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RECOIL REACTIONS OF CARBON-11 IN n-HEXANE AND CYCLOHEXANE[1]

by Charles E. Lang and Adolf F. Voigt

Abstract

Cyclohexane and n-hexane have been irradiated with x-rays from a 47 Mev electron synchrotron to produce the reaction $C^{12}(\gamma, n)C^{11}$. The distribution of the recoil C^{11} in hydrocarbons of low molecular weight has been studied using gas chromatographic separation with a scintillation counter monitoring the exit gas stream. Cyclohexane was irradiated at 30, 0 and -78°C and n-hexane at 30°. The total C^{11} produced was determined by irradiating carbon under comparable conditions, burning it to CO_2 and measuring its activity in the same manner. Under most conditions acetylene-C^{11} was the most abundant radioactive product with up to 15% of the total C^{11} appearing in this form. Methane-C^{11} and ethylene-C^{11} were produced in 2 to 7% yield depending on conditions. Radioactive ethane, propane and propylene were separated; 4-carbon compounds were observed as a group. Since the yield of C^{11} was small, no attempts were made to analyze for it in the parent compound or others of similar size. The results are discussed in terms of various mechanisms for recoil reactions. It appears that they can be explained on the basis of random fragmentation of the irradiated material by the very energetic C^{11} atoms and subsequent reactions of $C^{11}H_x$ radicals with these fragments.

Introduction

To a large extent investigations of the Szilard-Chalmers effect in organic systems have been concerned with the recoil effects of halogens in organic halides. Although these studies have elucidated several important concepts including phase, scavenger, and isotope effects,[2] and have led to the formulation of various models[2, 3] the nature of the Szilard-Chalmers effects in organic systems is as yet imperfectly understood.

Because of the difficulties in working with the carbon isotopes, the study of carbon recoils, which would be of particular relevance, has received much less attention. However, within the last several years a growing interest in the use of carbon-14 recoils for synthesis of labeled compounds has been evident.[4] Wolf and co-workers have studied recoil reactions of carbon-14 produced by the $N^{14}(n,p)C^{14}$ reaction in a variety of organic substrates. For example, after the irradiation of a mixture of benzene and 2-methylpyrazine[5] C^{14} was found in benzene and toluene to the extent of 1.9 and 1.0% of the total produced. Following hydrolysis of irradiated acetamide[6], C^{14}-labeled acetic and propionic acids were isolated; their combined activity represented about 13% of the total. A study by Mackay and Libby[7] of the effects of C^{14} recoils in n-pentane and isopentane, using aniline or aliphatic amines as the nitrogen source of the C^{14}, revealed the production of a variety of labeled 5-membered and larger hydrocarbons. Hydrocarbons of less than 5-members were not resolved but as a group represented 7% of the activity in n-pentane and about 5% in isopentane.

Only a few investigations have been made involving carbon-11 recoils and these have mainly been in inorganic systems.[8] The short half-life of carbon-11, 20 minutes, was a considerable deterent to its use until the development of gas chromatography made possible the rapid separation of tracer amounts of volatile compounds. Recently Suryanarayana and Wolf[9] in a study of the chemical effects of carbon-11 produced by the $C^{12}(n, 2n)C^{11}$ reaction in benzene found that about 4.5% of the total activity produced was accounted for in benzene and 2.2% in toluene.

In the present study the recoil products examined are the low molecular weight compounds containing C^{11} produced by the irradiation of n-hexane and cyclohexane. The reaction $C^{12}(\gamma, n)C^{11}$ was induced with x-rays from the Iowa State University synchrotron. The cross section for the photonuclear process is not large and the beam intensity was only moderate. Hence, the activity produced was not sufficient for a determination of all of the products and the more volatile, low molecular weight products were the only ones studied. It was considered that the comparison of a straight chain and a cyclic hydrocarbon would give a better insight into the mechanism of the recoil chemical reaction.

Experimental

Materials.-Eastman Kodak Company Spectro Grade cyclohexane and Phillips Petroleum Co. Research Grade n-hexane (99.96 mole % purity) were used after drying over sodium wire. The various gases used to establish elution sequences and positions were CP Grade from the Matheson Co. Helium used as a carrier gas was obtained from the U. S. Bureau of Mines with a purity in excess of 99.99%. Carbon Pearls obtained from Cabot Co. were freed of absorbed oxygen, nitrogen and water by flushing with helium at 800° for 12 hours. The carbon was stored under a helium atmosphere.

Chromatographic Columns.-It was necessary to employ a variety of columns because no single column could effectively resolve all of the products. A ten foot silica gel (14-20 mesh) column was used to separate methane, ethane, and ethylene. After its preparation, the silica gel column was heated to about 150°C and flushed for several hours with helium gas in order to remove any adsorbed material. It was always flushed for at least two hours before use in a particular analysis. In some of the early runs a 12 foot ethylacetoacetate column was used (67 grams of ethylacetoacetate to 100 grams of celite). This column separated methane, ethane—ethylene, propane, propylene-propyne, and acetylene-isobutane, but was of limited usefulness due to its failure to separate propylene from propyne and acetylene from isobutane. A more useful separation was provided by a mixed column with a six foot length of diisodecylphthalate and 16 foot length of dimethylsulfolane. This "DMS-DIDP" column, prepared with 40 grams of organic liquid to 100 grams of 28-35 mesh celite, separated methane, ethane-ethylene, propylene, propane, isobutane, and n-butane. Propyne and the other four carbon materials had retention times greater than that of n-butane. It was observed for the DMS-DIDP column that the isobutane peak preceded the acetylene peak which is contrary to the elution sequence reported by Fredericks and Brooks[10]. A 12 foot dioctylphthalate column (43 grams of dioctylphthalate to 100 grams of 48-65 mesh celite) provided a good separation of compounds of intermediate molecular weight such as n-hexane and cyclohexane. All columns with the exception of the silica gel column were prepared by addition of the organic liquids in suitable solvents to Johns-Mansville Celite-22 firebrick which had been previously cleaned, fired and sieved.

Bombardments.-Approximately 1 gram air-free samples contained in sealed pyrex ampoules were irradiated in the x-ray beam of the Iowa State University electron synchrotron operated at 47 Mev for a constant time period of 1 hour. The cross section of the $C^{12}(\gamma, n)C^{11}$ integrated from threshold to 47 Mev reaction is ~ 60 Mev-mb[11] and in an average run a total activity of the order of 0.3 mc/ml was produced. The only emitter observed in these experiments was carbon-11.

Low temperature bombardments at 0 and -78-C were made in a tube designed so that the appropriate coolant surrounded the ampoule during the irradiation.

A 5 mm thick Synthane plug positioned in front of the ampoule was irradiated in every run and the C^{11} activity produced in the plug served as a monitor for the beam. The activity of the Synthane monitor was determined by counting the C^{11} annihilation photo peak with a NaI(Tl) scintillation crystal and a Nuclear Chicago gamma-ray spectrometer, Model 1820.

Product Analysis. - The Szilard-Chalmers products were analyzed and counted according to a procedure suggested by Evans and Williard[12]. In the present investigation the products of the interest were the gaseous hydrocarbons from methane through the butanes. As produced by the irradiation, these materials were dissolved in the irradiated liquids. Solid samples were melted before analysis. The products were removed from solution by "flushing" the liquid with helium which carried the product onto the column of a Consolidated Electrodynamic Corporation gas phase chromatograph, Model X 26-201. The small amount of less volatile material picked up by the helium carrier was removed from the gas stream by adsorption on the chromatographic column and did not interfere with the subsequent analysis of the radioactivity.

After separation, the counting rates of the products as flowing gases were determined by passing the gas stream through a vial which was placed in the well of a NaI(Tl) well-type scintillation crystal. The crystal, 1.5 inches in diameter by 1 inch thick with a 0.75 inch hole, had reasonably good efficiency for the detected radiation which was the 0.51 Mev annihilation gamma-ray from the positron emitted by C^{11}. The crystal was mounted on an RCA 5819 photomultiplier tube, and the pulses were sent through a cathode follower to a Nuclear-Chicago, Model 162 scaling unit which provided a combination linear amplifier and discriminator and reduced the background to permit the detection of low counting levels.

The output from a Nuclear Chicago Model 1620 Ratemeter and from the thermal conductivity cell were displayed on a dual pen Brown recording potentiometer. Flow rates were determined using a soap-film flow meter suggested by Keulemans[13]. The Szilard-Chalmers products were identified by comparing their elution times to those of known samples. Liquid products were analyzed by the same procedure except that a 0.1 ml liquid sample was introduced directly onto the column by injection with a hypodermic syringe.

Total Activity. - Eight samples of air-free Carbon Pearls were bombarded under a helium atmosphere in the same geometry as the hydrocarbon samples. From these runs, 25 approximately 50 mg portions of carbon were ignited in a stream of oxygen and the volatile oxides were counted as flowing gases according to the procedure previously described. All transfers of the carbon samples before ignition were made in a dry box. The standard deviation of the 25 activity determinations was about 10%.

Activity Calculations. - For each component, the area under the curve of count rate vs time was measured with a planimeter and corrected to the time at which the synchrotron beam was shut off, using a value of 20.4 minutes for the half-life of C^{11}. The result, the counts recorded, was also standardized to a constant synchrotron flux and 1 gram sample. No correction was necessary for decay during the interval between the beginning and end of an activity peak since this time period was small compared to the C^{11} half-life. The corrected area was multiplied by the flow rate at which the particular component was eluted to obtain a value for the activity of the component[14]. The ratio of this value on a molar basis to the analogous value obtained from the carbon bombardments yielded the percent of total activity associated with the particular component.

Results

In Table I, results are summarized for the irradiation of liquid n-hexane and cyclohexane at 30° C and of solid cyclohexane at 0 and -78° C. The values listed are averages of the number of determinations which is given in parentheses before the value. The standard deviations in the relative yields range from 10 to 20% with an average of about 14%. Since the standard

Table I

Organic Yields of the Low Molecular Weight Hydrocarbons from the $C^{12}(\gamma, n)C^{11}$ Process in Cyclohexane and n-Hexane

	Yields from Cyclohexane, %						Yields from n-Hexane, %	
Product	30°C		0°C		-78°C		30°C	
Methane	(10)[a]	6.7[b]	(6)[a]	5.3[b]	(4)[a]	5.7[b]	(11)[a]	5.6[b]
Ethane	(4)	0.64	(1)	0.28	-		(4)	1.0
	(4)	4.2[c]					(6)	7.4[c]
Ethylene	(6)	2.7	(5)	2.1	(3)	1.7	(4)	6.3
Acetylene	(6)	14	(6)	11	(4)	4.2	(8)	15
Propane	-		-		-		(2)	0.52
Propylene	(6)	0.89	(6)	0.99	(4)	0.85	(8)	3.1
4-Carbon	(4)	1.8	(6)	2.3	(1)	1.3	(7)	3.2

a Number of determinations
b Average value of yield
c Ethane and ethylene were not resolved in these runs and the values represent the sum of the two products

deviation in the determination of the total yield was about 10%, the overall error in the yields was estimated as approximately 17%.

Cyclohexane. - The irradiation of liquid cyclohexane yielded a number of carbon-11 labeled hydrocarbons. Acetylene was the major product, followed by methane, ethylene and 4-carbon compounds. Ethane and propylene, the products of lowest yield among those detected, were produced in about equal amounts. No attempt was made to resolve the 4-carbon material which may be any combination of 4-carbon hydrocarbons other than isobutane. The production of carbon-11 labeled propane or isobutane was not observed and no attempt was made to analyze for propyne.

The phase studies showed that methane, acetylene, ethane and ethylene all decreased in amount with a change from the liquid to solid phase. In the case of ethane, no activity was observed in the runs at -78° C and its identification at zero degrees is doubtful since it was observed in only one run. Ethylene and acetylene also decreased with a decrease in temperature in the solid state while the methane yield remained essentially constant. The amount of propylene produced was apparently constant with respect to both phase and temperature. The change in the amount of 4-carbon compounds with temperature and phase is probably not much outside the experimental error, so that the apparent high value at zero degrees cannot be considered to be real.

A few qualitative experiments were run on the nature of the liquid products in irradiations at 30° C. Labeled cyclohexane and at least three other compounds of slightly lower molecular weight were observed.

n-Hexane. - The nature and amounts of products produced in hexane at 30° show strong similarities to those in liquid cyclohexane. However, propane was also observed and for almost every compound the relative amount produced is greater for n-hexane. Only in the case of methane was less produced in n-hexane than in cyclohexane. The major product was acetylene which was followed by ethylene, methane, 4-carbon compounds, propylene, ethane and propane. The 4-carbon and propylene amounts were about the same. The experiments to determine liquid products at 30° showed the formation of labeled hexane together with at least two other non-volatile compounds.

No phase or temperature studies could be made on n-hexane because the low temperature at which it freezes, -94° C, could not be maintained for the period of the irradiation under the conditions used in these experiments.

Discussion

Liquid n-Hexane and Cyclohexane. - The energy of recoil for an atom resulting from a γ, n reaction can be calculated from the following equation in which the momentum imparted to the atom by the impinging gamma-ray is neglected,

$$E_r = (E + Q) \frac{M}{m + M} . \tag{1}$$

In this equation, E is the gamma-ray energy and Q the energy released in the nuclear reaction; M and m are the masses of the recoiling atom and the neutron respectively. The yield of C^{11} as a function of the energy of the bremsstrahlung depends both on the cross section vs energy curve for the reaction $C^{12} (\gamma, n)C^{11}$ and the energy spectrum of the beam. Published yield curves[11] indicate that the highest yield occurs with bremsstrahlung between 20 and 30 Mev with the peak in the production curve at 23 Mev. Since Q for the reaction is -18.7 Mev, most of the values of E_r will lie between 0.1 and 1 Mev with an average value of about 0.4 Mev.

If the recoiling atom does not sever all of its bonds in the recoil process, a portion of the energy appears as internal energy of the complex. The internal energy is given by[15]

$$E_i = E_r \frac{M}{M + M'} \tag{2}$$

in which M is the mass of the recoiling atom and M' is the mass of the substituents attached to it. Even in the most extreme case in which M' is one, the internal energy of the carbon-11 recoil complex would be about 30,000 ev which is greatly in excess of the 4 ev carbon-hydrogen bond energy. Consequently rupture of all bonds to the carbon-11 is assured.

The unbonded carbon-11 recoil atom is undoubtedly ionized as a reulst of its high kinetic energy. The energy of an electron having the same velocity as the recoiling atom is given by

$$E_e = \frac{M_e}{M} E_r \qquad (3)$$

in which $\underline{M_e}$ is the mass of the electron. If $\underline{E_e}$ is above the binding energy of an electron $\underline{E_B}$, there will be a finite probability that the moving atom will lose the electron. This probability falls off for $\underline{E_e} < \underline{E_B}$ [16]. Taking the first, second and third ionization potentials of carbon as 11.3, 24.4 and 47.9 ev[17], the minimum values of the recoil energy necessary to cause a loss of 1, 2 and 3 electrons are 0.23, 0.49 and 0.98 Mev. On this basis of charge of +1 is quite likely, a charge of +2 will occur frequently, and charges of greater than +2 are less likely.

Consequently it would be expected that carbon-11 recoil atoms would be produced with initial energies of about 0.1 to 1 Mev and charges of +1 or +2. These recoil atoms slow down, dissipating their energy by a combination of ionization and excitation processes and collisions in which bonds are broken and radicals produced. When the energy of the recoiling atom drops below about 48 ev, carbon-hydrogen radicals such as $C^{11}H$, $C^{11}H_2$ and $C^{11}H_3$ will form. The corresponding singly charged species are also possible. However, only for $C^{11}H_3$ in cyclohexane and n-hexane and possibly for $C^{11}H$ in cyclohexane are the ionization potentials for the formation of singly charged ions less than those for the organic solvents[18].

If it is assumed that the carbon-11 recoil atoms are incorporated into various hydrogen complexes when they reach the end of their path, a mechanism can be constructed by which the observed Szilard-Chalmers chemistry of liquid n-hexane and liquid cyclohexane is explained using the Willard "random fragmentation" model[2]. That is, products are formed, either in hot or thermal regions, as a result of reactions of $C^{11}H$, $C^{11}H_2$ and $C^{11}H_3$ with free radicals which the carbon-11 produces in slowing down. In the absence of scavenger experiments the relative contributions of hot and thermal reactions can not be assessed; it is assumed that both occur.

It is difficult to explain the formation of acetylene in terms of any radical mechanism except one which involves $C^{11}H$ radicals. Since production of CH_2 radicals is likely in both irradiated compounds as recoil atoms are slowed down, interaction of $C^{11}H$ with CH_2 by means of the reaction:

$$:\underset{\cdot}{C}^{11}H + :CH_2 \longrightarrow {}^{\circ}C^{11}H = CH_2 \longrightarrow C^{11}H \equiv CH + H^{\cdot}, \qquad (4)$$

is suggested as a synthesis path for acetylene. The CH_2 radical could also react with $C^{11}H_2$ and $C^{11}H_3$ by means of the reactions

$$:C^{11}H_2 + :CH_2 \longrightarrow C^{11}H_2 = CH_2 \tag{5}$$

and

$$\cdot C^{11}H_3 + :CH_2 \longrightarrow C^{11}H_3 - \underset{\cdot}{C}H_2 \xrightarrow{H\cdot} C^{11}H_3 - CH_3 \tag{6}$$

$$\llcorner\!\!\longrightarrow C^{11}H_2 = CH_2 + H\cdot \tag{7}$$

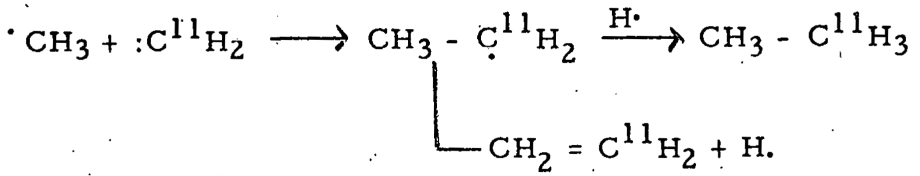
On the basis of the smaller yields of ethane and ethylene compared to that of acetylene it seems likely that both $C^{11}H_2$ and $C^{11}H_3$ are present in much lower concentrations than $C^{11}H$.

A number of reactions are possible between the $C^{11}H$, $C^{11}H_2$ and $C^{11}H_3$ and the methyl, ethyl and propyl radicals. These are present in the n-hexane system, as they are in electron radiolysis of hexane[19], and can be produced from cyclohexane by multiple bond rupture together with subsequent hydrogen abstraction. Reactions of the type

$$\cdot CH_3 + :\underset{\cdot}{C}{}^{11}H \longrightarrow CH_3 - \underset{\cdot\cdot}{C}{}^{11}H \longrightarrow CH_2 = C^{11}H_2 \tag{8}$$

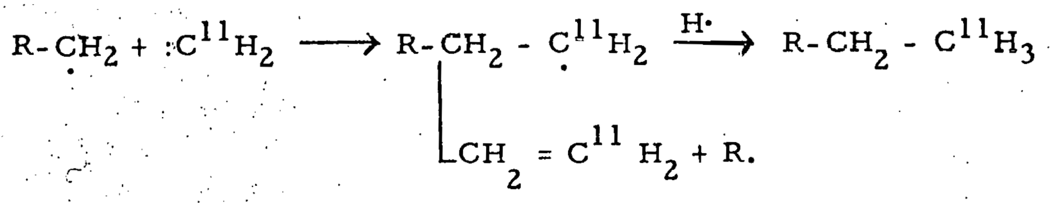
$$RCH_2\cdot + :\underset{\cdot}{C}{}^{11}H \longrightarrow RCH_2 - \underset{\cdot\cdot}{C}{}^{11}H \longrightarrow RCH = C^{11}H_2 \tag{9}$$

are certainly possible with hot $C^{11}H$ radicals and likely with cold radicals as well. Of the following reactions,



$$\cdot CH_3 + :C^{11}H_2 \longrightarrow CH_3 - \dot{C}^{11}H_2 \xrightarrow{H\cdot} CH_3 - C^{11}H_3 \tag{10}$$

$$\longrightarrow CH_2 = C^{11}H_2 + H. \tag{11}$$



$$R-\dot{C}H_2 + :C^{11}H_2 \longrightarrow R-CH_2 - \dot{C}^{11}H_2 \xrightarrow{H\cdot} R-CH_2 - C^{11}H_3 \tag{12}$$

$$\longrightarrow CH_2 = C^{11}H_2 + R. \tag{13}$$

$$\cdot CH_3 + \cdot C^{11}H_3 \longrightarrow CH_3 - C^{11}H_3 \tag{14}$$

$$R-\dot{C}H_2 + \cdot C^{11}H_3 \longrightarrow R-CH_2-C^{11}H_3, \tag{15}$$

those which lead to the saturated materials can proceed in the thermal region while those which lead to ethylene are known to occur in hot processes[20]. Since $C^{11}H$ is taken to be the most abundant carbon-11 hydrogen complex, the unsaturated compounds with three or more carbons, reaction 9, are favored over the corresponding saturated materials, reactions 12 and 15. This is in agreement with the relative yields of propane and propylene in both n-hexane and cyclohexane. Ethylene is favored by a number of reaction paths, reactions 5, 7, 8, 11 and 13; consequently, the rather large yields of ethylene from both compounds is expected. Presumably methane is produced by means of hydrogen abstraction in either thermal or hot processes.

Compounds of higher molecular weight are also produced. Some of these were detected, e. g. C^{11} labeled hexanes from n-hexane and compounds with 4 to 6 carbons from both n-hexane and cyclohexane. Since the activity produced was insufficient for specific identification, little can be said other than conjecture. Products of reactions of various radicals, such as butyl, pentyl, and hexyl with the C^{11}- bearing complex would be expected and the $C^{11}H_2$ radical would react with the original substrate to form labeled heptanes. The fact that most of the gaseous products are found in lower yields from cyclohexane than from n-hexane is probably due to the production of relatively fewer methyl, ethyl and propyl radicals in the former.

Phase and Temperature Effects. - The study of the effect of temperature on the yields from cyclohexane indicates that for the volatile compounds detected there is a definite reduction in yield with reduction in temperature. This is particularly true for acetylene but to a lesser extent for the other compounds. The effect may be due in part to change in phase but the differences in the yields of acetylene in the solid state irradiations at 0 and -78° are very pronounced. There is much less effect for methane and the yields of propylene are largely insensitive to temperature or phase changes. These results are insufficient as yet to serve as a basis for discussing the mechanism, but it seems likely that thermal reactions play a fairly important role in the observed processes. Scavenger experiments will enable relative assessment of the thermal and hot reactions.

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