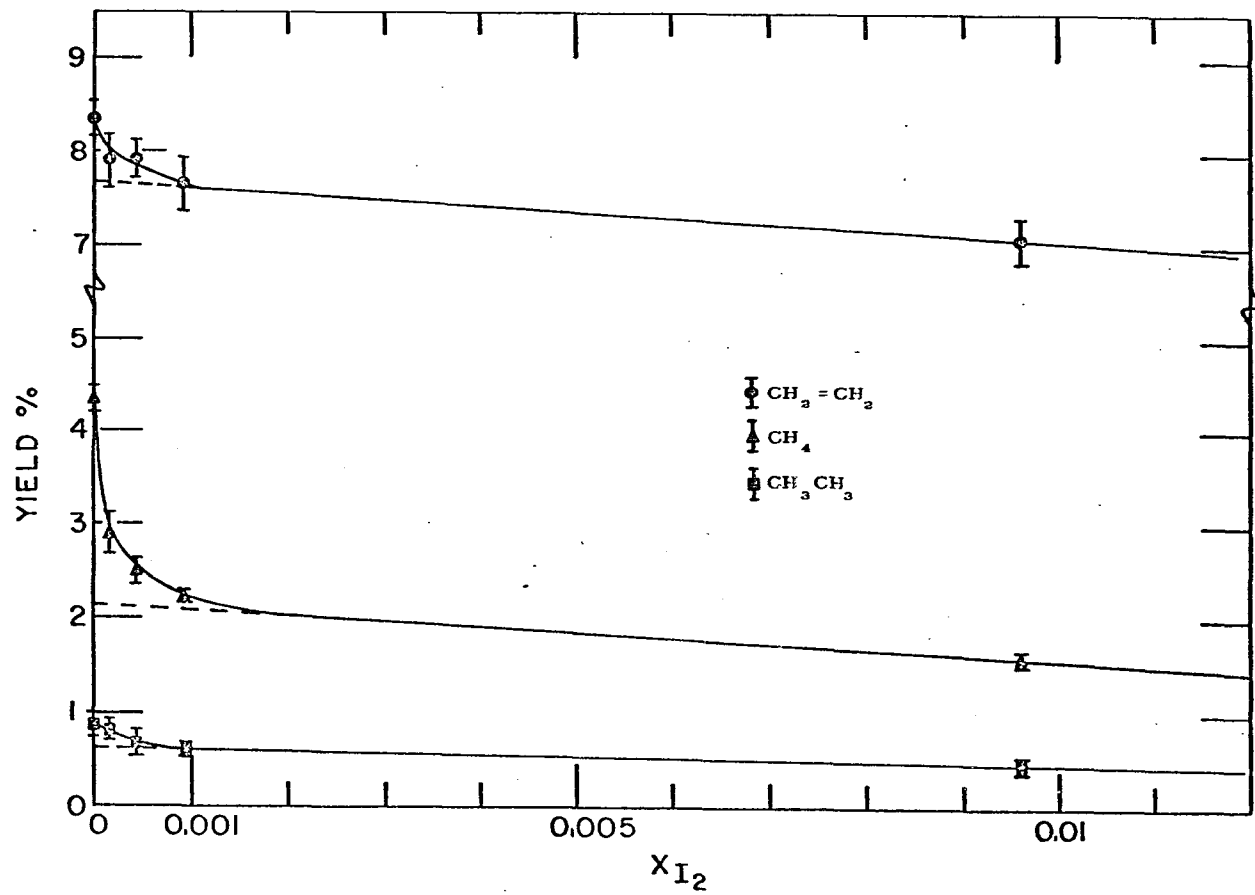


Figure 10. Iodine scavenger dependence of product yields in diethyl ether, dose 2×10^{-2} eV/molecule

Similar results were obtained in the methanol system (see Table 7) which very likely indicates that in most unscavenged systems studied part of the ethylene yield involves a radical precursor. The addition of scavenger quantities of DPPH does not appear to affect the yields of ethylene- ^{11}C or ethane- ^{11}C in methanol (Table 7). No definite explanation to account for these results can be presented at the present time. Possibly, as a result of the large size of the DPPH radical and its low solubility in methanol ($<10^{-3}\text{M}$), the abstraction reaction of the vinyl- ^{11}C and ethyl- ^{11}C radicals may be more than competitive with the scavenging reaction.

The production of ethane- ^{11}C in these systems is believed to result from insertion of $^{11}\text{CH}_2$ into a primary C-H bond followed by decomposition of the excited adduct to an ethyl- ^{11}C radical. The excited radical may rapidly abstract hydrogen within the solvent cage or may reach thermal energies and be scavenged by added radical scavengers. The expected result of increasing the iodine scavenger concentration is observed in the diethyl ether and methanol systems (Table 15 and 7 and Figure 10). The ethane- ^{11}C yield in the scavenged 1- and 2-propanol systems is approximately proportional to the number of primary C-H bonds in the molecule (Table 16).

Methane- ^{11}C is believed to result from a mechanism similar to that proposed for the production of ethane- ^{11}C . The major difference is that the methylene insertion adduct decomposes to $^{11}\text{CH}_3\cdot$ and that the initial insertion may also be into secondary or tertiary C-H bonds. A large fraction of the methane yield results from abstraction reactions of a thermal methyl radical. Evidence for this conclusion has been

presented earlier in the discussion of the $^{11}\text{CH}_4$ yields in the methanol and ethanol systems. This fact was further verified by the studies of the methane yield dependence on the iodine scavenger concentration in the diethyl ether and methanol systems (Tables 15 and 7 and Figure 10). If the yields of $^{11}\text{CH}_3\text{I}$ and $^{11}\text{CH}_4$ in the iodine scavenged methanol and ethanol systems are taken to represent the total $^{11}\text{CH}_3\cdot$ produced, then approximately 6% of the radioactive carbon reacts as $^{11}\text{CH}_3\cdot$ radicals.

Quantitative correlations of the structural dependence of the products yields has proved very difficult. Although statistical insertion of the primary reactants (e.g. ^{11}C , ^{11}CH and $^{11}\text{CH}_2$) may occur, the decomposition step will depend upon the structural features and energy content of the complex. The structural dependence of the yield of ethylene- ^{11}C and ethane- ^{11}C in the 1- and 2-propanol systems has previously been discussed. The higher yield of acetylene- ^{11}C in the 2-propanol system is very likely a result of the greater number of primary C-H bonds in the molecule. The carbon insertion adduct resulting from primary C-H bond insertion can fragment to acetylene by the breaking of a C-C and C-H bond while the adduct resulting from secondary C-H insertion requires the breaking to two C-C bonds to form the same product. The latter process is statistically less probable.

Carbon monoxide- ^{11}C was of particular interest since it is produced in relatively large yields in these systems and represents a major reaction mechanism for recoil carbon that has not been previously studied. The deoxygenation of a variety of oxygen containing organic compounds by vapor deposited carbon has been reported by Skell, et al. (110). The formation of carbon monoxide from compounds such as acetone,

methyl ethyl ketone, cyclopentanone, propylene oxide, diethyl ether, and tetrahydrofuran was observed. Water and the simple alcohols were not deoxygenated. This lack of deoxygenation may be a result of favorable competition from the O-H insertion reactions, since this possibility is not available for the other compounds.

Deoxygenation with formation of ^{11}CO is observed in all the systems investigated in this study. The yield of this product in the iodine scavenged systems can be correlated directly to a simple statistical model if the following suppositions are made; 1) Any primary or secondary C-H is 1.0 sites, tertiary C-H is 0.0 sites, and $\text{O}=\text{C}-\text{H}$ is 0.0 sites, 2) Any -O- whether C-O-H or C-O-C is 1.0 sites and 3) Any C=O is 2.7 sites. The site probability was obtained by using methanol and acetone as prototype molecules. The results of the statistical calculations of the product yields are presented in Table 17. The agreement between the calculated and the experimental yield is much better than should be expected on the basis of this naive model. Although this model has a number of ambiguities that need further clarification, these results do allow some definite conclusions to be formulated concerning the mechanism for ^{11}CO production.

The statistical nature of the ^{11}CO yield is indicative of the reactions of an indiscriminate reagent. The fact that the yields are predictable on an absolute basis in the alcohol and diethyl ether systems may indicate that the ^{11}CO results from a reaction which occurs over a definite range of recoil energy, above or below which the reaction probability is low. The high site probability for the reaction with the $\text{C}=\text{O}$ group may result from the larger electron cloud or from a larger

Table 17. Statistical nature of carbon monoxide yield in iodine scavenged systems^a

Target Molecule	CO Sites	Total Sites	CO Yield, Percent ^b	
			Calc.	Exp.
Methanol	1.0	4.0	25.0	24.5 ±0.3
Ethanol	1.0	6.0	16.7	17.0 ±0.6
1-Propanol	1.0	8.0	12.5	12.7 ±0.2
2-Propanol	1.0	7.0	14.3	14.5 ±0.2
Diethyl Ether	1.0	11.0	9.1	9.40±0.1
Acetone	2.7	8.7	31.0	30.7
Methyl Acetate	3.7	9.7	38.2	40.6 ±1.0
Methyl Formate	3.7	6.7	55.2	54.4 ±0.2

$${}^a X_{I_2} = 1 \times 10^{-3}$$

^bYields calculated at dose of 2×10^{-2} eV/molecule except for acetone where the listed value is a result of one low dose run, 7×10^{-3} eV/molecule.

energy region (possibly down to thermal energy) over which the reaction may occur. Since Skell, et al. (110) observed deoxygenation of acetone and diethyl ether for the vapor deposited carbon atoms, the excitation function for CO production may extend to thermal energies.

These results also demonstrate that the reaction site probability is independent of whether the bond is a C-O-H or C-O-C bond. A possible rationalization of these facts may be that the reaction is localized at the oxygen atom and that the reaction occurs at sufficiently high energies that the substituent groups do not affect the overall reaction

sequence. If this is the case, the reaction may be a result of the recoil carbon atom interacting with the nonbonding electrons of the oxygen atom.

The tertiary C-H bond in 2-propanol and the C-H bond in methyl formate were assigned a site probability of zero. These assignments cannot be completely justified. A possible rationale in the case of 2-propanol may be that the tertiary C-H bond is sterically hindered from attack by the methyl groups. If the tertiary C-H bond is assigned a site probability of 1.0, then the data indicates that the -O- bond on a tertiary carbon atom is more reactive than a similar bond on a secondary carbon atom (i.e. a -O- bond on a tertiary carbon atom should be assigned a site probability >1.0). A combination of both of these factors is possible but at the present time, the data do not allow a more definite conclusion to be drawn. In the case of methyl formate, a reasonable explanation for the C-H bond site assignment is not apparent which indicates that further study of the structural dependence of the ^{11}CO yield is required if a more definitive model is desired.

The effect of the iodine scavenger concentration on the yield of ^{11}CO in diethyl ether is presented in Table 15 and illustrated in Figure 9. The shape of the curve is very difficult to rationalize on the basis of a simple reaction model but does demonstrate that a small fraction of the ^{11}CO yield may result from complex and as yet unknown mechanisms.

CONCLUSIONS

Recoil carbon-11 products resulting from the irradiation of liquid methanol, ethanol, 1-propanol, 2-propanol, acetone, diethyl ether, methyl acetate and methyl formate with 70 MeV bremsstrahlung have been identified and their yields determined. The effects of changes in dose and of the presence of iodine as scavenger were measured. The results were interpreted in terms of the reactions of ^{11}C , ^{11}CH , $^{11}\text{CH}_2$ and $^{11}\text{CH}_3$ with the parent compound and the reactions of these radicals, other radical intermediates or product molecules with radiation produced radicals or added scavengers.

In all systems studied, radiation modification of the primary products was observed. For the methanol and ethanol systems, where a study of the complete product spectrum was attempted, relationships were established between a number of the dose dependent products. In methanol, the solvated electron and the $\cdot\text{CH}_2\text{OH}$ radical were shown to be the primary radicals responsible for the dose dependence of the yields of labelled products: carbon monoxide, carbon dioxide, acetaldehyde and 1,2-propanediol.

A complete reaction scheme was proposed for the reactions of recoil carbon in methanol. It was observed that the intermediate carbenes, $^{11}\text{CH}_2$, $\text{H}-^{11}\text{CCH}_2\text{OH}$ and $\text{CH}_3\text{O}-^{11}\text{CH}$ insert more readily in the O-H than the C-H bond. No evidence for C-O insertion reactions by ^{11}CH or the intermediate carbenes was obtained although carbon atoms appear to react with this bond. This reactions may be by way of cyclic intermediate, thus accounting for the production of acetaldehyde and methyl acetate.

The ethanol data was interpreted in light of the proposed reaction sequence in methanol. However, because of the increased complexity of this system, a detailed analysis of the data was more difficult. The reactions attributed to the solvated electron in methanol were not observed in ethanol because the radiolysis product acetaldehyde acts as an efficient electron scavenger. In ethanol, the radical $\text{CH}_2\dot{\text{C}}\text{HOH}$ was shown to participate in a number of the reaction sequences involving thermal radical intermediates. The extreme scavenger dependence of the dialkoxymethane yields in methanol and ethanol was attributed to the scavenging of radical intermediates by iodine and the subsequent reaction of the products, α -iodoethers, with the solvent.

The influence of molecular structure on the yields of the C_1 and C_2 products was studied in all of the compounds. The yield of ethylene- ^{11}C in iodine scavenged 1- and 2-propanol and the dependence of its yield in methanol and diethyl ether on the iodine concentration were used as a basis of a proposed mechanism for the production of ethylene, involving the insertion of the methyne radical into a primary C-H bond followed by rapid unimolecular decomposition.

The yields of ^{11}CO , one of the major products resulting from the reactions of recoil carbon in these systems, were interpreted in terms of a statistical model for carbon atom reactions. Although a few ambiguities exist in the model, the data give important insights into the mechanism for its production. In the alcohol and ether systems, ^{11}CO was considered to result from the reaction of an energetic carbon atom with the nonbonding electrons on oxygen. Deoxygenation with formation of carbon monoxide was also observed to occur at the $\text{C}=\text{O}$ group.

The formation of ^{11}CO was nearly three times as probable at a >C=O group as at a C-O-H or C-O-C group.

The yields of all products were determined on an absolute basis and the sample dose was estimated using cobalt glass dosimetry. No degradative studies were performed although such information would be useful. Because of the limitations present at the synchrotron, phase studies were impossible. Redesign of the acceleration chamber and irradiation port is now under way and phase studies at lower doses may be a future possibility.

As occurs in any research project, more questions develop than are answered and much research is still required in these systems if the details of the proposed reaction sequences are to be fully understood. It is sincerely hoped that this research will provide stimulation for further investigation in this area.

BIBLIOGRAPHY

1. Szilard, L. and Chalmers, T. A., *Nature*, 134, 462 (1934).
2. Fermi, E., Amaldi, E., D'Agostino, O., Rasetti, F. and Segre', E., *Proc. Roy. Soc., Ser. A*, 146, 483 (1934).
3. Amaldi, E., D'Agostino, O., Fermi, E., Pontecorro, B., Rasetti, F. and Segre', E., *Proc. Roy. Soc., Ser. A*, 149, 522 (1935).
4. Glueckauf, E. and Fay, J. W., *J. Chem. Soc.*, 390 (1936).
5. Fay, J. W. and Paneth, F. A., *J. Chem. Soc.*, 384 (1936).
6. Suess, H., *Z. Phys. Chem. (Leipzig)*, 45, 297 (1940).
7. Barkas, W. H., Carlson, P. R., Henderson, J. E. and Moore, W. H., *Phys. Rev.*, 58, 577 (1940).
8. Libby, W. F., *Science*, 93, 283 (1941).
9. Libby, W. F., *J. Am. Chem. Soc.*, 69, 2523 (1947).
10. Friedman, L. and Libby, W. F., *J. Chem. Phys.*, 17, 647 (1949).
11. Miller, J. M., Gryder, J. W. and Dodson, R. W., *J. Chem. Phys.*, 18, 579 (1950).
12. Miller, J. M. and Dodson, R. W., *J. Chem. Phys.*, 18, 865 (1950).
13. Capron, P. C. and Oshima, Y., *J. Chem. Phys.*, 20, 1403 (1952).
14. Estrup, P. J. and Wolfgang, R., *J. Am. Chem. Soc.*, 82, 2665 (1960).
15. Estrup, P. J. and Wolfgang, R., *J. Am. Chem. Soc.*, 82, 2661 (1960).
16. Wolfgang, R., *J. Chem. Phys.*, 39, 2983 (1963).
17. Goldhaber, S. and Willard, J. E., *J. Am. Chem. Soc.*, 74, 318 (1952).
18. Hornig, J. F., Levey, G. and Willard, J. E., *J. Chem. Phys.*, 20, 1556 (1952).
19. Levey, G. and Willard, J. E., *J. Am. Chem. Soc.*, 74, 6161 (1952).
20. Willard, J. E., *Ann. Rev. Nuclear Sci.*, 3, 193 (1953).
21. Suryanarayana, B. and Wolf, A. P., *J. Phys. Chem.*, 62, 1369 (1958).
22. Harbottle, G. and Sutin, N., *J. Phys. Chem.*, 62, 1344 (1958).

23. MacKay, C. and Wolfgang, R., *Radiochim. Acta*, 1, 42 (1962).
24. Willard, J. E., *Ann. Rev. Phys. Chem.*, 6, 141 (1955).
25. Harbottle, G. and Sutin, N., *Advan. Inorg. Chem. Radiochem.*, 1 267 (1959).
26. Wolf, A. P., *Ann. Rev. Nuclear Sci.*, 10, 259 (1960).
27. Willard, J. E., *in* Chemical effects of nuclear transformations, Vol. 1, pp. 215-217, Vienna, Austria, International Atomic Energy Agency, 1961.
28. Harbottle, G., *in* Radioisotopes in the physical sciences and industry, Vol. 2, pp. 375-391, Vienna, Austria, International Atomic Energy Agency, 1962.
29. Siuda, A., Polish Atomic Energy Commission Information Center Report, 6, (1963).
30. Campbell, I. G., *Advan. Inorg. Chem. Radiochem.*, 5, 135 (1963).
31. Walton, G. N., *Radiochim. Acta*, 2, 108 (1964).
32. Wolf, A. P., *Adv. in Phys. Org. Chem.*, 2, 201 (1964).
33. Willard, J. E., *in* Chemical effects of nuclear transformations, Vol. 1, pp. 221-235, Vienna, Austria, International Atomic Energy Agency, 1965.
34. Wolfgang, R., *Progr. Reaction Kinetics*, 3, 97 (1965).
35. Wolfgang, R., *Ann. Rev. Phys. Chem.*, 16, 15 (1965).
36. James, A. T. and Martin, A. J. P., *Analyst (London)*, 77, 915 (1952).
37. James, A. T. and Martin, A. J. P., *Biochem. J.*, 50, 679 (1952).
38. Evans, J. B. and Willard, J. E., *J. Am. Chem. Soc.*, 78, 2909 (1956).
39. Ruben, L. and Kamen, M., *Phys. Rev.*, 59, 349 (1941).
40. Yankwich, P. E., Rollefson, G. K. and Norris, T. H., *J. Chem. Phys.*, 14, 131 (1946).
41. Yankwich, P. E., *J. Chem. Phys.*, 15, 374 (1947).
42. Norris, L. and Snell, A., *Nucleonics*, 5, No. 3, 18 (1949).
43. Schrodtt, A. G. and Libby, W. F., *J. Am. Chem. Soc.*, 76, 3100 (1954).

44. Yankwich, P. E. and Vaughan, J. D., *J. Am. Chem. Soc.*, 76, 5851 (1954).
45. Wolf, A. P., Redvanly, C. S. and Christian, R., *Nature*, 176, 831 (1955).
46. Wolf, A. P., *Angew. Chem.*, 71, 237 (1959).
47. Wolf, A. P., Gordon, B. and Anderson, R. C., *J. Am. Chem. Soc.*, 78, 2657 (1956).
48. Wolf, A. P., Redvanly, C. S. and Anderson, R. C., *J. Am. Chem. Soc.*, 79, 3717 (1957).
49. Yang, J. Y. and Wolf, A. P., *J. Am. Chem. Soc.*, 82, 3315 (1960).
50. Visser, R., Redvanly, C. R., Sixma, F. L. J. and Wolf, A. P., *Rec. Trav. Chim. Pays-Bas*, 80, 533 (1961).
51. Wolf, A. P., *in* Chemical effects of nuclear transformations, Vol. 2, pp. 3-15, Vienna, Austria, International Atomic Energy Agency, 1961.
52. Oae, S., Redvanly, C. S. and Wolf, A. P., *Abstracts Am. Chem. Soc.*, 146, 31C (1964).
53. Yankwich, P. E., *Can. J. Chem.*, 34, 301 (1956).
54. Yankwich, P. E. and Cornman, W. R., *J. Am. Chem. Soc.*, 78, 1560 (1956).
55. MacKay, C. F. and Libby, W. F., *J. Am. Chem. Soc.*, 79, 6366 (1957).
56. Cacace, F., Giacomello, G. and Zifferero, M., *in* Chemical effects of nuclear transformations, Vol. 2, pp. 51-55, Vienna, Austria, International Atomic Energy Agency, 1961.
57. Yang, J. Y. and Wolf, A. P., *J. Am. Chem. Soc.*, 82, 4488 (1960).
58. Cacace, F. and Wolf, A. P., *J. Am. Chem. Soc.*, 84, 3202 (1962).
59. Yost, D. M., Ridenour, L. N. and Shinohara, K., *J. Chem. Phys.*, 3, 133 (1935).
60. Rowland, F. S. and Libby, W. F., *J. Chem. Phys.*, 21, 1493 (1953).
61. MacKay, C. and Wolfgang, R., *J. Am. Chem. Soc.*, 83, 2399 (1961).
62. Lang, C. E. and Voigt, A. F., *J. Phys. Chem.*, 65, 1542 (1961).
63. Stoecklin, G. and Wolf, A. P., *J. Am. Chem. Soc.*, 85, 229 (1963).

64. Ache, H. J. and Wolf, A. P., J. Am. Chem. Soc. 88, 888 (1966).
65. Dubrin, J., MacKay, C. and Wolfgang, R., J. Chem. Phys., 41, 3267 (1964).
66. Ache, H. J. and Wolf, A. P. in Chemical effects of nuclear transformations, Vol. 1, pp. 107-120, Vienna, Austria; International Atomic Energy Agency, 1965.
67. Dubrin, J., MacKay, C. and Wolfgang, R., J. Am. Chem. Soc., 86, 4747 (1964).
68. Skell, P. S. and Engel, R. R., J. Am. Chem. Soc., 87, 1135 (1965).
69. Skell, P. S. and Engel, R. R., J. Am. Chem. Soc., 87, 1135 (1965).
70. Skell, P. S. and Engel, R. R., J. Am. Chem. Soc., 87, 2493 (1965).
71. Skell, P. S. and Engel, R. R., J. Am. Chem. Soc., 88, 3749 (1966).
72. Skell, P. S. and Engel, R. R., J. Am. Chem. Soc., 89, 2912 (1967).
73. MacKay, C., Polak, P., Rosenberg, H. E. and Wolfgang, R., J. Am. Chem. Soc., 84, 308 (1962).
74. Marshall, M., Wolfgang, R. and MacKay, C., Tetrahedron Lett., 29, 2033 (1963).
75. Dubrin, J., MacKay, C. and Wolfgang, R., J. Am. Chem. Soc., 86, 959 (1964).
76. Rack, E. P. and Voigt, A. F., J. Phys. Chem., 67, 198 (1963).
77. Wolf, A. P. and Stoecklin, G., Abstracts Am. Chem. Soc., 146, 32C (1964).
78. MacKay, C., Nicholas, J. and Wolfgang, R., J. Am. Chem. Soc., 89, 5758 (1967).
79. Safrany, D. R., Reeves, R. R. and Harteck, P., J. Am. Chem. Soc., 86, 3160 (1964).
80. Braun, W., McNesby, J. R. and Bass, A. M., Chem. Eng. News, 44, No. 39, 52 (1966).
81. Doering, W. von E., BATTERY, R. G., Laughlin, R. G. and Chaudhuri, N., J. Am. Chem. Soc., 78, 3224 (1956).
82. Doering, W. von E. and Prinzbach, H., Tetrahedron, 6, 24 (1959).
83. Frey, H. M. and Kistiakowsky, G. B., J. Am. Chem. Soc., 79, 6373 (1957).

84. Mesich, F. S., Deactivation of reaction complexes in the recoil chemistry of ^{11}C , unpublished Ph.D. thesis, Ames, Iowa, Library, Iowa State University of Science and Technology, 1965.
85. Jewett, G. L., Recoil chemistry of carbon-11 in C_5 hydrocarbons, fragmentation and stabilization, unpublished Ph.D. thesis, Ames, Iowa, Library, Iowa State University of Science and Technology, 1967.
86. Frey, H. M., J. Am. Chem. Soc., 80, 5005 (1958).
87. Anet, F. A. L., Bader, R. F. W. and Van der Auwera, A. M., J. Am. Chem. Soc., 82, 3217 (1960).
88. Carr, R. W. Jr., J. Phys. Chem., 70, 1970 (1966).
89. Richardson, D. B., Simmons, M. C. and Dvoretzky, I., J. Am. Chem. Soc., 83, 1934 (1961).
90. Carr, R. W. and Kistiakowsky, G. B., J. Phys. Chem., 70, 118 (1966).
91. Butler, J. N. and Kistiakowsky, G. B., J. Am. Chem. Soc., 82, 759 (1960).
92. Schuler, R. H., J. Phys. Chem., 68, 1618 (1964).
93. Clark, D. E. and Voigt, A. F., J. Am. Chem. Soc., 87, 5558 (1965).
94. Edwards, W. J. and McCallum, K. J., Can. J. Chem., 34, 189 (1956).
95. Sharman, L. J. and McCallum, K. J., J. Am. Chem. Soc., 77, 2989 (1955).
96. McCallum, H. J. and Edwards, W. J., in Chemical effects of nuclear transformations, Vol. 2, pp. 57-62, Vienna, Austria, International Atomic Energy Agency, 1961.
97. Dubrin, J., MacKay, C., Pandow, M. L. and Wolfgang, R., J. Inorg. Nucl. Chem., 26, 2113 (1964).
98. MacKay, C., Pandow, M., Polak, D. and Wolfgang, R., in Chemical effects of nuclear transformations, Vol. 2, pp. 17-26, Vienna, Austria, International Atomic Energy Agency, 1961.
99. Moll, N. G. and Thompson, W. E., J. Chem. Phys., 44, 2684 (1966).
100. Pandow, M., MacKay, C. and Wolfgang, R., J. Inorg. Nucl. Chem., 14, 153 (1960).
101. MacKay, C., Pandow, M. and Wolfgang, R., J. Geophys. Res., 68, 3929 (1963).

102. Cacace, F. and Wolf, A. P., *J. Am. Chem. Soc.*, 87, 5301 (1965).
103. Cacace, F. Stoecklin, G. and Wolf, A. P., *Radiochim. Acta*, 5, No. 3, 155 (1966).
104. Diehm, R., The reactions of recoil carbon atoms in the acetamide system, unpublished Ph.D. thesis, Lawrence, Kansas, University of Kansas, 1964. Original not available; abstracted in *Nuclear Science Abstracts*, 20, 496 [Abstract No. 4026] (1964).
105. Ache, H. J. and Wolf, A. P., *Radiochim. Acta*, 6, No. 1, 32, (1966).
106. Schrodt, A. G. and Libby, W. F., *J. Am. Chem. Soc.*, 78, 1267 (1956).
107. Stief, L. J. and De Carlo, V. J., *J. Chem. Phys.*, 43, 2552 (1965).
108. Skell, P. S. and Engel, R. R., *J. Am. Chem. Soc.*, 87, 4663 (1965).
109. Skell, P. S. and Harris, R. F., *J. Am. Chem. Soc.*, 87, 5807 (1965).
110. Skell, P. S., Plonka, J. H. and Engel, R. R., *J. Am. Chem. Soc.*, 89, 1748 (1967).
111. Skell, P. S. and Harris, R. F., *J. Am. Chem. Soc.*, 88, 5933 (1966).
112. Sprung, J., Winstein, S. and Libby, W. F., *J. Am. Chem. Soc.*, 87, 1812 (1965).
113. Marshall, M., MacKay, C. and Wolfgang, R., *J. Am. Chem. Soc.*, 86, 4741 (1964).
114. Nicholas, J. E., MacKay, C. and Wolfgang, R., *J. Am. Chem. Soc.*, 87, 3008 (1965).
115. Nicholas, J., MacKay, C. and Wolfgang, R., *J. Am. Chem. Soc.*, 88, 1610 (1966).
116. Nicholas, J., MacKay, C. and Wolfgang, R., *Tetrahedron*, 22, 2967 (1966).
117. Baxendale, J. H. and Mellows, F. W., *J. Am. Chem. Soc.*, 83, 4720 (1961).
118. Morton, A. A. and Mark, J. G., *Ind. Eng. Chem.*, 6, 151 (1943).
119. Fieser, L. F., *Experiments in organic chemistry*, 3rd ed., revised, Boston, Mass., D.C. Heath and Company. c1957.
120. Hersh, C. K., *Molecular sieves*, New York, N. Y., Reinhold Publishing Corp. 1961.

121. Arthur, P., Haynes, W. M., and Uarga, L. P., *Anal. Chem.* 38, 1630 (1966).
122. Hammond, W. A., *Drierite*, Columbus, Ohio, Stoneman Press. c1961.
123. De Vries, D. B. and Voigt, A. F., U.S. Atomic Energy Commission Report, IS-866 [Iowa State University of Science and Technology, Ames. Inst. for Atomic Research], 1964.
124. Matkovich, C. E., Recoil reactions of C-11 in binary mixtures of liquid hydrocarbons, unpublished M.S. thesis, Ames, Iowa, Library, Iowa State University of Science and Technology, 1967.
125. Wolfgang, R. and Rowland, F. S., *Anal. Chem.*, 30, 903 (1958).
126. Clark, D. E., Reactions of recoil carbon-11 in liquid hydrocarbons, unpublished Ph.D. thesis, Ames, Iowa, Library, Iowa State University of Science and Technology, 1965.
127. Rack, E. P., Lang, C. E. and Voigt, A. F., *J. Chem. Phys.*, 38, 1211 (1963).
128. Korthoven, P. J. M. and Carlson, F. S., U.S. Atomic Energy Commission Report, IS-1501 [Iowa State Univ. of Science and Technology, Ames. Inst. for Atomic Research], 1967.
129. Kreidl, N. J. and Blair, G. E., *Nucleonics*, 14, No. 3, 82 (1956).
130. Kreidl, N. J. and Blair, G. E., *Nucleonics*, 17, No. 10, 58 (1959).
131. Blair, G. E., *J. Am. Ceramic Soc.*, 43, 426 (1960).
132. Schall, P., *Nucleonics*, 17, No. 10, 68 (1959).
133. Sutton, H. C. and Rotblat, J., *Nature*, 180, 1332 (1957).
134. Hammer, C. L. and Bureau, A. F., *Rev. Sci. Instrum.*, 26, 594 (1955).
135. Hammer, C. L. and Bureau, A. F., *Rev. Sci. Instrum.*, 26, 598 (1955).
136. Bureau, A. F. and Hammer, C. L., *Rev. Sci. Instrum.*, 32, 93 (1961).
137. Cook, B. G., Baglin, J. E. E., Bradford, J. N. and Griffin, J. E., *Phys. Rev.*, 143, 724 (1966).
138. Harvey, B. G., *Ann. Rev. Nuclear Sci.*, 10, 235 (1960).
139. Bohr, N., *Kgl. Danske Videnskab. Selskab, May-fys. Medd.*, 18, No. 8 (1948).
140. Herzberg, G., *Atomic spectra and atomic structure*, New York, N.Y., Dover Publications, Inc., 1944.

141. Massey, H. S. W. and Burhop, E. H. S., *Electronic and ionic impact phenomena*, Oxford, England, Oxford University Press, 1952.
142. Friedman, L., Long, A. and Wolfsberg, M., *J. Chem. Phys.*, 27, 613 (1957).
143. Wilmenius, P. and Lindholm, E., *Arkiv Fys.*, 21, 97 (1962).
144. Theard, L. M. and Burton, M., *J. Phys. Chem.*, 67, 59 (1963).
145. Ekstrom, A. and Garnett, J. L., *J. Phys. Chem.*, 70, 324 (1966).
146. Meshitsuka, G. and Burton, M., *Radiat. Res.*, 8, 285 (1958).
147. Thomas, J. K., Gordon, S. and Hart, E. J., *J. Phys. Chem.*, 68, 1524 (1964).
148. Grossweiner, L. I. and Matheson, M. S., *J. Phys. Chem.*, 61, 1089 (1957).
149. Hoffmann, R. W. and Haeuser, H., *Tetrahedron Lett.*, 197 (1964).
150. Franzen, V. and Fikentscher, L., *Ann. Chem., Liebigs*, 617, 1 (1958).
151. Hart, E. J., Thomas, J. K. and Gordon, S., *Radiat. Res. Suppl.*, 4, 74 (1964).
152. Hart, E. J., Gordon, S. and Thomas, J. K., *J. Phys. Chem.*, 68, 1271 (1964).
153. Holian, J., Scholes, G. and Weiss, J. J., *Nature*, 191, 1386 (1961).
154. Scholes, G., Simic, M. and Weiss, J. J., *Nature*, 188, 1019 (1960).
155. Cram, D. J. and Hammond, G. S., *Organic chemistry*, 2nd ed., New York, N.Y., McGraw-Hill Book Co., Inc., 1964.
156. Simmons, L., *Chem. Rev.*, 55, 301 (1955).
157. McCabe, C. L. and Warner, J. C., *J. Am. Chem. Soc.*, 70, 4031 (1948).
158. Spinks, J. W. T. and Woods, R. J., *An introduction to radiation chemistry*, New York, N.Y., John Wiley and Sons, Inc., 1964.
159. Hayon, E. and Weiss, J. J., *J. Chem. Soc.*, 3962 (1961).
160. Hirota, K. and Hatada, M., *Bull. Chem. Soc. Jap.*, 34, 1644 (1961).
161. Kurihara, T. and Hotta, H., *Bull. Chem. Soc. Jap.*, 37, 1448 (1964).
162. Ausloos, P. and Trumbore, C. N., *J. Am. Chem. Soc.*, 81, 3866 (1959).

163. Hummel, R. W., *Trans. Faraday Soc.*, 56, 234 (1960).
164. Hirota, K., Iizuka, S., Ochi, H. and Hatada, K., *Bull. Chem. Soc. Jap.*, 36, 115 (1963).

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APPENDIX

Table 18. Chromatographic columns used for product separations^a

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1. 18'-30% Carbowax 20M (F&M Scientific) on Chromosorb W A. W. DMCS, 45-60 Mesh (F&M Scientific).
 2. 18' and 30'-30% Tripropionin (K&K Laboratories) on Chromosorb P, 45-60 Mesh (F&M Scientific).
 3. 30'-35% 2-Ethylhexyl Acetate (Eastman Organic) on Chromosorb P, 45-60 Mesh (F&M Scientific).
 4. 28'-30% Diisodecyl Phthalate (Monsanto) on Chromosorb W A. W., 45-60 Mesh (F&M Scientific).
 5. 20'-30% Triisovalerin (K&K Laboratories) on Chromosorb W A. W. DMCS, 45-60 Mesh (F&M Scientific).
 6. 20'-30% Di Butoxy Tetraglycol (Carbide and Carbon Chemicals) on Chromosorb W. A. W. DMCS, 45-60 Mesh (F&M Scientific).
 7. 14' - Molecular Sieve-Linde Type 5A (Matheson Coleman & Bell) 40-60 Mesh.
 8. 10' - Silica Gel (Fisher Scientific), 14-20 Mesh.
 9. 20'-20% Tricaprylin (K&K Laboratories) on Anakrom PA, 50-60 Mesh (Analabs).
 10. 20'-25% Ethyl Cinnamate (Matheson Coleman & Bell) on Chromosorb W A. W., 45-60 Mesh (F&M Scientific).
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^aAll columns were fabricated from 8 mm Pyrex tubing.