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DEACTIVATION OF REACTION COMPLEXES IN THE RECOIL CHEMISTRY OF ^{11}C

by

Frank Gerald Mesich

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INTRODUCTION

Recoil Chemistry

The study of the chemistry of atoms with energies above thermal or ground state energies is called Hot Atom Chemistry. Recoil chemistry may be considered a subdivision of hot atom chemistry in that the reactions studied are those of kinetically energetic atoms produced and given this energy by a nuclear transformation. Hot atom chemistry is concerned with the study of reactions which occur at energies above threshold energy. In a chemical reaction, there is a dependence of collisional efficiency on energy. This efficiency will increase from zero at the threshold energy, reach a maximum at some energy, and decrease as the energy of the atom becomes too high for the formation of a stable product. Unfortunately, the energy dependence of collisional efficiency is not known in most cases. The study of reactions at thermal or near-thermal energies, while being experimentally convenient, is limited to threshold processes.

Some information about the energy dependence of the reactions of energetic species has been gained through mass-spectrographic techniques (1,2). This information is of limited usefulness in the interpretation of the reactions of recoil atoms because of the ionic form of the hot species and the dependence of the interactions on long range ion-dipole forces.

Energetic atoms or fragments may also be produced photochemically. This technique has the advantage that the energies of the fragments can be known, but the disadvantage that the translational energy of the fragments is low (2000 Å = 2.3 ev). Ionizing radiation may also be used but typical ionization potentials lie in the range of about 10 ev, still relatively low in energy.

Most of the recent studies of the reactions of hot atoms have used the recoil from a nuclear transformation as the source of energetic atoms. The energies produced can range from a few electron volts to several MeV. An additional factor which makes this method convenient is that in many cases the recoil atom is radioactive and small amounts of tagged products may be followed with relative ease by the use of radiochemical techniques.

Historical Background

The historical development of hot atom chemistry may be traced back to 1904 when Brooks (3) observed that the decay products of the radioactive element radon displayed a greater volatility than expected. The chemical effects associated with this phenomenon were first investigated by Lind and Bardwell (4) in 1924. They measured the rate of reaction between hydrogen and oxygen both in the presence and in the absence of recoil atoms. Fermi and his co-workers (5) found in 1934 that upon neutron irradiation of various elements with atomic number greater than 30, the products formed were isotopic with the target elements and could not be separated from them by normal chemical means. The (n,γ) reaction of iodine in ethyl iodide was studied in the same year by Szilard and Chalmers (6) and the results presented in a now-classic paper. Consideration of conservation of momentum suggested that a separation of an atom from its parent compound by neutron irradiation should be possible. Neutron irradiation of ethyl iodide was followed by the addition of iodine carrier in the presence of a reducing agent. Precipitation was then carried out with silver ion, demonstrating the fact that a substantial fraction of the radioactive iodine was present in inorganic form, differing from the parent compound. They then postulated that this effect could be observed in other systems provided that the following criteria are met:

1. The product of the nuclear reaction is radioactive.
2. Isotopic exchange between the recoil atom and atoms

in the parent compound does not occur.

Soon after this work, it was shown that irradiation with thermal neutrons could cause an effect similar to that demonstrated with fast neutrons (7). The effect was then suggested as being due to the recoil energy imparted to the iodine atom by the emission of a gamma ray in the $^{127}I(n,\gamma)^{128}I$ nuclear reaction. Since this time, such reactions of recoil atoms have often been termed Szilard-Chalmers reactions.

Soon after it was demonstrated that the recoil atoms could have interesting chemical properties, Glückauf and Fay (8) initiated a study of the (n,γ) reaction in several liquid phase alkyl halides. Carrier materials were added to the parent compound after irradiation and fractional distillations were carried out in order to determine the final state of the radio-iodine. The distillations showed the presence of organic compounds other than the parent compound and gave the first indications that chemical synthesis could be the result of the reactions of the recoil atom. The fact that the chemical bonds between a recoil atom and its parent compound were broken in almost every case was first mentioned by Suess (9) and Libby (10). This meant that activity found in the parent compound was due to the reentrance of the recoil atom into another molecule. In 1940 the (γ,n) reaction was also shown to be useful for the study of hot atom chemistry (11), giving results qualitatively similar to those of the (n,γ) reaction in ethyl bromide.

The primary problems concerned with hot atom chemistry at this time were analytical in nature. Distillation techniques were the most widely used for the separation and identification of products. This involved the addition of carriers to the reaction mixture. One had to guess at the correct carriers to add, the analysis was tedious and long half-life materials were required. Because of the requirement for a long half-life, irradiation times were long and the associated radiation dose often high, in some cases affecting the product distribution. In 1952 James and Martin (12,13) described a procedure for the analysis of organic compounds involving the use of gas-liquid chromatography. The use of gas chromatography applied to the analysis of products formed in the reactions of recoil atoms was first described by Evans and Willard (14) in 1956. They applied the technique to the products formed in the recoil chemistry of organic halides. With this development, the study of hot atom chemistry could be extended to the reactions of atoms with relatively short half-lives as the analysis of a wide range of products could be made in a period of an hour or less. Since 1953, several reviews have been published covering the entire field of hot atom chemistry (15-24).

Carbon Recoil Chemistry

The study of the recoil chemistry of carbon has attracted considerable recent interest. The carbon isotopes which may be conveniently produced are ^{14}C and ^{11}C. Carbon-14 is produced by the $^{14}N(n,p)^{14}C$ reaction giving recoil atoms with an energy of 0.042 MeV. Its half-life is very long, 5730 yr., and the cross section for the nuclear reaction with thermal neutrons is 1.75 barnes (25). The long half-life simplifies the analytical problems but irradiation times must be very long to produce workable amounts of activity at available neutron fluxes (10^{11}-10^{14} n/cm^2/sec.). Irradiation times may range from days to weeks with the accompanying radiation doses quite high. In some cases this high radiation dose causes radiation damage in the system and affects product distributions. Another serious drawback to the use of nucleogenically produced ^{14}C is the requirement for a nitrogen source in the sample rendering the study of pure hydrocarbon systems impossible.

Much of the recent work on the recoil chemistry of carbon involves the use of the short-lived carbon-11 isotope. Although the short half-life, 20.4 min. (25), precludes a lengthy analysis, ^{11}C atoms may be produced by a variety of methods using fairly short irradiation times contributing only a low dose to the sample. The following reactions have been used for the production of ^{11}C: $^{14}N(p,\alpha)^{11}C$, $^{12}C(n,2n)^{11}C$, $^{12}C(p,pn)^{11}C$, $^{12}C(\gamma,n)^{11}C$ and $^{16}O(p,pn\alpha)^{11}C$. Typical carbon-11 recoil energies are in the range of ~0.4-2.1 MeV. The bond energy of a typical chemical bond will be on the order of a few ev and the recoil carbon will in every case have sufficient recoil energy to break all of its chemical bonds. Another method of production of ^{11}C has been used by Wolfgang and co-workers at Yale University. The procedure makes use of a linear accelerator in which carbon-12 atoms are accelerated to 120 MeV and passed through a platinum foil, the carbon undergoing a neutron stripping reaction, and the ^{11}C is scattered into the reaction vessel.

The discovery of ^{11}C by Yost, Ridenour and Shinohara (26) and ^{14}C by Ruben and Kamen (27) included the first studies of these atoms in inorganic solids. Rowland and Libby (28) studied the reactions of ^{11}C in sodium carbonate and in solid and liquid carbon dioxide. Their work concerned itself only with CO and CO_2 production. It is probable that sulfuric acid used in their systems reacted with some of the original products, converting them to CO and CO_2. In 1955 Sharmon and McCallum (29) also studied the reactions of ^{11}C in sodium carbonate. They observed a variety of products, the highest yield being $(COOH)_2$ at 39% with OHCCOOH accounting for 24% of the activity. Small amounts of other acids and alcohols were also observed with only a trace of CO. The reactions of carbon-14 recoiling in ammonium bromide were studied by Yankwich and Vaughan (30) who found 80% of the activity in methylamine, 7.5% in methane and 1.8% in methyl bromide. This work was significant in that it was the first in which almost all the activity could be assigned to known products.

The study of the reactions of recoil carbon atoms in the gaseous phase has been especially fruitful in elucidating the nature of the reactions taking place. These studies have been carried out using ^{11}C because of the greater ease of production of the atoms in the gaseous phase. Gas phase studies have been carried out on a variety of inorganic molecules and oxides. In the reaction of ^{11}C in O_2 (31-34), CO (33,34), CO_2 (33,34), SO_2 (34) and NO_2 (34), ^{11}CO was the major product.

In studies of NO and NO_2, significant amounts of ^{11}CO and ^{11}CN were observed (34). The fact that ^{11}CO and ^{11}CN were observed supports the interpretation that the attack of the carbon atom on pi-bonded inorganic molecules is "end-on" rather than into the pi bond.

Early work on the reactions of ^{14}C with ammonia indicated that $^{14}CH_4$ was the major product (35). The reactions of ^{11}C in the same system (33) showed only a small methane yield, indicating that the high radiation dose received in the neutron irradiations had caused severe radiation damage in the primary ^{14}C-containing products.

Studies have been made of the reactions of recoil carbon atoms with a number of hydrocarbons in the gas phase. These studies generally include the use of radical scavengers and inert gas moderators. Systems studied include CH_4 (36,37), C_2H_6 (38,22), C_3H_8 (22,33,36,38), isobutane (22,39), n-butane, 2,2-dimethylpropane, 2,3-dimethylbutane, cyclopropane, cyclobutane, cyclopentane and cyclohexane (22). The major product in each system was acetylene. Other unsaturated products were also produced in relatively high yields in these gas phase reactions.

The gaseous system which has had the most complete study is ethylene and the reaction mechanisms proposed for this system are of interest. The products found contained greater yields of C_{n+1} compounds than the spectrum of products from the corresponding alkane (40). Allene was found to be a major product in the ethylene system as well as the usual acetylene (41-44). Degradation experiments showed that most of the allene was center labeled, $HC{=}^{11}C{=}CH$ (41). This indicated that in contrast to the reactions of carbon with inorganic pi-bonded compounds, the attack of the carbon on the ethylene was in a large number of cases directed into the pi bond. Double tracer techniques involving deuterated ethylene demonstrated that the allene contained all the hydrogens from the original ethylene molecule (42), also indicating attack on the double bond. Similar studies have been reported on the formation of acetylene (43). A relatively complete determination of the product spectrum from ethylene has been reported (45) along with the effects of phase change and scavenger on the product spectrum. A substantial amount of 5-carbon products was observed which are thought to be the products of radical reactions.

The study of the reactions of ^{11}C in liquid hydrocarbons is in some respects more difficult than similar work in the gaseous phase. Moderator effects cannot be conveniently observed and the behavior of radical scavengers in the liquid phase is not as well understood as the behavior in the gaseous phase.

As the number of carbon atoms in the parent compound is increased, the product spectrum becomes more varied. For this reason the study of hydrocarbons with more than four carbon atoms has been largely limited to the gaseous products. The products emphasized are usually methane, ethane, ethylene and acetylene with acetylene generally being the most abundant of the four. The dependence of these products on phase has been studied in cyclohexane by Lang and Voigt (46). Rack and Voigt (47) reported the effects of increasing radiation dose on the two-carbon products from cyclohexane with and without iodine scavenger. They found that in unscavenged systems, yields of methane, ethane and ethylene increase with dose while the acetylene yield remains essentially constant. The addition of a radical scavenger decreased the yield of all except acetylene and the dose dependence disappeared. This was reported as being due to the elimination of the radical contributions to the product formation. Similar studies on benzene, cyclohexane, n-hexane, 2-methyl pentane and 2,2-dimethyl butane gave the same results (48). The possible use of oxygen as a scavenger in liquid systems has been investigated for the systems cyclohexane and n-hexane (49). It was found that no effect on the product distribution could be observed at oxygen concentrations up to 7.3 x 10^{-3} mole fraction.

Up to this time, most of the data on the gaseous products from 5- and 6-carbon liquid hydrocarbons was reported as ratios of the yield of a given product to the yield of acetylene. Recently, the percentage yields of the various gaseous products have been reported for a number of hydrocarbons (50, 51). In each case acetylene was the major gaseous product.

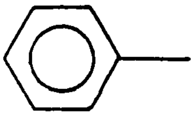
Relatively complete determinations of the product spectrum have been made on only a few cases. Stöcklin and Wolf (38) have reported that 16.5% of the activity produced in the irradiation of ethane is found in products having one more carbon than the parent molecule. The irradiation of liquid ethylene produced 21.7% 3-carbon products (45). Other important and interesting products from the irradiation of ethylene include a variety of 5-carbon products, pentene-1, 10%, pentadienes, 7.7% and pentyne-1, 6.5% with acetylene accounting for 17.5% of the activity. In liquid propane, the major product again is acetylene, 18.2%, with a large amount of ethylene, 12.8%, and 25.3% of the activity found in products containing one more carbon than the parent (33,38).

Isolation and identification of products resulting from hydrocarbons that are liquid at room temperature presents difficulties due to the variety of products which are formed. The alkanes with one more carbon than the parent have been studied in n-pentane by Schrodt and Libby (52), MacKay and Libby (53) and Wolf (54). These determinations all involved the use of ^{14}C and were complicated by the necessity for a nitrogen source in the sample. The results reported by Wolf indicate a relative statistical replacement of hydrogen atoms in the parent with recoil carbons to form hexanes. He determined the ratios of 2-methyl pentane: 3-methyl pentane: n-hexane as 4.3:2.1:6.5 compared to a calculated statistical ratio of 4:2:6, well within the experimental error. The results of Libby and co-workers disagreed with these results and the disagreement was attributed to impurities present in the samples irradiated by Libby.

The reactions of ^{14}C in benzene have been studied by Schrodt and Libby (52) and by Wolf (54). The results of Schrodt and Libby, using aniline as a nitrogen source, showed 2.5% benzene, 1.7% toluene, 3.2% diphenylmethane and 2.1%

triphenylmethane with over 75% of the activity boiling over 359°C. Wolf (54) carried out degradation studies on the toluene formed from benzene and on n-hexane formed from n-pentane to determine the position of the ^{14}C. The results are tiven in Table 1.

Table 1. Degradation[a] of toluene-^{14}C and n-hexane-^{14}C

		CH_3	CH_3-CH_2-CH_2-$CH_2CH_2CH_3$		
Expected	0%	100%	100%	0%	0%
Found	12%	88%	97%	3%	0%

[a]Data of Wolf (54).

The influence of phase, temperature and radical scavenger on the reactions of ^{11}C with benzene was studied by Wolf and Suryanarayana (55). This work concentrated on the formation of benzene and toluene using gas chromatography for separation of the products. Their results are summarized in Table 2. DPPH used as a radical trap lowered the benzene activity while not appreciably affecting the toluene. This indicated that at least some of the benzene was formed from a low energy radical precursor. The toluene was thought to be the result of the reaction of a high energy carbon atom with a benzene molecule.

The reduction in benzene yield with change from liquid to solid phase also indicated that the formation of benzene was due to a radical mechanism and was somewhat diffusion dependent. The effect of temperature led to the same conclusion.

Table 2. Products from ^{11}C + benzene[a]

Experimental conditions	% Benzene	% Toluene
Liquid benzene	4.63	2.28
Liquid benzene + DPPH	2.90	2.32
Solid benzene at 0°	2.46	2.56
Solid benzene at -78°	2.63	2.39
Solid benzene at -195°	3.10	2.94

[a] From reference (55).

Reaction Mechanisms and Theoretical Models

There have been two types of approach to the explanation of the reactions of hot atoms, the physical model or mechanistic approach, and the theoretical model. Purely mathematical attempts to predict the product distribution have had limited success, however there are several treatments worth mentioning.

The first attempt to explain the reactions was proposed by Libby in 1947 (56) who proposed that "billiard ball" collisions of the hot atom with the substrate could be used as a working hypothesis. As an example he used the reaction of recoil ^{82}Br with ethyl bromide to produce $C_2H_5{}^{82}Br$. This process was considered to be the result of the collision of an energetic recoil atom with another Br atom in a parent molecule and was called a hot reaction. Fox and Libby (57) later modified the model to include an epithermal region slightly above thermal energies in order to explain the presence of labeled products other than the parent compound. Reactions in the epithermal region required that the atom have sufficient energy to collide inelastically with a parent molecule, but not enough energy to escape from the solvent cage where radicals produced in the collision could react with the hot atom.

The maximum energy that a recoil atom can transfer in an elastic collision is given by the well known equation:

$$E_M = \frac{4m_1m_2}{(m_1+m_2)^2} E_I \qquad \text{(Eq. 1)}$$

where E_I is the energy of the incident atom, m_1 is the mass of the incident atom, E_M is the maximum transferable energy and m_2 the mass of the target atom.

Libby (56), using the billiard ball hypothesis, derived an expression for organic retention:

$$R = \varepsilon/d \qquad \text{(Eq. 2)}$$

in which R is the organic retention, the fraction of recoil atoms found in organic compounds, ϵ is the threshold energy required for an atom to escape from the cage and d is the bond dissociation energy.

As more information on product distributions became available, the billiard ball hypotheses became less adequate in explaining the reactions. Willard (58) proposed a model known as the "random fragmentation" theory. This approach assumed that in the condensed phases the recoil atom at the end of its track found itself surrounded by a variety of radicals. Combination with these radicals would give a random distribution of products. This theory has been shown to be invalid in a number of cases in which the product distribution is not random but biased in favor of certain products (59-63).

Another theoretical approach using the cage model of Libby was that of Miller, Gryder and Dodson (64). In this model, molecules were dissociated by the impact of the hot atom and combination occurred in the liquid cage. Capron and Oshima (65) also used the same approach with slight modification. In a second paper, Miller and Dodson (66) suggested a theoretical approach free of any mechanistic assumptions. Estrup and Wolfgang (67) proposed a model which was similar to that of Miller and Dodson (66) but refined the treatment considerably. Their basic equation was the same:

$$P = \sum_j \int_{E_L}^{E_1} f_j p_j(E) n(E) dE \qquad \text{(Eq. 3)}$$

in which P is the total probability that a hot atom will combine while undergoing a moderating collision, f_j is the relative probability of collision with component j, $p_j(E)$ is the reaction probability per collision and n(E)dE is the number of collisions made by a hot atom in the energy range E to E + dE. The assumptions made in the evaluation of n(E) are as follows:

1. The recoil atom is initially free and must lose some energy before undergoing reaction.

2. Energy loss is by elastic collision only.

3. The minimum energy required for reaction, E, is large compared to thermal energies.

For the yield of an individual product, they obtain:

$$\frac{N_i}{N_s} = \frac{f}{\alpha} I_i - \frac{f^2}{\alpha^2} K_i + \frac{f^3}{\alpha^3} L_i - \ldots \qquad \text{(Eq. 4)}$$

in which N_i is the number of products of type i, N_s is the total number of hot atoms, α is the average logarithmic energy loss per collision, I_i is the integral of the probability that the hot atom will react at energy E to form product i and K_i, L_i, ... are corrections for the fact that the hot atom may have reacted to give a product at a higher energy. Experimental values A_i and A_s were substituted for N_i and N_s, keeping only the first two terms to give:

$$-\frac{\alpha}{f}\,\frac{A_i}{A_s} = I_i - \frac{f}{\alpha}\,K_i \qquad \text{(Eq. 5)}$$

in which $f = \dfrac{XS}{\sum_j X_i S_i}$, X is the mole fraction of reactant in the mixture, S the collision cross section of X for the hot atom, and X_i and S_i the mole fraction and cross section of component i.

From this expression, I_i can be evaluated by plotting $(\alpha/f)(A_i/A_s)$ versus f/α and taking the intercept. The equation has been tested for data on tritium recoil reactions with gaseous methane and the experimental and calculated results agree quite well (68).

Gordus and Hsiung (69,70) have given a somewhat different treatment using classical mechanics. Their theory includes bond rupture predictions and a random walk with steps of unequal length to explain the initial impulse given the recoil atom. Their model considers the molecule as a set of rigid spheres joined by springs. Unfortunately, this theory and those given above do not lend themselves to the prediction of product distributions in more complex systems such as the reactions of recoil carbon in liquid phase hydrocarbons. Such reactions are, at present, best explained by physical models.

Four operational criteria have been used in differentiating between hot and thermal reactions. The first of these is the dependence of the product distribution on phase. Theoretically, the result of a hot reaction should be independent of phase. Thus if a given product does not change with a change in phase, it may be assumed to be the result of a hot reaction. A product which does show a phase dependence may or may not, however, be due to a hot reaction. The distinction is by no means clear.

The second criteria concerns the temperature dependence of the product distribution. The yield of a compound formed by a hot reaction should be insensitive to temperature changes in a given phase.

Radical scavengers have also been used to differentiate between hot and thermal reactions. Oxygen, iodine and bromine have been used, as well as a variety of organic radical scavengers such as DPPH, diphenylpicryl hydrate. Care must be taken in determining whether a compound added as a radical scavenger is actually acting as a radical trap or competing with the substrate for the hot atom. The actions of a scavenger are somewhat easier to understand in the gaseous than in the condensed phases.

The use of an inert moderator is the most convenient method of distinguishing between hot and thermal reactions in the gas phase. With proper addition of moderator, the hot atom will be degraded in energy to the thermal region through collisions with the moderator without undergoing chemical reactions. An inert gas such as xenon used as a moderator can serve a dual purpose. The ionization potential of xenon is low and the hot atom will be neutralized by charge-transfer reactions with the inert gas. Interpretation of the results is straightforward. If the yield of a product decreases with the addition of more scavenger, the product may be considered as having been formed by a reaction in the hot region. The application of moderators to liquid phase studies has not been successfully accomplished.

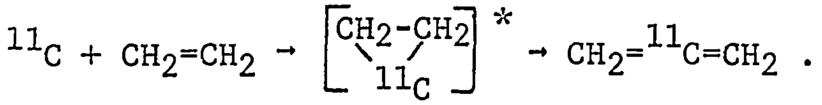
In 1961 MacKay _et al_. (33) suggested a reaction mechanism consisting of the insertion of a hot carbon atom into a carbon-hydrogen bond. MacKay and Wolfgang (36) determined the identity of the products from the reaction of ^{11}C with simple hydrocarbons, and found the product spectrum consistent with the insertion mechanism. For example, the reaction of ^{11}C with ethane would be

$$CH_3CH_3 + {}^{11}C \rightarrow \left[CH_3CH_2 - {}^{11}C\text{-}H\right]^{*} \qquad \text{(Eq. 6)}$$

with the excited complex then decomposing to form acetylene or other fragments.

Further evidence for the insertion mechanism comes from isotopic labeling experiments. Reaction of ^{11}C with CH_3CD_3 yields mostly C_2H_2 and C_2D_2 rather than C_2HD indicating a one-step decomposition of the excited complex to form the acetylene. The implication that the adduct will decompose rather than stabilize in the gas phase is borne out by the fact that isotopic labeling showed that most of the propane formed from ethane arose from a radical precursor rather than from the insertion complex (42).

In an alkene, the ^{11}C seems to show a preference for attack on the double bond rather than carbon-hydrogen insertion. Greater yields of C_{n+1} products are, for example, produced in ethylene than in ethane (40). The mechanism for this reaction has been given as



$$^{11}C + CH_2{=}CH_2 \rightarrow \left[\begin{array}{c} CH_2\text{-}CH_2 \\ \diagdown \;\; \diagup \\ {}^{11}C \end{array}\right]^{*} \rightarrow CH_2{=}{}^{11}C{=}CH_2\ . \qquad \text{(Eq. 7)}$$

This mechanism is analogous to the reactions of CH_2 (71,72) and O atoms (73) in bridging the double bond.

The formation of methane seems to be due to the abstraction of H by $^{11}CH_3$ radicals at thermal energies. Results obtained through the use of iodine scavenger in liquid hydrocarbons indicate that the yield of $^{11}CH_3I$ balances the reduction in methane yield (70). Similar reductions in the methane yield with addition of scavenger have been reported by Rack, Lang and Voigt (48) and Clark (51) in studies of liquid hydrocarbons.

The formation of saturated products has been suggested as being due to the formation and reaction of the $^{11}CH_2$ radical (20) and the ^{11}CH radical has been suggested as a plausible precursor to ethylenic products (75, 76).

Purpose of Investigation

Much of the justification for the insertion mechanism in liquid hydrocarbons has been inferred from the yields of gaseous products. The products most completely studied have been methane and the C_2H_x products. It was felt that more information was needed about the higher boiling compounds formed, particularly the C_{n+1} products from C_n hydrocarbons in the liquid phase.

Therefore, the primary purpose of this investigation is to develop methods for the separation and identification of the higher boiling products, with particular emphasis on radio-gas chromatographic techniques. The product spectra obtained are used as a test of the validity of the insertion mechanism in the liquid phase.

EXPERIMENTAL

Materials

Hydrocarbons used in the irradiations were Research Grade chemicals obtained from Phillips Petroleum Company. The purity of the chemicals was listed at greater than 99 mole percent. They were used without further purification.

Reagents used for the gas chromatographic analysis were obtained from either the Burrell Corp. or from F and M Scientific Corporation. Solid supports used were Chromosorb P, Diatoport P and Diatoport W, all of 45-60 mesh. 14-20 mesh silica gel used as a column packing was obtained from Fisher Scientific Company. Before use it was washed with hot concentrated nitric acid, then with distilled water, and thoroughly dried in an oven at 150°C in order to remove all traces of the nitric acid.

Standardization of columns was made using Commercial Grade gases from The Matheson Company and with liquid hydrocarbons, either Phillips Research Grade or from a Chem-Supply Kit obtained from F and M Scientific Corporation.

Sample Preparation

Pure hydrocarbon samples were prepared in pyrex or quartz bulblets holding about 0.3 ml. of liquid. The bulblets were prepared with thin necks facilitating sealing. In order to eliminate dissolved oxygen and other gaseous impurities, the samples were prepared using a freeze-thaw vacuum degassing procedure.

In this procedure the sample was attached to a vacuum line before sealing and the hydrocarbon was frozen with liquid nitrogen. The valve to the vacuum line was then opened and the frozen sample degassed. The valve was closed and the sample was allowed to melt. This freeze-thaw procedure was repeated three times and the sample was then frozen and sealed under vacuum with a torch. Elimination of oxygen was sufficiently complete so that no CO or CO_2 peaks could be observed after irradiation of a sample.

Sample Irradiation

Irradiations were conducted using the Iowa State University electron synchrotron operated at its maximum energy, ~70 MeV, with the accelerated electrons directed into a lead target, 0.32 cm in thickness. The bremsstrahlung beam produced in the target passed through the sample. The procedure used in the irradiations has been discussed by Hammer and Bureau (77,78, 79).

The $^{12}C(\gamma,n)^{11}C$ nuclear reaction was used to produce the

20.4 min carbon-11. The cross section curve for this reaction has maxima at gamma-ray energies of 21.6, 22.0, 23.2 and 25.4 MeV (80). Using these energies, the recoil energies of the ^{11}C at the cross section maxima may be calculated using the following equation.

$$E_R = (E_\gamma + Q)\frac{m_1}{m_1+m_2} \qquad \text{(Eq. 8)}$$

where E_R is the recoil energy of the ^{11}C, E_γ is the incident gamma ray energy, Q is the energy of reaction, -18.7 MeV, m_1 is the neutron mass and m_2 the mass of the ^{11}C. The recoil energies corresponding to the cross section maxima are 0.24, 0.27, 0.37 and 0.56 MeV. As gamma rays of energies up to 70 MeV are present, the average recoil energy of the carbon-11 is estimated to be ~0.5 MeV. Approximately 10^9 carbon-11 atoms are produced in a typical irradiation.

Several factors contribute to the total radiation dose received by the sample. In addition to the bremsstrahlung, there are contributions to the dose from x-rays and electrons of various energies.

The electron beam of the synchrotron is discontinuous with a pulse duration of about 4 x 10^{-8} sec and time between pulses of about 1.7 x 10^{-2} sec. Each burst contains 10^8-10^{11} electrons with an average number per burst of about 10^9 (51).

Using this average value with 70 MeV as the operating energy, the total energy delivered by the beam is ~2.5 x 10^{20} ev/min.

The dose rate actually received by the sample has been estimated by Rack, Lang and Voigt (48) as ~10^{19} ev/gm-min. Their estimate was made on the basis of the disappearance of iodine color in irradiations of 2,2-dimethylbutane. Clark (51) used two separate methods of determining dose rate in the synchrotron. Fricke dosimetry gave a value of ~1.2 x 10^{19} ev/gm-min and the use of a cobalt glass dosimeter gave ~10^{19} ev/gm-min. The procedures used in these determinations were limited because of the high dose rate and contributions of different types of radiation but the agreement between the three methods indicated an actual dose rate on the order of 10^{19} ev/gm-min.

These measurements of dose rate may be somewhat misleading in that they are average measurements over a relatively long period of time. The pulsed nature of the synchrotron beam causes the actual instantaneous dose rate during a pulse to be about 2.1 x 10^{25} ev/gm-min. The beam diameter is ~0.13 in. at the sample. As the diameter of the sample is somewhat larger than this, the dose received in the region of ^{11}C production is increased even more.

Radio-Gas Chromatographic Techniques

The yields of products produced in an irradiation are extremely low. If it is assumed that 10^9 carbon-11 atoms are produced, and that a typical product contains 10% of the activity, only 10^{-16} moles of the product are formed. Compounds in this small abundance are not detectable by normal chemical analyses. Even the use of gas chromatographic techniques using mass detectors must be ruled out. The detection of the products must be made using radiochemical techniques. As the reactions of interest are those involving the ^{11}C-atoms, the radioactivity of the ^{11}C-atoms may be used to detect the products. The carbon-11 is a positron emitter with a half life of 20.4 min. The short half life requires that an analysis be completed in a period of an hour or less. As the ^{11}C decays to ^{11}B, the products are destroyed so that trapping of certain products for identification purposes is impractical.

In this work a NaI(Tl) well-type crystal was used to detect the annihilation radiation from the decay of the ^{11}C and the requirements of rapidity of analysis were met by using high-temperature, high flow rate radio-gas chromatography.

The experimental apparatus is shown in Fig. 1. Some of the products formed in the irradiation of hydrocarbons are

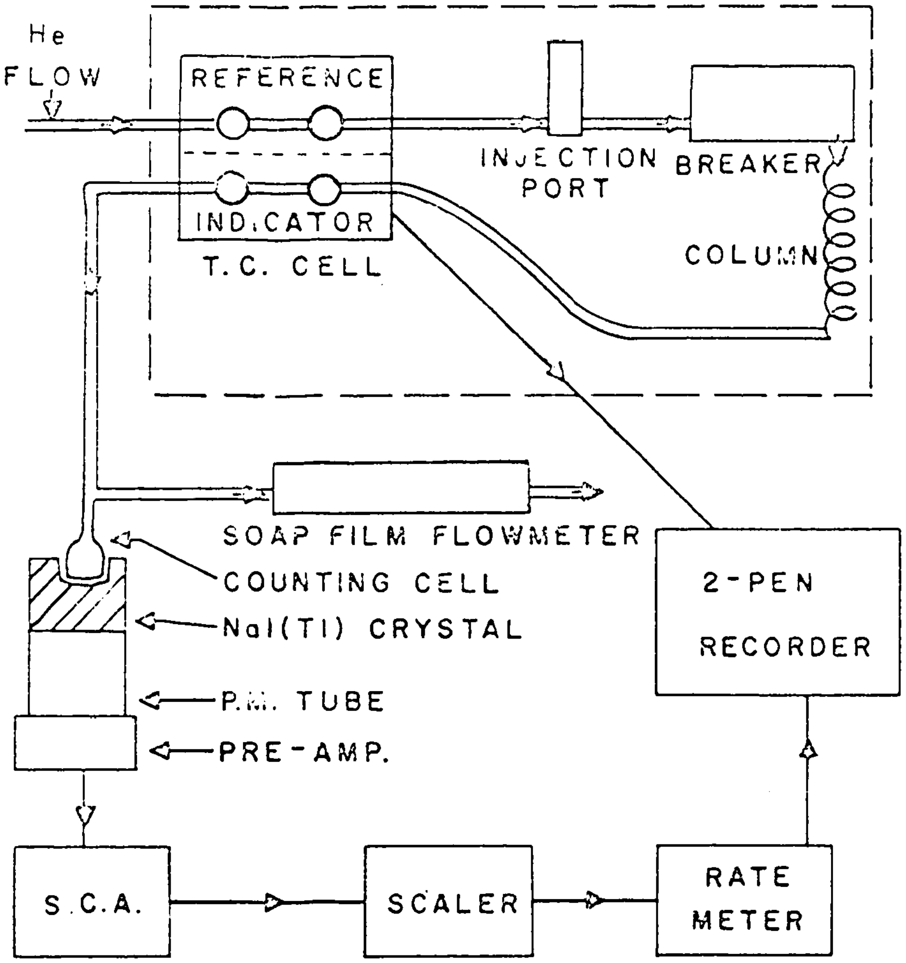


Fig. 1. Diagram of chromatograph

gases. This requires that the sample be broken in the carrier gas stream of the chromatograph as close as possible to the inlet of the column. The sample breaker and chromatograph were designed and constructed by Mr. R. G. Clark and Mr. W. Stensland of the Ames Laboratory.

After the sample is separated on the column, it passes through a hot wire thermal conductivity detector. The thermal conductivity cell was of primary use in calibration of the columns. Helium was generally used as carrier gas because of the large difference in thermal conductivity between the helium and the hydrocarbons. The output from the thermal conductivity detector was recorded by one pen of a Briston Dynamaster two-pen recorder as peaks whose areas were proportional to the relative amounts of compounds carried through the cell. The thermal conductivity detector was not of use in the analysis of radioactive products as its sensitivity was approximately 10^{-10} moles of material.

The effluent gas was passed from the thermal conductivity cell through a glass counting cell set in the well of a 5 x 5 cm NaI(Tl) crystal. In order to reduce the background radiation and provide a steady baseline, thus increasing the sensitivity of the system, a single channel analyzer used in the integral mode was incorporated into the counting system. This was used to discriminate against low energy pulses corresponding to γ-ray energies of ~0.4 MeV.

The product yields could be measured in two ways. A Nuclear Chicago Model 186 scaler could be used to manually integrate the peaks. The signals from the scaler were passed through a counting rate meter and could be displayed on the recorder using the second pen. The capability for simultaneous recording of the thermal conductivity and radiation detectors was useful in product identification through addition of carrier.

If individual peaks were completely resolved as in Fig. 2A, the yield of product could be easily determined either by direct integration using the scaler or by planimetering the peak to find its area. If, as was often the case, resolution was incomplete, as in Fig. 2B, a stripping procedure was used to determine the respective areas. In this case, the peaks were assumed to be primarily Gaussian in shape with a small amount of tailing allowed for. The expected shape of the peak was drawn in and the areas determined with a planimeter. Some tailing of peaks was unavoidable due to dead space in the chromatograph and the large sample size. The tailing was

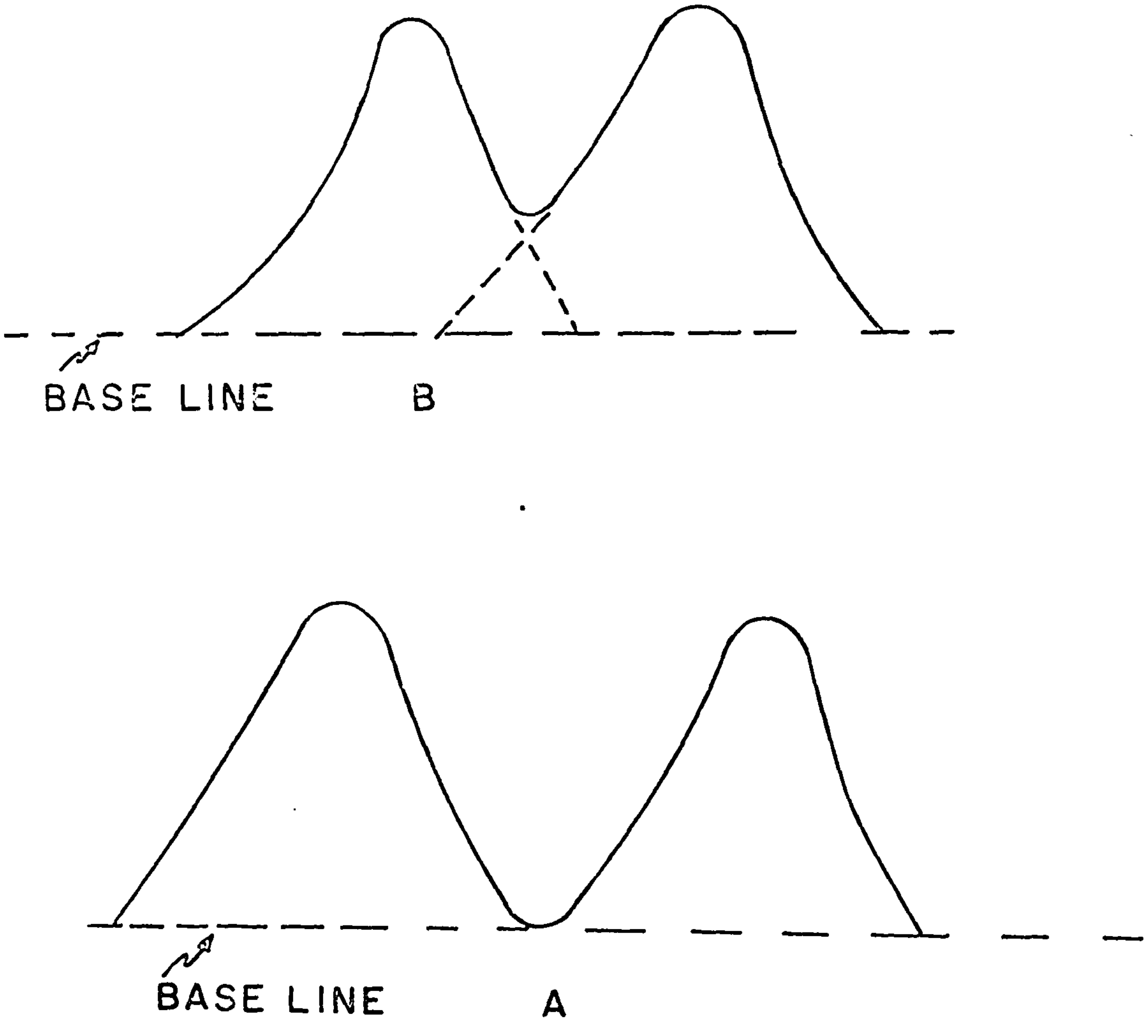


Fig. 2. Peak shapes found in analyses

minimized by use of high flow rates and temperatures and accounted for only a few percent of the peak area. If two overlapping peaks were approximately the same in area, as was generally the case, the areas could be determined with very little error. In extreme cases where the ratios of the areas approached 10:1, the error introduced into the measurement of the smaller peak could be as high as 10% of its area.

The peak areas were converted to counts and the activity of each product was corrected for decay taking the time when the synchrotron was shut off as $t = 0$. The correction factor, $e^{\lambda t}$, was determined by taking the time at the center of the peak.

The flow rate was carefully measured during a run using a soap film flowmeter. Changes in flow rate tended to introduce error in the activity measurements and care was taken to keep the flow rate as steady as possible. In a normal run, the flow rate could be kept steady to within ± 1%. The activity of a given product may be calculated using the following equation:

$$A_o = k \frac{Af}{V} \qquad \text{(Eq. 9)}$$

where A_o is the activity, A the observed counts, k is a constant depending on flow rate, f is the flow rate and V the volume of the counting cell. A similar expression has been given by Wolfgang and Rowland (81) for use in a flow-proportional counter. Since k/V is a constant over a given flow rate range, the measure of activity was taken as $A_o' = Af$.

In order to convert the product yields into percentages, it was necessary to calibrate the counting system. An auxiliary counting system was used to determine the dose received by a sample. In the auxiliary counter the sample was counted in a fixed geometry with a 2.5 x 2.5 cm Na(Tl) crystal and this measurement used as a monitor of the dose received. The methylcyclopentane system was used as a standard for calibration. The percentage of acetylene in this compound has been well established as 17.8 (51). The procedure involved the irradiation of methylcyclopentane samples, counting them on the auxiliary counter and the analysis of the gaseous products. This analysis was made using two different columns, silica gel and DMS-DIDP. The activity A_o of the acetylene peak was calculated using the appropriate decay corrections, and the corrected counts B from the auxiliary counter were obtained. The ratio of the two counting systems G' = A/B was calculated and taken to correspond to a yield of 17.8% for acetylene. Using this factor a corresponding factor G was obtained for the n-hexane yield from irradiation of n-pentane. This factor corresponded to a yield of 12.2% and by calculating a factor $G_S = A/B$ for any given product, its percentage yield could be calculated by the following equation.

$$\frac{G_S}{G} \times 12.2 = P\% \qquad \text{(Eq. 10)}$$

The value of G for the counting system used was determined as 20.5.

One of the most difficult analytical problems was due to the sample size. The entire sample, 0.3 ml, injected on the column would in general completely flood columns of the size used. Products appearing before the parent compound were resolved with a fair degree of ease, but at normally useful temperatures and flow rates the elution of the parent compound would tail for up to 45 min and mask or prevent elution of higher boiling products. One solution of this problem would have been to use a larger column. This was not feasible for the reason that retention times increased to a point where the remaining activity was undetectable. Usual procedure calls for temperatures slightly below the boiling point of the compound of interest. It was found that by increasing the operating temperature to 30-40°C above the boiling point of the parent, the elution time could be reduced to a few minutes. Using flow rates of ~100 ml/min, about double those normally used, the time required for essentially complete elution of the parent compound could be reduced to 3 min or less. Each column was used at an optimum temperature and flow rate. Under these conditions the parent compound could be eluted in a reasonable length of time and fairly good separations could be obtained for most of the expected products.

Column packings were prepared by dissolving a weighed amount of the liquid phase in a suitable solvent, mixing it with an appropriate amount of solid phase and evaporating the solvent using a flash evaporator. This procedure gave dry, uniform packing material. The liquid phases used included Apiezon-L and Apiezon-M, used for separation of aromatic compounds, D. C. 200 and D. C. 703, good for general hydrocarbon analyses and Nujol (Paraffin oil) which gave very specific boiling point analyses. The columns used were constructed of glass and were helical in shape. Packing was accomplished by applying suction on one end of the column and introducing the packing material with vibration at the other end. The glass construction was convenient in that tightness of packing could be visually observed. A column was considered to be sufficiently packed when no movement of the packing material could be observed with vibration. Typical liquid loadings on the column packings were 20-40% by weight. The solid phase found to give the least tailing in this work was Diatoport W.

Separations of hydrocarbon gases were carried out using two column materials. Silica gel gave good separations of methane, ethane, ethylene and acetylene. As a gas-solid chromatographic material the tailing was more pronounced than in gas-liquid chromatography but separations were sufficiently good so that the products could be resolved. The dual column, DMS-DIDP, gave similar separations with less tailing but with the drawback that ethane and ethylene had similar retention times and could not be resolved.

Identification of the products was made through careful calibration of the chromatographic columns. A series of known compounds was injected on to the column and the retention times noted. A related measurement was used to determine separation factors, the retention volume, V_0. This quantity which may be obtained by multiplying the retention time for a given compound by the flow rate, represents the volume of gas necessary to elute the compound. The retention volume may be used to calculate the number of theoretical plates in the column for a given compound.

The separation ability of a column is given by its HETP or height equivalent to a theoretical plate, calculated by dividing the length of the column in cm by the number of theoretical plates. By the use of the retention volumes as a guide, the flow rate and temperature were adjusted for each column to give maximum separation of the products in the shortest possible time. Retention volumes were tabulated for the various columns and retention volumes from hot runs were calculated and compared to the standards. Agreement was in the range of ± 20 ml for the comparison of carrier free hot products with the elution of macro amounts of standards. Carrier amounts of suspected products were added in a number of runs and the thermal conductivity peaks resulting were compared directly with the tagged product.

The column of widest general use was 20% Nujol on Diatoport W. Retention volumes and separation factors determined for this column are given in Table 3. It was found that a plot of boiling point versus log V_0 for a series of non-cyclic hydrocarbons gave a linear behavior. A similar behavior with the curve displaced was found for cyclic hydrocarbons. This behavior was used to determine the boiling points of several compounds which could not otherwise be identified. The boiling point of a given compound could be found within $1.5^{\circ}C$ for

Table 3. Retention data for a 29 ft Nujol column, packed 20% by weight on Diatoport W at an operating temperature of 65°C and flow rate of 86 ml/min

Compound	B.P. (°C)	R'_t(min)[a]	a[b]	V_o(ml)
Air	---	2.80	0.23	241
Methane	-161.5	2.80	0.23	241
Ethylene	-103.9	3.00	0.25	253
Acetylene	- 83.6	3.00	0.25	253
Ethane	- 88.3	3.20	0.27	275
Propylene	- 47.0	3.61	0.30	310
Propane	- 42.2	3.75	0.31	322
Propyne	- 23.3	3.80	0.32	327
Isobutylene	- 6	5.33	0.44	458
Isobutane	- 10.2	5.33	0.44	458
Butene-1	- 5	5.33	0.44	458
Butane	- 0.6	5.80	0.49	499
Isopentane	+ 28	9.92	0.83	853
Pentene-1	+ 30.0	10.64	0.88	915
n-Pentane	+ 36.2	12.00	1.00	1032
2-Methylbutadiene-1,3	+ 34	12.00	1.00	1032
2,2-Dimethylbutane	+49.7	16.16	1.38	1390
Cyclopentene	+44.2	19.09	1.59	1642
2,3-Dimethylbutane	+58.1	21.06	1.76	1811
2-Methylpentane	+60	21.25	1.78	1827
Cyclopentane	+49.5	21.57	1.80	1855
3-Methylpentane	+64	24.10	2.01	2073
Hexene-1	+63.5	24.29	2.07	2089
cis-Hexene-2	+68	27.43	2.28	2359
n-Hexane	+69.0	27.95	2.33	2404
trans-Hexene-2	+68	29.29	2.44	2519
1,2-Hexadiene	+78	34.90	2.91	3001
Methylcyclopentane	+72	37.00	3.08	3182
Benzene	+80.1	43.63	3.64	3752
Cyclohexane	+81.4	50.33	4.19	4328
n-Heptane	+98.4	70.00	5.84	6020

[a] R' is the retention time for a given compound standardized to R_t for n-pentane as 12.00 min.

[b] a is the separation factor related to the retention of n-pentane being taken as 1.00, R_t(compound)/R_t(n-pentane).

non-cyclic hydrocarbons. Boiling points for cyclic hydrocarbons were within ~$3^\circ C$. The plot is given in Fig. 3.

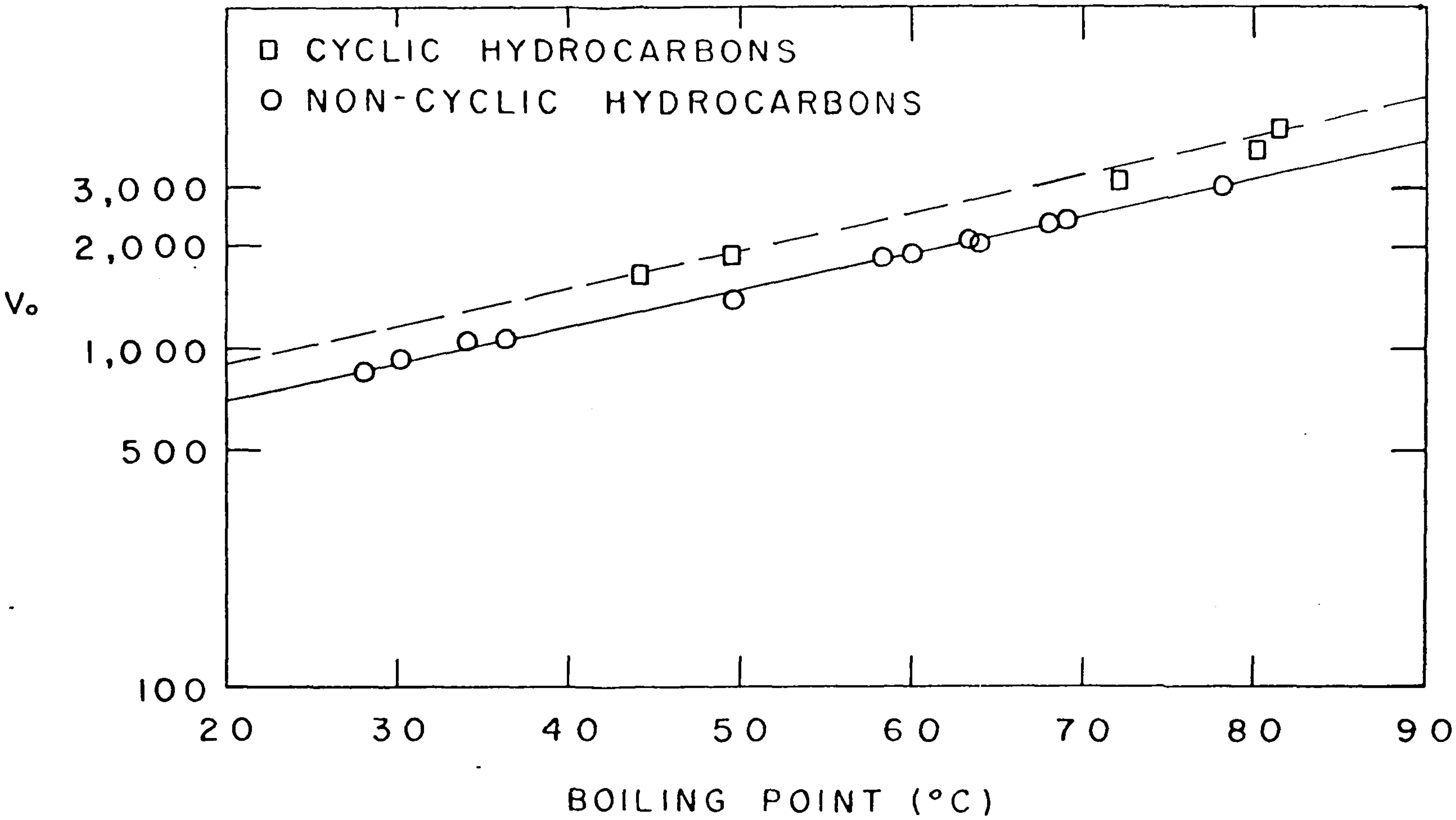


Fig. 3. Dependence of V_0 on boiling point

RESULTS

Dose Calculations

The total number of carbon-11 atoms present at any time t during an irradiation is given by:

$$N = \frac{\sigma\phi N_o}{\lambda}(1-e^{-\lambda t}) \qquad \text{(Eq. 11)}$$

in which N is the number of carbon-11 atoms present at time t, σ the reaction cross section, ϕ the flux, N_o the number of parent atoms present at t = 0 and λ the decay constant, 3.40×10^{-3} min^{-1} for carbon-11.

The total number of carbon-11 atoms N_T produced during an irradiation of time t is:

$$N_T = \sigma\phi N_o t . \qquad \text{(Eq. 12)}$$

By combining Eq. 11 and Eq. 12 one may write:

$$N_T = \lambda N \left[\frac{t}{(1-e^{-\lambda t})}\right]. \qquad \text{(Eq. 13)}$$

Since the activity is given by:

$$A = -\frac{dN}{dT} = \lambda N, \qquad \text{(Eq. 14)}$$

the total number of atoms produced may be written as:

$$N_T = A_o \left[\frac{t}{(1-e^{-\lambda t})}\right] \qquad \text{(Eq. 15)}$$

in which A_o is the activity present at the end of an irradiation. Since A_o may be calculated from Eq. 9 as $A_o = Af$, the dose received by a sample may be calculated by:

$$D = \Sigma A_i \cdot f \left[\frac{t}{(1-e^{-\lambda t})}\right] \qquad \text{(Eq. 16)}$$

in which A_i is the activity observed in any given product. The quantity D is proportional to the number of radioactive atoms produced and may be used as a measure of the total dose received in a sample during an irradiation.

Dose Dependence of Product Yields

The effects of radiation dose on the yields of products formed from the reactions of carbon-11 in hydrocarbons have been studied by several authors (47-51). These studies were concerned only with the gaseous products, methane, ethane, ethylene and acetylene. These products are sometimes referred to as "fragmentation" products resulting from the breakdown of an excited complex formed in the initial reaction. It was felt that a similar study concerning the higher boiling products of these reactions would be of interest.

The experiments concerning the effects of dose on the product yields were performed preliminary to the determination of actual product percentages. Hence the results are presented as ratios of the activity of a given product or group of products A_n to the total observed activity ΣA_i.

Although most of the products were separated in the analyses, the results are generally reported for groups of products. The behavior of individual products in these groups was similar to that of the group as a whole.

Three systems were chosen for this study; n-pentane, cyclopentane and benzene. Dose studies made on the gaseous products from similar hydrocarbons have demonstrated that the product with the highest dose dependence is methane, showing a substantial increase in yield with increasing dose. Ethane and ethylene show slight increases with dose while acetylene is essentially unaffected (47-51).

In this series of experiments, only the products containing 3 or more carbon atoms were analyzed. The products of major interest were those containing one more carbon atom than the parent. Tables 4 and 5 present the yields found in n-pentane and cyclopentane, respectively. Results are given for two product groups in each, C_{3-5} and C_6. The dose dependence of these product groups is shown graphically in Figs. 4-7.

The analysis of the products resulting from irradiation of benzene showed only four identifiable products, methane, acetylene, toluene and benzene. The results of this study are presented in Table 6 and Figs. 8-10 graphically show the

Table 4. Effect of dose on products from irradiation of n-pentane

Run number	Irradiation time (min)	$R^a(C_{3-5})$	$R(C_6)$	$D^b(\times 10^{-5})$
G	5	16.5	37.4	2.3
B	5	16.5	39.8	4.1
90	5	15.8	43.3	5.4
D	10	18.3	37.9	6.9
89	10	18.0	41.0	9.0
H	11.7	17.1	38.7	10.6
A	15	16.6	43.3	12.0
M	30	18.2	44.9	13.4
I	30	18.0	41.6	14.2
E	15	18.4	42.8	14.3
91	20	16.9	37.5	15.1
F	20	15.2	40.3	17.3

[a] $R(C_n) = \frac{A_n}{\Sigma A_i}$.

[b] $D = \Sigma A_i \cdot f \cdot \frac{t}{(1-e^{-\lambda t})}$.

Table 5. Effect of dose on products from irradiation of cyclopentane

Run number	Irradiation time (min)	$R^a(C_{3-5})$	$R(C_6)$	$D^b(\times 10^{-5})$
108	10	6.4	61.4	5.4
111	20	6.7	59.7	7.1
106	5	6.2	60.0	7.4
105	15	6.2	60.1	19.6
110	15	6.4	60.3	26.9

[a] $R(C_n) = \frac{A_n}{\Sigma A_i}$.

[b] $D = \Sigma A_i \cdot f \cdot \frac{t}{(1-e^{-\lambda t})}$.

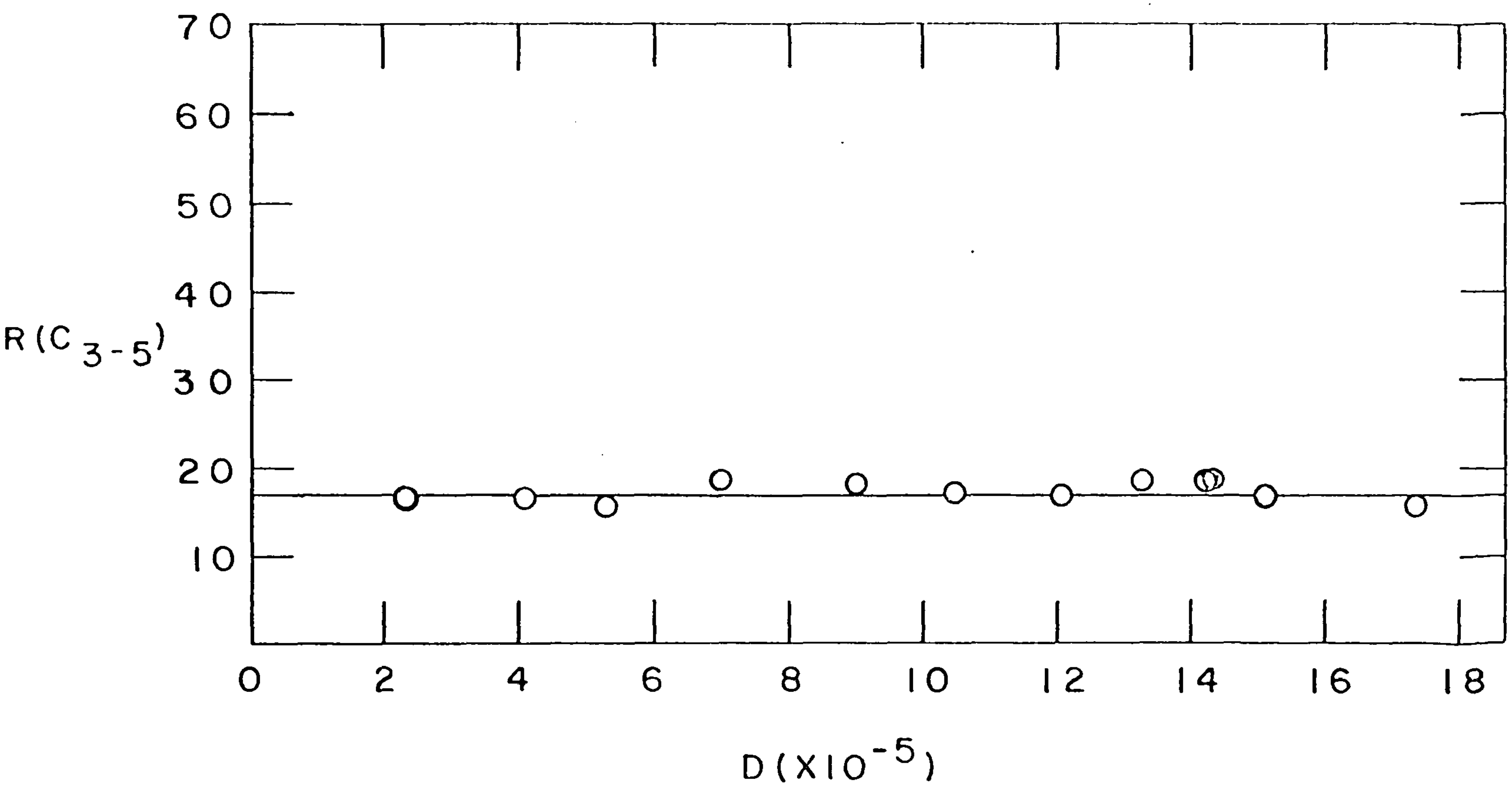


Fig. 4. Effect of dose on C_{3-5} yield from n-pentane

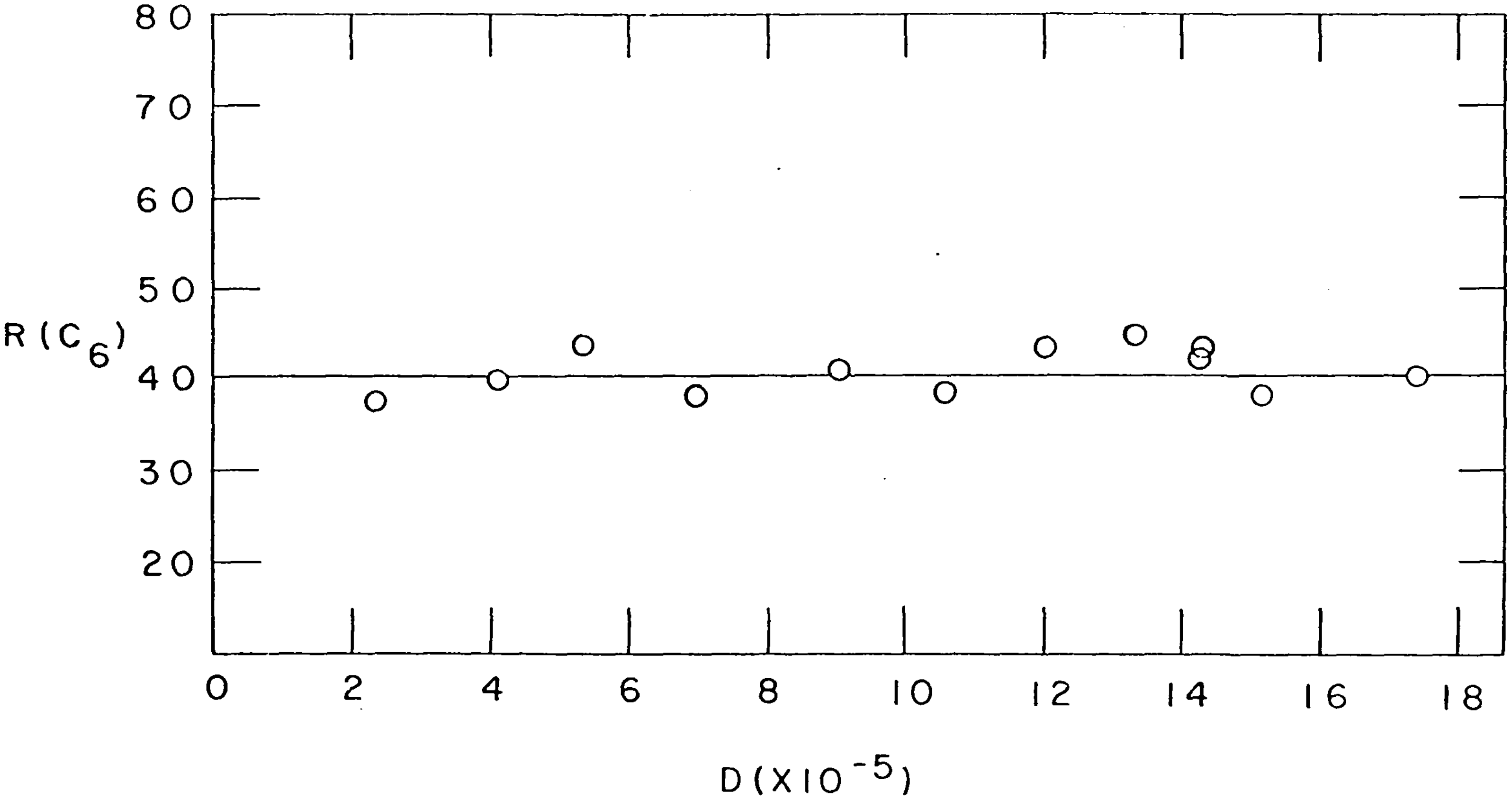


Fig. 5. Effect of dose on C_6 yield from n-pentane

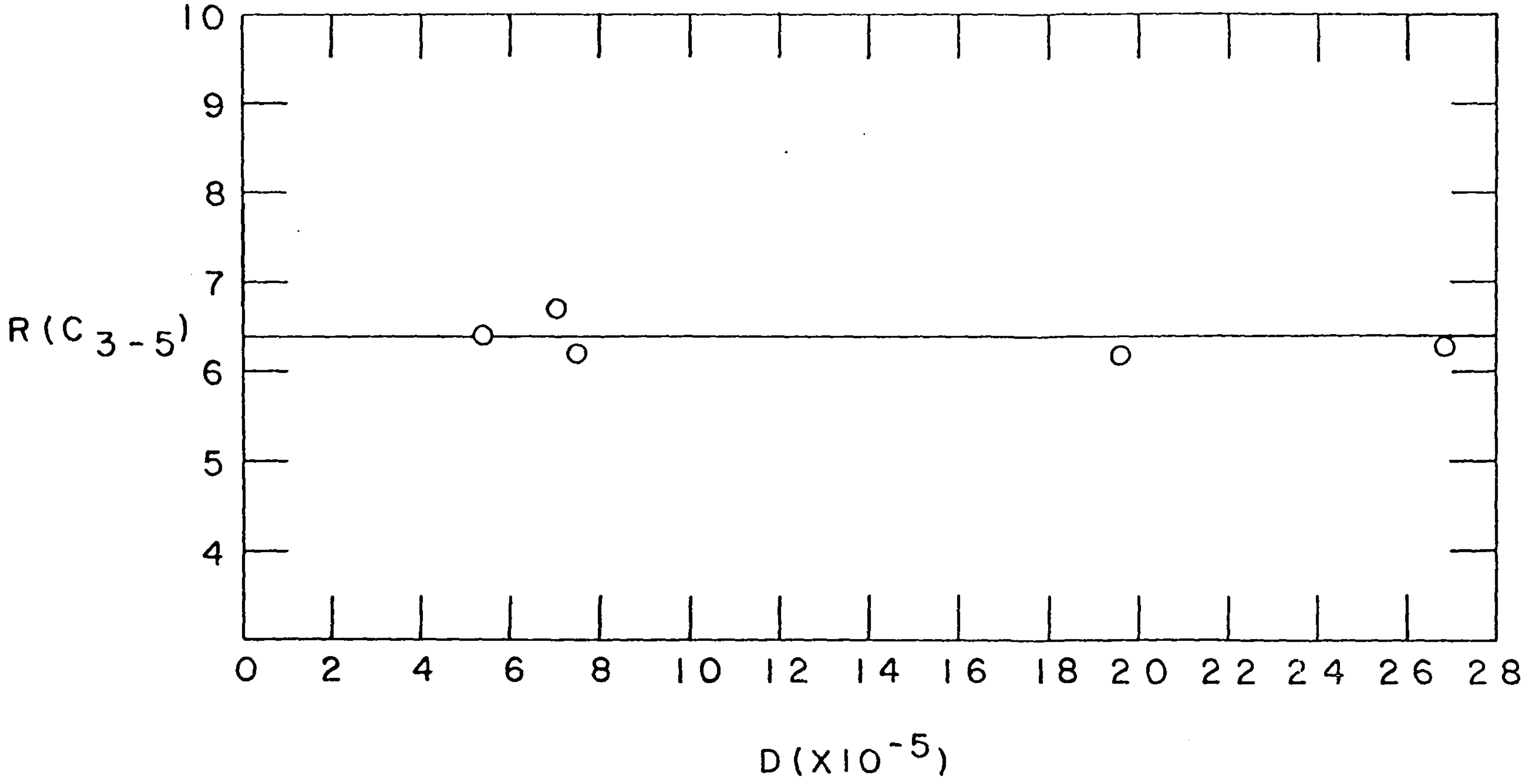


Fig. 6. Effect of dose on C_{3-5} yields from cyclopentane

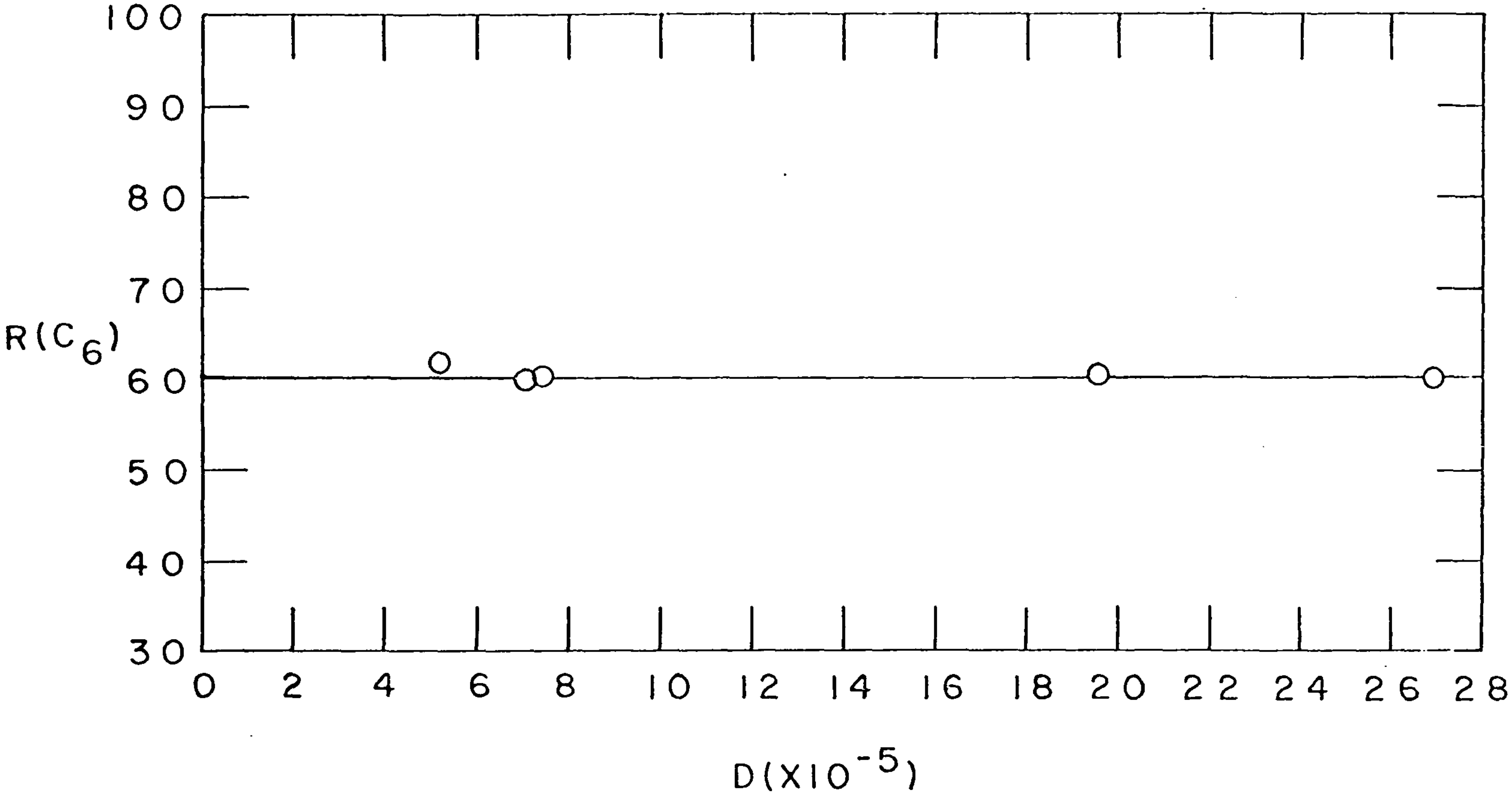


Fig. 7. Effect of dose on C_6 yields from cyclopentane

Table 6. Effect of dose on products from irradiation of benzene

Run number	Irradiation time (min)	$R^a(C_{1-2})$	R()	R(CH_3)	$D^b(\times 10^{-5})$
Q	5	29.0	48.0	23.0	0.73
97	5	30.0	48.0	22.0	2.10
98	10	31.2	45.8	24.0	3.29
117	20	26.1	48.6	25.4	4.59
120	15	30.6	49.2	20.2	5.20
119	20	27.5	48.2	24.3	5.49
99	20	30.4	46.8	22.8	6.97
T	30	28.5	47.4	24.1	8.41

[a] $R(C_n) = \frac{A_n}{\Sigma A_i}$.

[b] $D = \Sigma A_i \cdot f \cdot \frac{t}{(1-e^{-\lambda t})}$.

dose dependence of the C_{1-2}, benzene and toluene yields. Rack, Lang and Voigt (48) found no dose dependence for the acetylene yield. Fig. 8 indicates a similar behavior of combined methane and acetylene.

Product Distributions

Six compounds were selected for the determination of product distributions. With the exception of benzene, five carbon compounds were used in order to keep the product distribution as simple as possible while irradiating compounds which were liquid at room temperature. Hydrocarbons of different types were chosen so that the effects of structure on

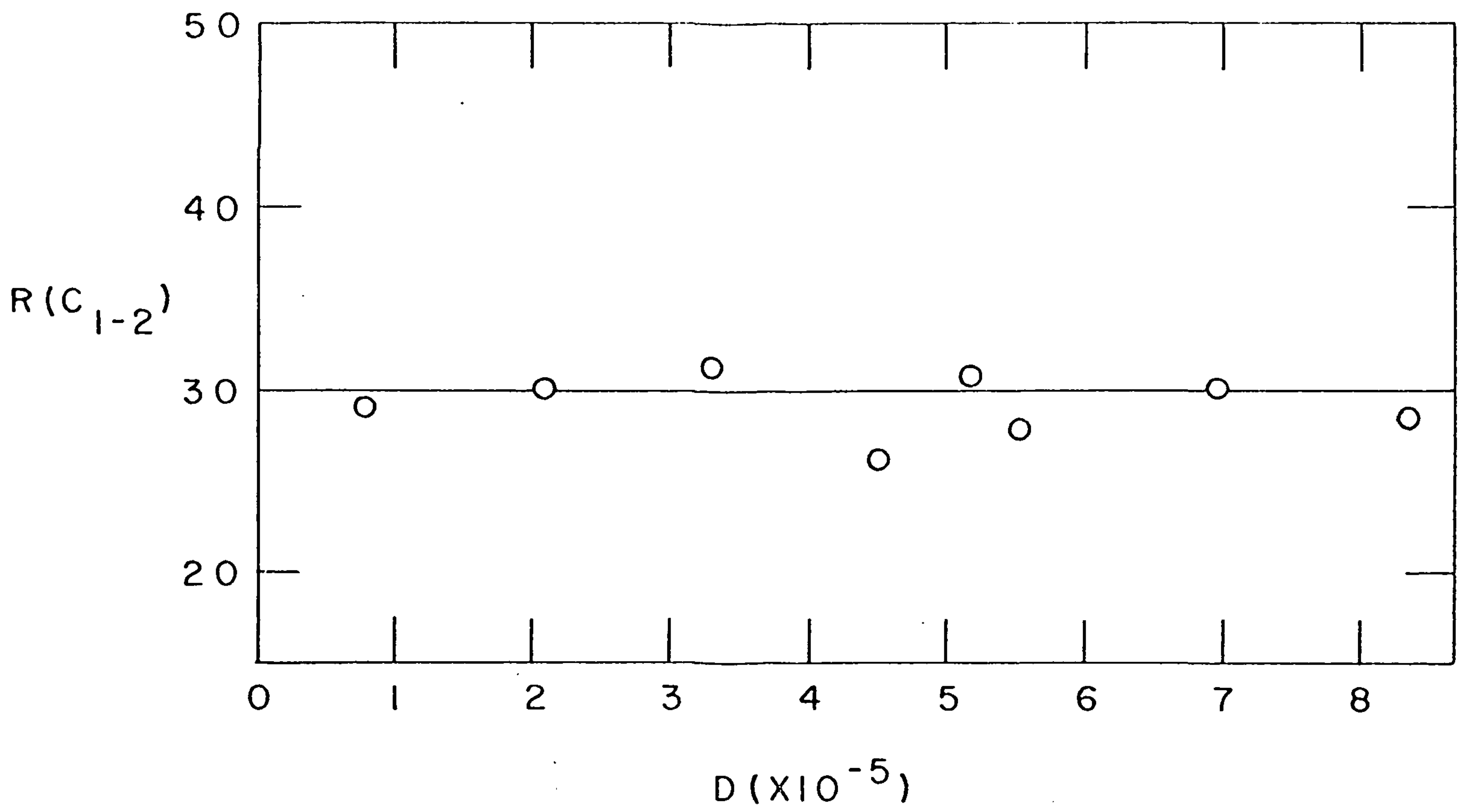


Fig. 8. Effect of dose on C_{1-2} yields from benzene

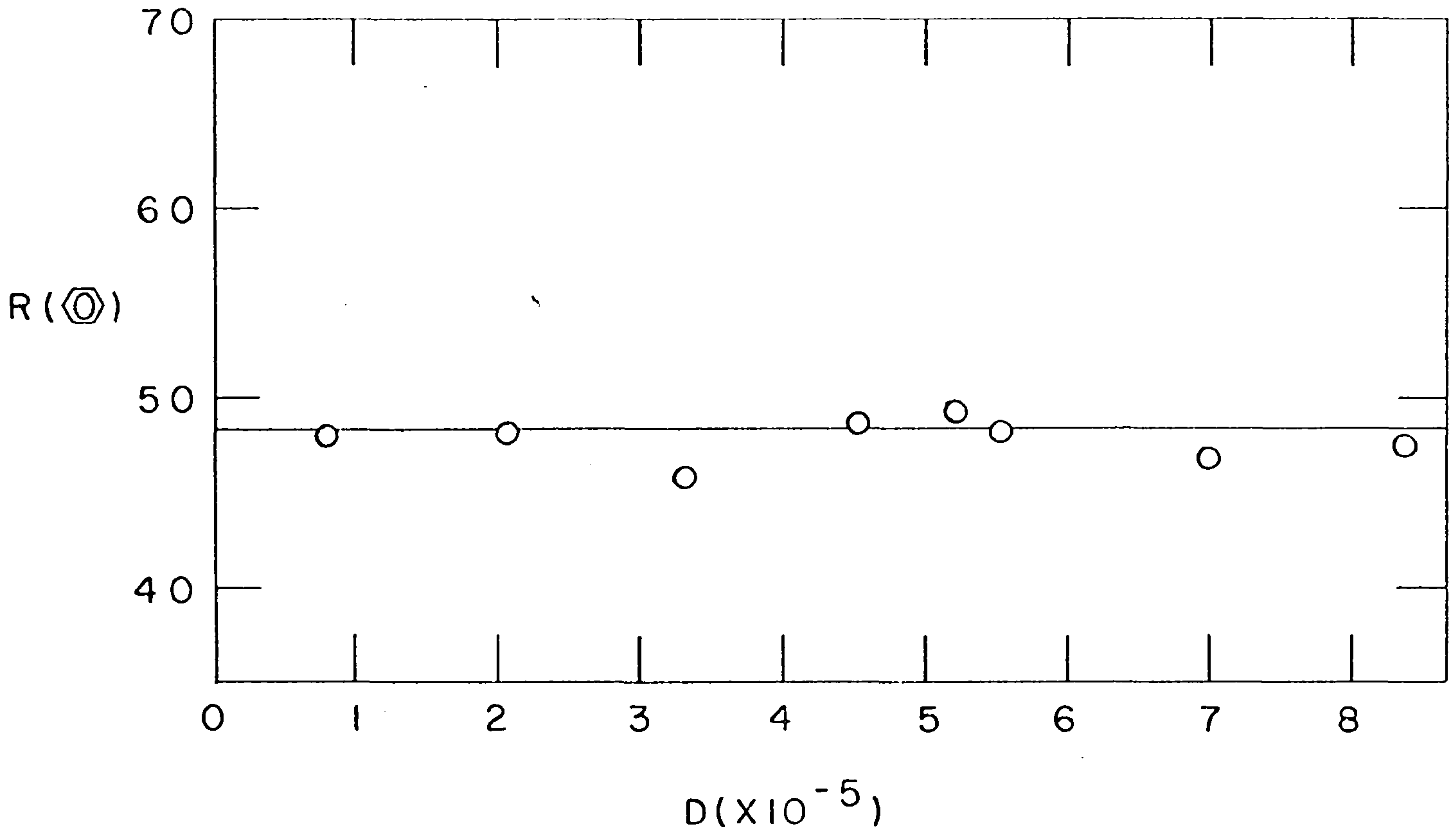


Fig. 9. Effect of dose in benzene yields from benzene

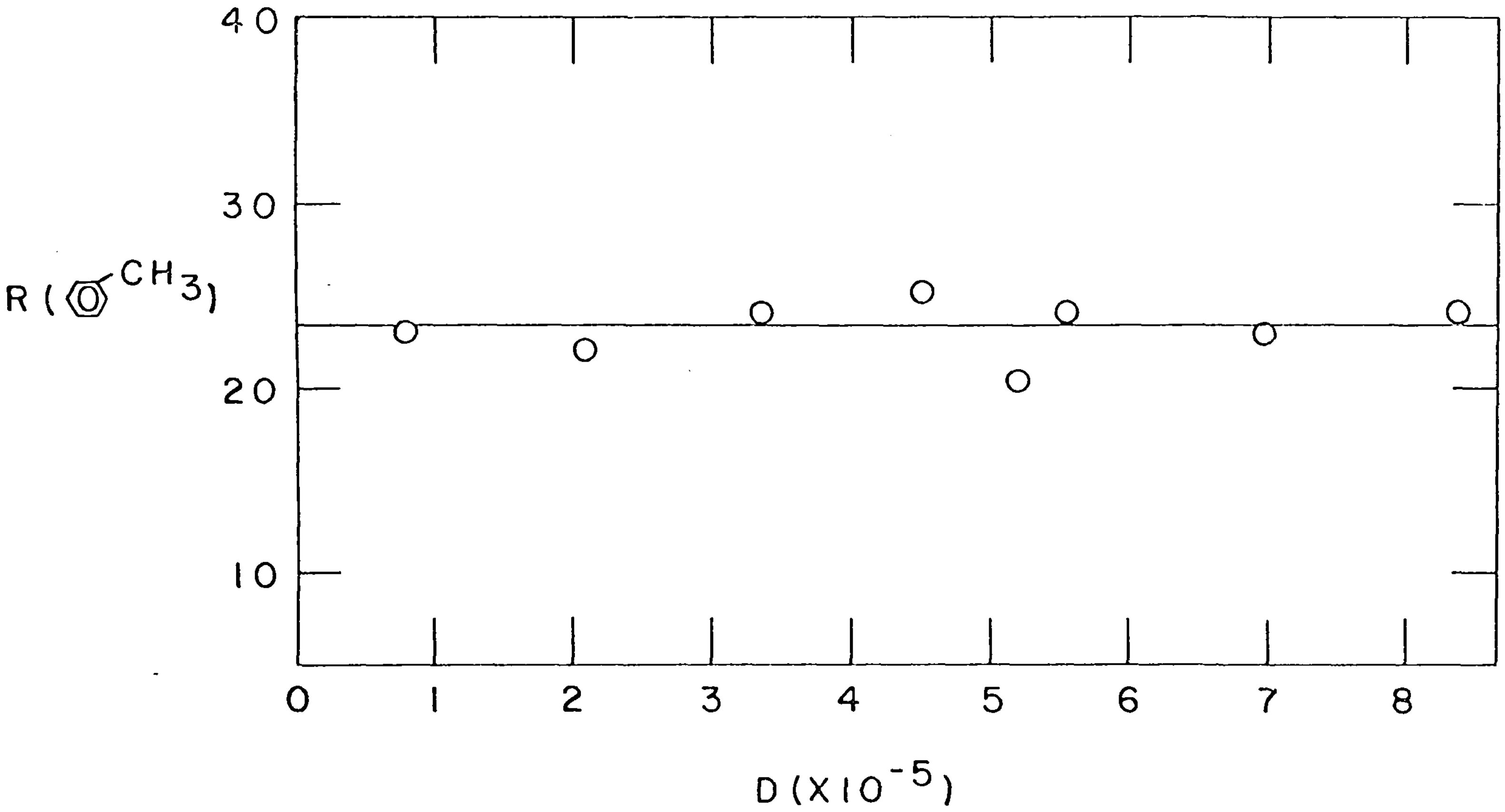


Fig. 10. Effect of dose on toluene yield from benzene

the nature and yields of the higher boiling products could be determined. These compounds included straight chain, branched chain and cyclic alkanes, n-pentane, isopentane and cyclopentane, straight chain and cyclic alkenes, pentene-1 and cyclopentene, and an aromatic compound, benzene.

Analyses could be performed for products boiling up to $\sim 200^{\circ}C$. Due to limitations in the heating system of the chromatograph, $200^{\circ}C$ was the maximum temperature which could be used. At least two columns were used in the analysis of each system. The results reported are the averaged values for at least three runs. Separate analyses were performed on the product groups $C_{n>2}$ and C_{1-2} as a complete separation of all products could not be achieved in any one run. In general, the use of different columns enabled identifications of products to be made with a fair degree of certainty. Product separations varied from column to column. Ideally, a separation could be achieved by a column for every product. This, however, was not usually the case. As an example, n-hexane and hexene-1 were eluted at the same time using a D.C. 703 column while 3-methylpentane could be isolated. Using Nujol as a packing material, n-hexane could be resolved free of impurities but hexene-1 and 3-methylpentane were not separated.

A comparison of the results obtained for the two columns enabled determination of the true yields of hexene-1 and n-hexane.

Errors in the product yields are estimated to be ± 10% for the larger yields. The error in systems with relatively few products is less than that in the more complicated systems for the reason that the resolution of the peaks was improved. In the case of products with measured yields of <2%, the background was usually of the same order as the activity in the peak leading to more error in peak integration. Peak widths became a problem in systems containing a large number of products. Ideally, a sensitive counting system would be used in order to obtain high counting rates with correspondingly low statistical error. High counting rates, however, also contributed to the broadening of peaks making resolution of the products difficult. In view of the number of products found in each system, fairly low counting rates were used in order to reduce overlap of peaks. The same counting geometry was used in the analyses of all the systems. This was done to avoid errors introduced by the recalibration which would be necessary if changes were made in the counting geometry. In benzene and cyclopentane, in which 50% or less of the activity was recovered, the counting rates in the peaks were low. In benzene, due to the simplicity of the product spectrum, this presented few problems, but in the more complicated cyclopentene system, the low activity contributed to a fairly large error in product yield determinations. In the cyclopentene system, the yields given should be considered as only approximate.

Product identifications were generally made by comparison of the retention volume for a given product with that of a known standard. Carrier amounts of suspected products were injected during many runs in order to compare the peaks obtained with the radioactivity peaks. In several instances, two or more products are reported together. Separation of these products could not be achieved using the available column materials.

The proposed product spectrum for cyclopentene contains several products which were not available for retention volume comparison. Tentative identifications were made on the basis of boiling points determined by use of Fig. 3, page 41b. Table 7 includes the tentative identifications of 2- and 3-methylcyclopentene, 1-methylcyclopentene and bicyclo[3.1.0] hexane from the cyclopentene system.

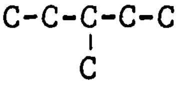
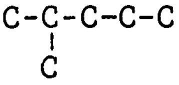
The pentene-1 system contained so many products that a complete analysis could not be performed with the available equipment. Several of the products from this system were identified by use of Fig. 3, page 41b, determining boiling points for the products. Identifications of these products are given in Table 7.

The product distributions determined are presented in Tables 8-13 along with the columns used.

Table 7. Identification of products by boiling point determination

V_o(ml)	B.P. (^oC) from Fig. 3	Suspected product	B.P. (^oC) of product
1282	46.7	1,2-pentadiene	44
1544	51.3	3-methylpentene-1	53
		4-methylpentene-1	53
1753	56.1	4-methylpentene-2	58
2037	62.4	1-hexene	63.5
		2-methylpentene-1	61.5
		1-5-hexadiene	60
2336	68.5	2-methylpentene-2	67
		2-hexene	68
		cyclopropylpropane	69
2673	73.3	1,3-hexadiene	72
2716	65.5	2-methylcyclopentene	65
		3-methylcyclopentene	66.5
3300	74.4	1-methylcyclopentene	76
3605	84.0	2,4-hexadiene	82
4214	80.0	bicyclo[3.1.0] hexane	79.5

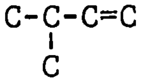
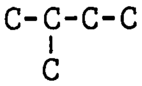
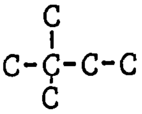
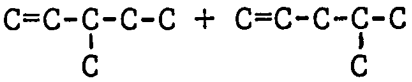
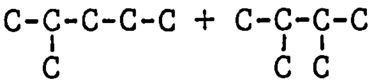
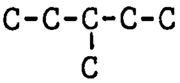
Table 8. Product distribution from irradiation of n-pentane

Product	Percentage	Columns used[a]
CH_4	8.4	1,2
C-C[b]	1.5	1,2
C=C	9.6	1,2
C≡C	22.1	1,2
C=C-C + C≡C-C	4.7	3,4,5
C_4	7.3	3,4,5
C=C-C-C-C	2.3	3,4,5
C-C-C-C-C	1.0	3,4,5
 $\mathrm{C{-}C{-}\underset{\underset{C}{\vert}}{C}{-}C{-}C}$	3.3	3,4,5
 $\mathrm{C{-}\underset{\underset{C}{\vert}}{C}{-}C{-}C{-}C}$	5.9	3,4,5
C-C-C-C-C-C	12.2	3,4,5
C=C-C-C-C-C	14.0	3,4,5
C-C=C-C-C-C	2.2	3,4,5
	ΣA_i = 94.7	

[a] 1. Silica gel
2. DMS-DIDP
3. Apiezon-L
4. D.C. 703
5. Nujol.

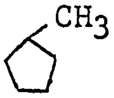
[b] Hydrogens are left off all following products.

Table 9. Product distribution from irradiation of isopentane

Product	Percentage	Columns used[a]
CH_4	7.7	1
C-C		1
C=C	15.7	1
C≡C	22.7	1
C=C-C + C≡C-C	<5	5
C_4	2.2	5
 $\mathrm{C-\underset{\underset{C}{\vert}}{C}-C=C}$	1.4	5
 $\mathrm{C-\underset{\underset{C}{\vert}}{C}-C-C}$	3.0	5
C-C-C-C-C + C=C-C-C-C	2.8	5
 $\mathrm{C-\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}-C-C}$	2.9	5
 $\mathrm{C=C-\underset{\underset{C}{\vert}}{C}-C-C + C=C-C-\underset{\underset{C}{\vert}}{C}-C}$	10.4	5
 $\mathrm{C-\underset{\underset{C}{\vert}}{C}-C-C-C + C-\underset{\underset{C}{\vert}}{C}-\underset{\underset{C}{\vert}}{C}-C}$	11.3	5
 $\mathrm{C-C-\underset{\underset{C}{\vert}}{C}-C-C}$	11.7	5
	ΣA_i = 98.8	

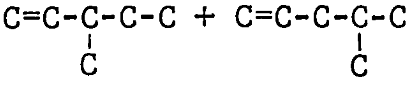
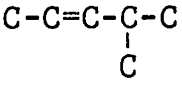
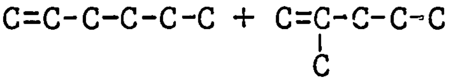
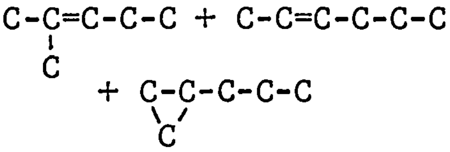
[a] 1. Silica gel
5. Nujol.

Table 10. Product distribution from irradiation of cyclopentane

Product	Percentage	Columns used[a]
CH_4	8.0	1
C-C	0.6	1
C=C	5.1	1
C≡C	13.5	1
C=C-C + C≡C-C	3.7	4,5,6
C_4	4.9	4,5,6
	3.0	4,5,6
C=C-C-C-C-C	3.4	4,5,6
	18.4	4,5,6
	10.0	4,5,6
	9.0	4,5,6
	ΣA_i = 79.6	

[a] 1. Silica gel
4. D.C. 703
5. Nujol
6. D.C. 200.

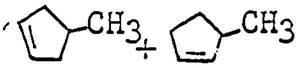
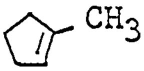
Table 11. Product distribution from irradiation of pentene-1

Product	Percentage	Columns used[a]
CH_4	2.8	1
C-C	0.5	1
C=C	6.5	1
C≡C	~18[b]	1
C=C-C	3.1	5
C≡C-C	2.9	5
C-C-C=C	3.6	5
C≡C-C-C	1.0	5
C=C=C-C-C	6.0	5
C=C-C-C-C	trace	5
 $\mathrm{C{=}C{-}\underset{C}{C}{-}C{-}C + C{=}C{-}C{-}\underset{C}{C}{-}C}$	5.3	5
 $\mathrm{C{-}C{=}C{-}\underset{C}{C}{-}C}$	8.0	5
 $\mathrm{C{=}C{-}C{-}C{-}C{-}C + C{=}\underset{C}{C}{-}C{-}C{-}C}$ + C=C-C-C-C=C	8.1	5
 $\mathrm{C{-}\underset{C}{C}{=}C{-}C{-}C + C{-}C{=}C{-}C{-}C{-}C + \underbrace{C{-}C}_{C}{-}C{-}C{-}C}$	7.4	5
C=C-C=C-C-C	9.0	5
C=C=C-C-C-C	11.4	5
C-C=C-C=C-C	3.0	5
	ΣA_i~98.4	

[a] 1. Silica gel, 5. Nujol.

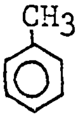
[b] C≡C yield was estimated. In this series of runs there was some decomposition of the C≡C and the product was not well resolved.

Table 12. Product distribution from irradiation of cyclopentene

Product	Percentage	Columns used[a]
CH_4	4.0	1,2
C-C	---	1,2
C=C	2.5	1,2
C≡C	12.1	1,2
C=C-C + C≡C-C	2.5	5
C_4	3.1	5
C=C-C=C-C	1.4	5
	trace	5
	8.0	5
	4.6	5
	6.4	5
	6.3	5
	3.6	5
	$\Sigma A_i = 54.5$	

[a] 1. Silica gel
2. DMS-DIDP
5. Nujol.

Table 13. Product distribution from irradiation of benzene

Product	Percentage	Columns used[a]
CH_4	0.3	2
C-C	---	2
C=C	---	2
C≡C	5.5	2
	11.4	3,4
	5.7	3,4
	$\Sigma A_i = 22.9$	

[a] 2. DMS-DIDP
3. Apiezon-L
4. D.C. 703.

DISCUSSION

Bond dissociation energies for carbon-hydrogen and carbon-carbon bonds are generally in the range of 2-4 ev. The average initial recoil energy of the carbon-11 atoms, ~0.5 MeV, can be assumed to be sufficient to break all bonds to the carbon. The carbon-11 then undergoes a number of collisions transferring momentum to atoms and molecules in the surrounding medium. The average distance which the atom travels from birth until it reaches the energy region in which it may react chemically has been calculated by DeVries (49) as $\sim 10^{-3}$ cm.

Due to the high initial energy, the carbon-11 atom is probably born as an ionic species. Lang (82) and DeVries (49) have calculated the maximum probable charge as +2. The carbon-11 atoms probably cannot undergo chemical reactions until they reach an energy range of <~20 ev. The charge on the atom at these energies is dependent on the number of charge changing collisions which the carbon atom undergoes during the cooling process.

The maxima in the cross sections for charge transfer processes determine the charge state of the reacting carbon. The cross sections are quite high at the maxima and tend to be higher for maxima occurring at lower energies (83,84). This fact indicates that the final charge state is determined by the the lowest energy process.

The resonance rule (84) may be used to calculate approximate energies for the maxima in the cross section curves for charge transfer processes. The maximum cross section for a process in which there is an energy change ΔE will occur when:

$$v_{max} = \frac{\alpha\,|\Delta E|}{h} \qquad \text{(Eq. 17)}$$

in which h is Planck's constant, α is an interaction distance, 7 x 10^{-8} cm. (83), and v_{max} is the relative velocity of the interacting particles at the energy of maximum cross section. Sample calculations applying the resonance rule to benzene and isopentane are given in Table 14.

Table 14. Charge transfer calculations using the resonance rule

	R = Benzene		R = Isopentane	
Reaction	$\|\Delta E\|$	E_{max}[a]	$\|\Delta E\|$	E_{max}
1) $C(^3P) + R = C^+ + R + e^-$	11.3	2×10^5	11.3	2×10^5
2) $C(^1D) + R = C^+ + R + e^-$	10.1	1.6×10^5	10.1	1.6×10^5
3) $C^+ + R = C(^3P) + R^+$	2.1	7.1×10^3	2.6	1.1×10^4
4) $C^+ + R = C(^1D) + R^+$	0.9	1.3×10^3	1.4	3.1×10^3
5) $C(^3P) + R = C(^1D) + R$	1.2	2.3×10^3	1.2	2.3×10^3

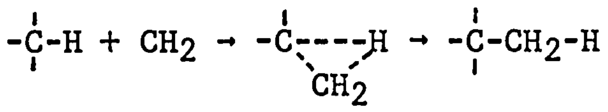
[a] $E_{max} = 0.5m\left[\frac{(|\Delta E|\alpha)}{h}\right]^2 = 1600(\Delta E)^2$ for ^{11}C.

The ionization potentials used in the above calculations are, benzene = 9.2 ev (85), isopentane = 8.7 ev (86), $C(^3P)$ = 11.3 ev (87) and $C(^1D)$ = 10.1 ev (88). These calculations indicate that by the time the carbon-11 atom drops below an energy of $\sim 10^3$ ev, it will be neutral.

The ground state of the carbon-11 atom is the ^3P state. The first excited state, ^1D, lies only 1.2 ev above the ground state (88). The resonance rule indicates that both the singlet and triplet states can enter into the reactions of the carbon-11 atom. From the available data, it is difficult to determine the electronic state of the carbon-11 atom producing a given product. Marshall _et al_. (44) have indicated that the $C(^1D)$ species is responsible for the reaction of carbon-11 with ethylene to produce allene. Although their argument for this proposal is reasonable, it is by no means proven. The energy available to the carbon atom is sufficiently high that the actual electronic state of the reacting atom may not be of prime importance in the determination of the final reaction product.

The possible reacting carbon species include C, CH, CH_2 and CH_3 radicals. The CH_2 or methylene radical may be conveniently produced through photochemical means and its reactions have been the subject of considerable interest. The reactions of C and CH may be reasonably considered to be similar to those of CH_2. In this light, a discussion of the reactions of methylene may be considered to be typical of the reactions of the C and CH radicals. The primary differences in these reactions are the modes of stabilization and decomposition of the reaction complex initially formed.

The chemistry of the methylene radical in hydrocarbons includes two basically different types of processes; reaction with carbon-hydrogen bonds and reaction with carbon-carbon multiple bonds. The most characteristic reaction of the methylene radical is insertion into a carbon-hydrogen bond. A "three-center" mechanism has been proposed for the process (89).



$$-\overset{|}{\underset{|}{C}}-H + CH_2 \rightarrow -\overset{|}{C}\underset{CH_2}{\cdots\cdots}H \rightarrow -\overset{|}{\underset{|}{C}}-CH_2-H \qquad \text{(Eq. 18)}$$

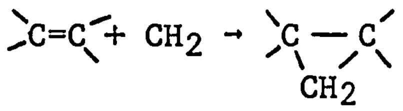
In the liquid phase, the insertion reaction was shown to be random with respect to the carbon-hydrogen bond attacked (72). The same authors also found that in cyclohexene there was no discrimination between aliphatic and allylic hydrogens. The product distribution found included 11% 1-methylcyclohexene, 26% 2-methylcyclohexene, 26% 3-methylcyclohexene and 37% Bicyclo[4.1.0]heptane (72). The rates of insertion of methylene into carbon-hydrogen bonds have been found to be comparable to the rates of insertion into carbon-carbon double bonds (72,89).

A second type of reaction between methylene and carbon-hydrogen bonds is hydrogen abstraction. This type of reaction is described by the following equation:

$$R\text{-}H + CH_2 \rightarrow CH_3 + R\ . \qquad \text{(Eq. 19)}$$

This reaction may occur either by a one-step process or by the decomposition of an insertion product (89,90).

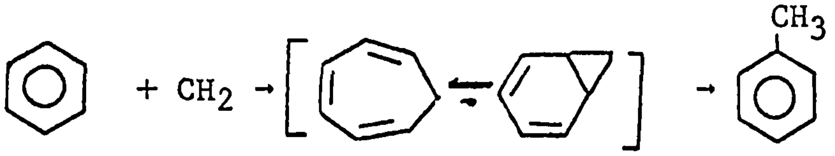
Carbon-carbon single bonds appear to be inert toward methylene insertion even in the case of highly strained small ring compounds such as spiropentane (91). Methylene is easily added to carbon-carbon double bonds forming a cyclopropane.



(Eq. 20)

This process has been of general use in the synthesis of cyclopropanes (92,93).

Methylene reacts with aromatic compounds to form interesting products. The photolysis of diazomethane in benzene yields 32% cycloheptatriene and 9% toluene (94,95). Norcaradiene has been observed by Meerwein <u>et al</u>. in the reaction mixture from the same system. The reaction has been described by the following process:

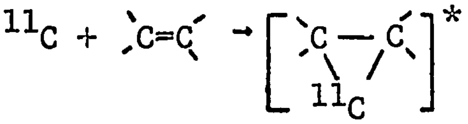


(Eq. 21)

The insertion mechanism has been widely applied to the reactions of ^{11}C-atoms in hydrocarbons (23,31-45, 47-51,97). The reactions of ^{11}C and ^{11}CH equivalent to those observed for methylene are as follows:

$$^{11}C + -\overset{|}{\underset{|}{C}}-H \rightarrow \left[-\overset{|}{\underset{|}{C}}-{}^{11}C-H\right]^* \qquad \text{(Eq. 22)}$$

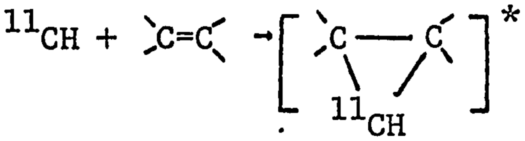
$$^{11}C + R\text{-}H \rightarrow {}^{11}CH + R \qquad \text{(Eq. 23)}$$



(Eq. 24)

$$^{11}CH + -\overset{|}{\underset{|}{C}}-H \rightarrow \left[-\overset{|}{\underset{|}{C}}-{}^{11}C-H_2\right]^* \qquad \text{(Eq. 25a)}$$

$$^{11}CH + R\text{-}H \rightarrow {}^{11}CH_2 + R \qquad \text{(Eq. 25b)}$$

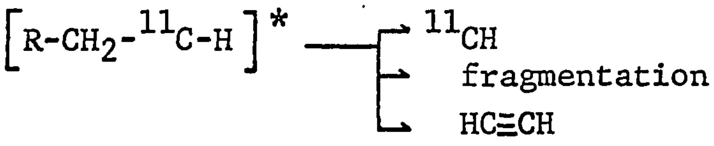


(Eq. 26)

The excited complexes formed in these reactions may either stabilize or decompose to give fragments with various numbers of carbon atoms. It appears as though the complexes formed from reactions with ^{11}C-atoms have a high probability of decomposing. Acetylene is a major product from each system and is thought to arise from the insertion of ${}^{11}C$-atoms (51) and decomposition of a complex similar to that formed in Eq. 22.

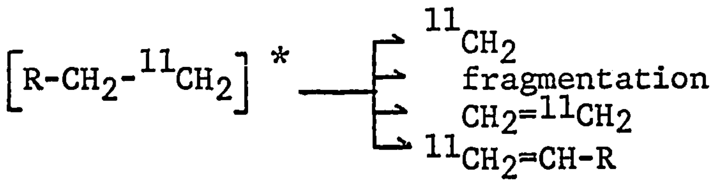
The insertion reactions of ${}^{11}C$, ${}^{11}CH$ and ${}^{11}CH_2$ radicals are used to explain the product distributions found in this study. Contributions of radiation damage to the yields of products containing more than two carbon atoms appear to be minimal. This may be seen from the zero slope of the curves given in Figs. 4-10. In order to minimize the effects of radiation damage on the C_1 and C_2 products, the experiments were run at low dose conditions, a typical run being 5-10 min in duration.

Insertion complexes similar to those formed in Eqs. 22, 25 and 18 may undergo several different reactions:



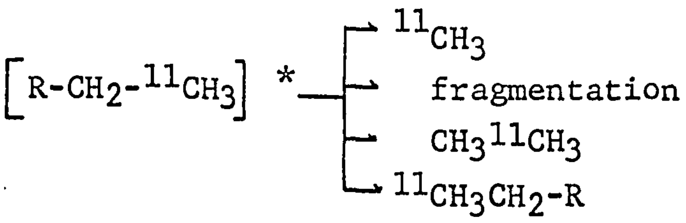
$$\left[R\text{-}CH_2\text{-}{}^{11}C\text{-}H\right]^* \rightarrow \begin{cases} {}^{11}CH \\ \text{fragmentation} \\ HC{\equiv}CH \end{cases}$$

(Eq. 27)



$$\left[R\text{-}CH_2\text{-}{}^{11}CH_2\right]^* \rightarrow \begin{cases} {}^{11}CH_2 \\ \text{fragmentation} \\ CH_2{=}{}^{11}CH_2 \\ {}^{11}CH_2{=}CH\text{-}R \end{cases}$$

(Eq. 28)



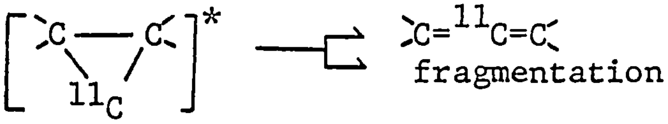
$$[R\text{-}CH_2\text{-}{}^{11}CH_3]^* \rightarrow \begin{cases} {}^{11}CH_3 \\ \text{fragmentation} \\ CH_3{}^{11}CH_3 \\ {}^{11}CH_3CH_2\text{-}R \end{cases}$$

(Eq. 29)

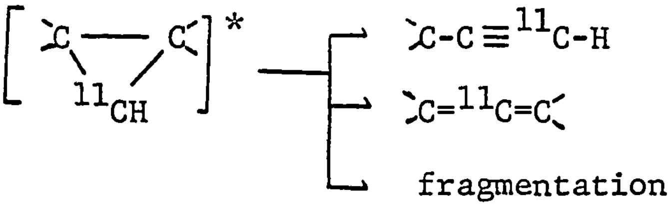
$$R\text{-}H + {}^{11}CH_3 \longrightarrow {}^{11}CH_4$$

(Eq. 30)

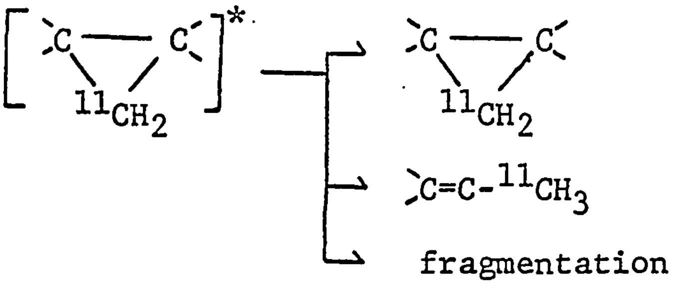
Complexes formed in Eq. 24, 26 and 20 may undergo the following reactions:



(Eq. 31)



(Eq. 32)



(Eq. 33)

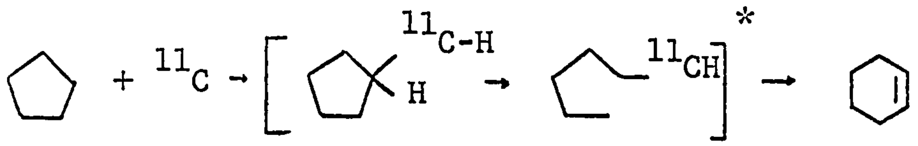
The products of the reactions of carbon-11 in hydrocarbons may be grouped into four types. Decomposition products, parent-like products and stabilization products compose the first three groups. Decomposition products contain fewer carbon atoms than the parent, parent-like compounds contain the same number of carbon atoms and stabilization products contain one more carbon atom than the parent. There is another product group containing compounds with more than one more carbon atom than the parent but no compounds of this type were isolated in this study.

The $^{11}CH_2$ radical appears to play a dominant role in the formation of the stabilization products found in n-pentane and isopentane (Tables 8 and 9, pages 58 and 59). The products resulting from the insertion of methylene into carbon-hydrogen bonds would be expected to show a random distribution. Indeed, this does appear to be the case. In n-pentane the calculated ratio of 3-methylpentane:2-methylpentane:n-hexane is 1:2:3. The experimentally determined ratio for these products is 0.8:1.4:3. This is considered to be random within the experimental error. The ratios of 2,2-dimethylbutane:2,3-dimethylbutane + 2-methylpentane:3-methylpentane were found to be 1.4:5.6:6 compared to the calculated ratios of 1:5:6 in isopentane. Again this result is considered to be random within the experimental error. These results are taken to indicate that the radical precursor of these products is the $^{11}CH_2$

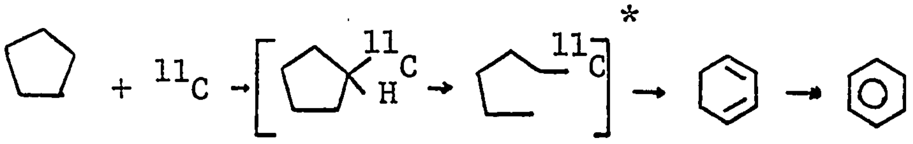
radical.

In the n-pentane and isopentane systems the alkenes found in highest yield were those containing only terminal double bonds. This could indicate two possible interpretations of the insertion reactions of ^{11}C or ^{11}CH radicals. The insertion of the radical into a carbon-hydrogen bond may not be random in the cases of ^{11}C and ^{11}CH radicals. Insertion into a primary carbon-hydrogen bond appears to be favored. Alternatively, it is possible that, although insertion is random, the insertion complex formed with a primary carbon-hydrogen bond has some mode of deexcitation not available to other insertion complexes. In either case, it appears as if the ^{11}C and ^{11}CH radicals undergo insertion at higher energies than the $^{11}CH_2$ radicals. The non-random insertion indicates that the reactions of ^{11}C and ^{11}CH are truly "hot" reactions while the reactions of the $^{11}CH_2$ radical are indistinguishable from those of thermal methylene radicals.

In the case of cyclopentane (Table 10, page 60), the only stabilization products which would be expected are methylcyclopentane and methylenecyclopentane from insertion of ^{11}CH or $^{11}CH_2$ into carbon-hydrogen bonds. However, although methylcyclopentane is observed in the expected high yield, 18.4%, methylenecyclopentane is not found. Instead, two six-carbon cyclic compounds are found, benzene and cyclohexene. Hexene-1 is also present in low yield. The methylcyclopentane can easily be explained in light of the insertion reactions of $^{11}CH_2$. Reaction schemes must be proposed for the benzene and cyclohexene formation of a different type from a typical insertion.



(Eq. 34)

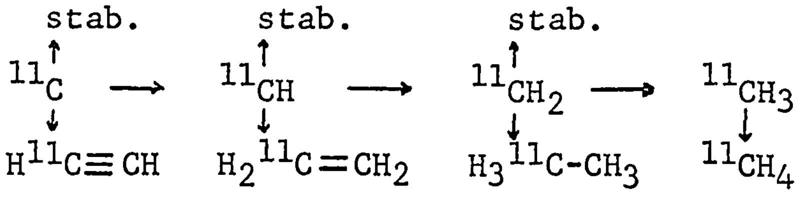


(Eq. 35)

Reactions 34 and 35 support the proposal that the ^{11}C and ^{11}CH radicals actually do react at high energies, having at least enough energy to rupture the cyclopentane ring.

The reactions of the ^{11}C atom in hydrocarbons containing double bonds lead to a product distribution considerably more complex than that found in alkanes. In pentene-1 (Table 11, page 61), the product distribution has not been completely established although most of the activity is found in observable peaks. Using the available equipment, it was not feasible to separate and identify every product. However, the separations which were achieved give some insight into the reactions in this compound. From the analyses obtained, it appears as though every compound which can be imagined as the result of an insertion reaction with pentene-1 can be found. In this system a considerable number of products are found which can be explained by the stabilization of the insertion complexes formed with the double bond by ^{11}C and ^{11}CH. These products consist mainly of the various dienes. Products of similar insertions into carbon-hydrogen bonds in n-pentane and isopentane account for 14.0 and 10.4% of the activity, respectively. In pentene-1, the diene yields total ~23.4% of the activity. This indicates that insertion of ^{11}C or $^{11}CH_2$ into the double bond forms an adduct which can dissipate the excess energy more easily than the adduct formed with carbon-hydrogen bond.

The yields of the gaseous products methane, ethane, ethylene and acetylene are lower in the pentene-1 system than in the n-pentane system. The reductions in these yields probably reflect the greater stability of the double bond insertion complex. If it is assumed that the radicals ^{11}C, ^{11}CH, $^{11}CH_2$ and $^{11}CH_3$ are responsible respectively for the formation of acetylene, ethylene, ethane and methane, one may again infer something of the energies of the different radicals. The reaction sequence may be written as:



$$\begin{tikzcd} \text{stab.} & \text{stab.} & \text{stab.} & \\ {}^{11}C \arrow[u] \arrow[d] \arrow[r] & {}^{11}CH \arrow[u] \arrow[d] \arrow[r] & {}^{11}CH_2 \arrow[u] \arrow[d] \arrow[r] & {}^{11}CH_3 \arrow[d] \\ H^{11}C\equiv CH & H_2{}^{11}C=CH_2 & H_3{}^{11}C\text{-}CH_3 & {}^{11}CH_4 \end{tikzcd} \qquad \text{(Eq. 36)}$$

neglecting other fragmentation products.

The acetylene yield apparently drops only slightly from n-pentane to pentene-1. This indicates that an appreciable fraction of the ${}^{11}C$ atoms undergo reaction at energies too high to be stabilized even by a double bond. The drop in the ethylene yield indicates that, although the ${}^{11}CH$ radicals still probably have energies above the thermal range, these energies are low enough that an appreciable number of the insertions of ${}^{11}CH$ into a carbon-carbon double bond result in stabilization of the reaction complex. The decrease in the methane and ethane yields probably reflect the fact that fewer ${}^{11}CH_2$ radicals are present in the system. This is reasonable considering that a large number of ${}^{11}CH$ radicals, the precursor to ${}^{11}CH_2$, have already entered into stable combination.

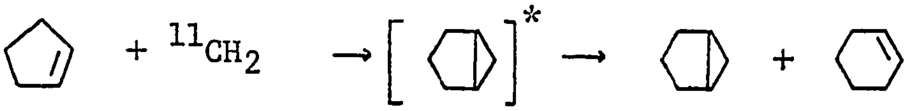
Almost all the activity could be accounted for in the n-pentane, isopentane and pentene-1 systems. Approximately 20%

of the activity in the cyclopentane system is found in unidentified products. In the next two systems to be discussed, cyclopentene and benzene, even less of the product spectra could be determined. The analytical techniques used were limited to the identification of products boiling under 200°C.

The product spectrum in cyclopentene would be expected to be similar to that obtained from cyclopentane. Similar products are formed but the yields are lower than those found in cyclopentane. Only ~54% of the activity could be assigned to identifiable products. The yield of the $^{11}CH_2$ insertion product, methylcyclopentene, is lower than that found for methylcyclopentane from cyclopentane. This reduction in yield is almost balanced by the appearance of a new product, tentatively identified as bicyclo[3.1.0]hexane which results from $^{11}CH_2$ insertion into the double bond. Benzene and cyclohexene are again found in this system as they were in cyclopentane. Benzene has also been reported as a major product from cyclopentadiene (97). The lower yields of these products from cyclopentene along with the recovery of only ~50% of the activity indicates that the ^{11}C and ^{11}CH radicals are undergoing some reaction which leads to high molecular weight products. The nature of this reaction is not yet known.

Cyclohexadiene might be considered as a logical product from both cyclopentane and cyclopentene. Cyclohexadiene is somewhat unstable with respect to benzene formation even at room temperature. The irradiations were carried out at ~40°C and the presence of the radiation flux makes it unlikely that the compound would be stable. A separation of cyclohexadiene from cyclohexene is difficult to achieve and the cyclohexene reported may have been contaminated with cyclohexadiene although inspection of the chromatograms indicated no such contamination.

In the cyclopentene system, there is another possible mechanism for the formation of cyclohexene:



(Eq. 37)

If this reaction does represent the primary mode of cyclohexene formation in this system, as seems reasonable because reactions of ^{11}C and ^{11}CH can more easily lead to cyclohexadiene or benzene, then the total contribution of the $^{11}CH_2$ radical toward stabilization products is 22.3% compared to 18.4% in the cyclopentane system indicating again the greater stability of insertion into the double bond.

Over 75% of the activity in the benzene system is found in high boiling compounds. The only product found that could be considered the direct result of $^{11}CH_2$ insertion was toluene in a yield of 5.7%. Methylene was earlier described as reacting with benzene to form a variety of products in the same boiling point range as toluene. The fact that none of these were observed supports the contention that in benzene, the reactions of ^{11}C and ^{11}CH lead to high boiling products, probably containing at least two benzene rings. The almost non-existent methane yield, 0.3%, and the low acetylene yield, 5.5%, lend support to this contention. Although an effort to identify diphenylmethane as a reaction product was unsuccessful, it is considered a likely product.

An interesting aspect of the benzene system is the presence of a relatively high yield of tagged benzene, 11.4%. This is a much higher parent-like product yield than was found in any of the other compounds studied. The parent-like compounds can be formed either by a direct replacement collision of a carbon atom in the parent with a recoil ^{11}C-atom causing the ^{11}C to impart almost all of its energy to the atom in the parent compound, or from a fragment formed from the decomposition of an excited insertion complex. In most instances, the author is inclined to favor the latter explanation. In benzene the possibility cannot be ruled out that the ^{11}C may interact with the π-bonding system as a whole in some unprecidented manner.

If it is assumed that the mechanisms given in this discussion are valid and the fragmentation products other than methane, ethane, ethylene and acetylene are ignored, the relative contributions of the various carbon radicals to the reactions may be tabulated. These results are presented in Table 15 for the three systems in which essentially all the activity was recovered.

Table 15. Relative contributions of ^{11}C, ^{11}CH, $^{11}CH_2$ and $^{11}CH_3$ to the formation of products in hydrocarbons

Parent	$^{11}CH_3$[a]	$^{11}CH_2$[b]	$^{11}CH+^{11}C$ [c]
n-pentane	8.4	22.9	47.9
isopentane	7.7	27.9	48.8
pentene-1	2.8	~25	~58

[a] From CH_4 formation.

[b] From CH_3CH_3 formation and addition of $^{11}CH_2$ to the parent.

[c] From $CH_2{=}CH_2$ and $CH{\equiv}CH$ formation and addition of a ^{11}CH or ^{11}C to the parent.

The data presented in Table 14 may be interpreted in view of reaction cross sections for the different species. The cross sections for the reactions of the radicals with n-pentane and isopentane appear to be essentially the same. In the case of pentene-1 the cross sections seem to be somewhat higher for the reactions with ^{11}CH and ^{11}C. This is probably due to the ability of the compound to stabilize the adduct formed from reactions of ^{11}CH and ^{11}C with the double bond. The cross section for reactions of $^{11}CH_2$ with pentene-1 is similar to the cross sections for the corresponding reaction in the alkanes. The lower methane yield from pentene-1 is then an indication of relatively fewer $^{11}CH_2$ radicals present in the system.

CONCLUSIONS

The product distributions resulting from the reactions of ^{11}C in six liquid hydrocarbons have been determined. The hydrocarbons chosen for this study were n-pentane, isopentane, cyclopentane, pentene-1, cyclopentene and benzene. Four product types were found, fragmentation products, parent-like products, stabilization products and products containing two or more carbon atoms than the parent.

The product distributions can be explained through consideration of a reaction mechanism involving insertion of ^{11}C, ^{11}CH or $^{11}CH_2$ radicals into carbon-hydrogen bonds or carbon-carbon double bonds, forming an excited reaction complex. Depending on the energy of the reacting species, the complex may either stabilize itself, giving a product with one more carbon than the parent, or decompose, leading to a variety of products.

A study of the effects of radiation damage on the product yields indicated that the yields of products containing more than two carbon atoms are essentially independent of dose.

Fragmentation of reaction complexes formed with ^{11}C or ^{11}CH radicals leads to the formation of such products as acetylene and ethylene. The high yields of these fragmentation products indicate that ^{11}C and ^{11}CH radicals still possess appreciable amounts of kinetic energy while undergoing insertion. The random distribution of stabilization products from the reactions of the $^{11}CH_2$ radicals indicates that the reactions of these radicals are similar to those of photochemically produced methylene radicals and that the energies of the reacting species are near the thermal range. The low yields of ethane, a product of fragmentation of the $^{11}CH_2$ reaction complex, support the view that the $^{11}CH_2$ radicals undergo reaction at near-thermal energies.

The reaction complexes formed by insertion of the carbon radicals into carbon-carbon double bonds appear to possess a higher degree of stability than complexes formed with carbon-hydrogen bonds. The product distributions from the reactions of ^{11}C with alkenes contain large numbers of highly unsaturated products resulting from the stabilization of reaction complexes formed with ^{11}C and ^{11}CH radicals. Even in these systems, however, appreciable acetylene and ethylene yields were found. It was also found that ^{11}C and ^{11}CH radicals could enter into reactions rupturing a cyclopentane ring. These results appear to be consistent with the interpretation that the ^{11}C and ^{11}CH react at energies well above the thermal range.

The results of this study can be interpreted in view of reaction cross sections. The cross sections for reaction of ^{11}C and ^{11}CH radicals appear to be higher for alkenes than alkanes, while the cross sections for reactions of $^{11}CH_2$ appear to have little structural dependence. The lower methane yields found in the alkenes probably reflect the higher cross sections for ^{11}C and ^{11}CH reactions and the correspondingly fewer $^{11}CH_2$ radicals which would be present in the reaction system.

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