Ethylene-¹¹C Formation in Alkyl Chlorides. Mechanisms and Isotope Effects¹

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Energetic carbon-11 atoms were allowed to react with specifically deuterated alkyl chlorides and with mixtures of protonated and perdeuterated alkyl chlorides. The doubly labeled ethylenes (¹¹C and D) formed in this process were analyzed by radiogas chromatography. The observed ¹¹C distribution in the isotopic ethylenes is consistent with the previously proposed "methylene insertion and decomposition mechanism". The results further suggest that in addition to methyne formation following $C(^{1}D)$ insertion into carbon-hydrogen bonds a fraction of methyne may be formed via hydrogen abstraction involving $C(^{1}D)$ and $C(^{3}P)$. Chlorine containing compounds seem to be able to divert $C(^{1}D)$ from forming methyne by chloromethyne formation.

Introduction

The hot atom chemistry of carbon has been discussed in review articles by Wolf² and Wolfgang³ in which the mechanistic approach to the chemistry of energetic carbon atoms has been documented.

One of the major products formed following the generation of carbon-11 atoms via nuclear processes, such as ${}^{12}C(p,pn){}^{11}C, {}^{14}N(p,\alpha){}^{11}C, {}^{12}C(n,2n){}^{11}C$, and others, in hydrocarbons is carbon-11 labeled ethylene. Evidence for methyne, [CH:], insertion into the C-H bonds of methyl groups being responsible in major part for the production of ethylene-¹¹C from the hydrocarbons was adduced from structure dependence studies and other data by Wolf and Stöcklin.⁴⁻⁶ An alternative to this mechanism was suggested by MacKay et al.,⁷ who proposed that carbon atom insertion into a C-H bond followed by rapid decomposition of the insertion complex produces a vinyl radical, which in turn can abstract a hydrogen from the substrate to give ethylene- ^{11}C .

Double label techniques have been used to study the mechanisms and isotope effects involved in the formation of ethylene-¹¹C following the nuclear process ${}^{12}C(p,pn){}^{11}C$ in a variety of mixtures of protonated and perdeuterated hydrocarbons, and specifically deuterated compounds.⁸

The results of these studies further supported methyne insertion into methyl groups as leading to ethylene- ${}^{11}C$ formation. They ruled out contributions made by the reactions (hydrogen abstraction) of ${}^{11}C_2$ species, possibly formed via "high energy stripping", 9,10 to the overall ethylene yield (in oxygen scavenged systems).

In the following similar double label techniques will be described which have been employed in the study of the formation of ethylene-¹¹C following ¹²C(p,pn)¹¹C in a series of mixtures of protonated and perdeuterated alkyl halides, specifically deuterated alkyl halides, and mixtures of protonated and perdeuterated hydrocarbons with carbon tetrachloride. The observed ¹¹C distribution among the various isotopic ethylenes will be discussed within the framework of the existing "insertion decomposition" mechanism^{2,7,8,11-16} of ethylene formation.

Experimental Section

Deuterated Alkanes. The specifically deuterated CD_3CH_2Cl and the perdeuterated compounds C_2D_6 , C_2D_5Cl , and $n-C_4D_9Cl$ were obtained from Merck Sharpe

TABLE I: Purity of Deuterated Compounds

compd	% purity	probable major impurity ^a		
C ₂ D ₆	97.2	C,D,H		
ĊĎ,ČD,Cl	98.8	C,HD₄Cl		
CD, CH, Cl	95.3	C,H,D,Cl		
$CD_{3}(CD_{2})_{3}Cl$	92.3	C₄HĎ,Cl		

^a Impurities identified by cracking pattern in the mass spectrum. Analysis done at BNL.

and Dohme, Ltd. Montreal, Canada. Mass spectral analyses and deuterium analyses were provided by Merck. Deuterium analyses were also carried out at BNL. Table I lists the analyses. The structure of the most probable impurity is based in each case on the cracking patterns of the labeled compounds. The results listed in subsequent tables have been corrected for those compositions.

Other Compounds. Phillips Research grade ethane, n-butyl chloride (Fisher Spectranalyzed Grade), and ethyl chloride (Matheson USP Grade) were used without further purification.

Airco Research Grade oxygen and xenon were used without further purification. Mass spectrometric assays provided by the supplier indicated less than 4 ppm of impurities.

Irradiation Techniques. The gas mixtures were contained in quartz vessels and subjected to a diffused beam of 33-MeV protons at the BNL 60-in. cyclotron in order to effect the ¹²C(p,pn)¹¹C reaction. Typical beam intensities were 1 μ A with exposure times ranging from 50 to 300 s. The radiation dose was 1.74×10^{-4} eV molecule⁻¹ $\mu A^{-1} \ s^{-1}$ as determined by acetylene to benzene dosimetry. 17 No change in the total ethylene- ${}^{11}C$ yields or in the relative ¹¹C distribution among the isotopic ethylenes was observed as a function of varying radiation dose within this range.

Samples were irradiated at room temperature in the gas phase at a pressure of 700 torr, and in the presence of 4.5mol % oxygen scavenger. There were the following exceptions: (1) Mixtures containing carbon tetrachloride and n-butyl chloride were heated to 80 °C during the bombardment to ensure the reactants being in the gaseous state. (2) The mixture of xenon, ethane, and ethane- d_6 contained 2.25 mol % oxygen, although the ratio of ethane to oxygen was the same as in all other samples.

Assay of the Isotopic Ethylenes. The assay of the isotopic ethylenes was carried out in a manner similar to

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TABLE II:	Ethylene	Yields in	Specifically	Deuterated	Alkyl	Chlorides	and	Mixtures	of Proto	nated and
Perdeuterate	d Alkanes	1	-		-					

		absolute vields				
substrate	¹¹ C ₂ H ₄	¹¹ C ₂ H ₃ D	¹¹ C ₂ H ₂ D ₂	¹¹ C ₂ HD ₃	¹¹ C ₂ D ₄	ethylene- ¹¹ C
$\begin{array}{r} C_{2}H_{5}Cl + C_{2}D_{5}Cl \\ n \cdot C_{4}H_{9}Cl + n \cdot C_{4}D_{9}Cl \\ 14\% \ CCl_{4} + (C_{2}H_{6} + C_{2}D_{6}) \\ 50\% \ Xe + (C_{2}H_{6} + C_{2}D_{6}) \\ CD_{3}CH_{2}Cl \end{array}$	$\begin{array}{c} 29.1 \pm 0.6 \\ 31.4 \pm 1.8 \\ 31.0 \pm 2.0 \\ 25.4 \pm 1.3 \\ 1.7 \pm 0.4 \end{array}$	$28.3 \pm 0.3 \\ 28.4 \pm 1.8 \\ 29.8 \pm 0.3 \\ 32.4 \pm 1.5 \\ 3.3 \pm 0.7$	$\begin{array}{c} 0.4 \pm 0.5 \\ 0.6 \pm 0.3 \\ 0.8 \pm 1.0 \\ 0.1 \pm 0.9 \\ 1.0 \pm 0.4 \end{array}$	$\begin{array}{c} 22.6 \pm 0.8 \\ 21.7 \pm 1.2 \\ 20.6 \pm 0.6 \\ 19.7 \pm 1.2 \\ 42.0 \pm 0.7 \end{array}$	$\begin{array}{c} 19.5 \pm 1.2 \\ 17.9 \pm 2.6 \\ 17.6 \pm 1.5 \\ 22.6 \pm 1.6 \\ 52.0 \pm 0.0 \end{array}$	$\begin{array}{c} 4.2 \pm 0.5 \\ 7.0 \pm 0.6 \\ 11.8 \pm 0.7 \\ 13.8^{a} \\ 3.7 \pm 0.1 \end{array}$

^a Only one determination.

that previously described.^{13,14,18} Carrier ethylenes were added to the irradiated mixture and the ethylenes-¹¹C were isolated from the bulk gas by gas chromatography. The mixture of the isotopic ethylenes-¹¹C was collected and subsequently separated into its various components: ¹¹C₂H₄, ¹¹C₂H₃D, ¹¹C₂H₂D₂, ¹¹C₂HD₃, and ¹¹C₂D₄ by a recycling gas chromatographic method^{13,18-20} using columns consisting of 30–60 mesh firebrick coated with 25% AgNO₃-saturated ethylene glycol.²¹

The assay technique used in this investigation can distinguish mass isomers of ethylene, but not positional isomers. For example, ¹¹CH₂=CD₂, CH_2 =¹¹CD₂, *cis*-CHD=¹¹CHD, and *trans*-CHD=¹¹CHD cannot be distinguished. These data have been corrected for the nonisotopic purity of the substrate, as discussed previously, and represent the arithmetic mean of the results of at least three experiments. The error limits cited are one standard deviation.

The radioactivity measurements were made in the usual way by gas effluent counting.²² The total gaseous ¹¹C activity was determined by counting an aliquot using conventional static gas counting techniques. The relative ¹¹C amounts in the various isotopic ethylenes were accurately determined by resolving the relative areas under each peak in the radioactivity curves corresponding to each one of the five possible products, with a Dupont 310 curve resolver. The instrument was calibrated for peak shape with standard compounds, e.g., $C_2H_4^{-11}C$ and $C_2D_4^{-11}C$.

Results and Discussion

Table II summarizes the relative yields of the various isotopic ethylenes-¹¹C (corrected for isotopic composition of the substrate) obtained following ¹²C(p,pn)¹¹C in equimolar mixtures of C₂H₅Cl-C₂D₅Cl, C₄H₉Cl-C₄D₉Cl, in the specifically deuterated compounds of CD₃CH₂Cl, and in equimolar mixtures of C₂H₆-C₂D₆ containing 14% CCl₄ and 50% Xe.

The failure to observe significant amounts of ${}^{11}C_2H_2D_2$ is in agreement with the conclusion made previously that an intermolecular mechanism of the type

$$\mathrm{RCH}_3 + {}^{11}\mathrm{C}_{\mathrm{hot}} \rightarrow {}^{11}\mathrm{C}_2 \xrightarrow{\mathrm{several steps}} {}^{11}\mathrm{C}_2\mathrm{H}_4 \qquad (1)$$

including "high energy stripping" or "abstraction" similar to that proposed for the "intermolecular" production of acetylene- ${}^{11}C^{9,10}$ does not contribute to ethylene- ${}^{11}C$ formation in acyclic alkanes.

Thus the present results shall be considered in view of the "¹¹CH-insertion" mechanism,^{2,4-6,11-15} eq 2-4. This mechanism predicts that ethylene-¹¹C production is preceded by ¹¹CH, the C-H bond of a methyl group.

CH Insertion-Decomposition Mechanism.

$$RH + {}^{11}C \rightarrow {}^{11}CH + R.$$
 (2)

$$R'CH_3 + {}^{11}CH \rightarrow [R'CH_2{}^{11}CH_2]$$
(3)

$$[\mathbf{R}'\mathbf{C}\mathbf{H}_2^{11}\mathbf{C}\mathbf{H}_2] \rightarrow \text{``other products''} \rightarrow \mathbf{R'} + \mathbf{C}\mathbf{H}_2 = \mathbf{1}^{11}\mathbf{C}\mathbf{H}_2$$
(4)

An inspection of the results in Table II reveals immediately that the isotopic ethylenes⁻¹¹C are not formed in the proportions which one would expect if hydrogen abstraction (step 2) and insertion (step 3) were to occur at random. As an example consider the results using $C_2H_5Cl-C_2D_5Cl$ (1:1) as substrate. One would predict random distribution yields of 25%. As discussed in the previous paper in this series⁸ ethylene formation exhibits two isotope effects, one in the formation of methyne (CH or CD), and again in the insertion step (¹¹CH or ¹¹CD insertion into a C-H or C-D bond).

The presence of these isotope effects in the individual reaction steps has been found to be reflected in the relative distribution among the various isotopic ethylenes- ^{11}C .

In the present case, e.g. in mixtures of $C_2H_5Cl-C_2D_5Cl$ the yields of those compounds whose formation includes H or D abstraction by ¹¹C atoms and subsequent insertion of CH or CD into methyl groups are C_2H_4 and ¹¹ C_2H_3D or ¹¹ C_2HD_3 and ¹¹ C_2D_4 , respectively. Thus the "formation isotope effect" can be assessed from the ratio ¹¹ $C_2H_4/$ ¹¹ C_2H_3D and ¹¹ $C_2HD_3/^{11}C_2D_4$.

On the other hand the "insertion isotope effect" can be recognized from comparison of the total yields of isotopic ethylene-¹¹C produced via CH and CD insertion into a CH₃ or CD₃ group; e.g., in the mixture $C_2H_5Cl-C_2D_5Cl$ the products ¹¹C₂H₄ and ¹¹C₂H₃D result from CH and CD insertion into the CH₃ group, whereas ¹¹C₂HD₃ and ¹¹C₂D₄ are formed via CH and CD insertion into the CD₃ group.

Table II shows the distribution of isotopic ethylenes observed in the systems studied in this investigation. All mixtures contain 4.5% oxygen as scavenger. The product ratios in Table III demonstrate the formation isotope effect for methyne to be significantly different from that found in alkanes⁸ with production of ¹¹CH being favored over ¹¹CD by a factor of 1.1 as compared with about 0.85 in the alkanes. Identical results were found in a $n-C_4H_9Cl/n$ - C_4D_9Cl mixture and with a mixture of 14% CCl_4 , 4.5% O_2 , and 81.5% C_2H_6/C_2D_6 (Table II). On the other hand, the insertion isotope effect as it can be assessed from the ratio $({}^{11}C_2H_4 + {}^{11}C_2H_3D)/({}^{11}C_2HD_3 + {}^{11}C_2D_4)$ in these systems is in the same direction, and of approximately the same magnitude, as found in alkanes (i.e., insertion into CH₃ is favored over insertion into CD_3 by an average of 1.41). Absolute yields of ethylene are reduced dramatically in chloroalkanes, although with increasing chain length, the ethylene yield approaches that in the equivalent alkane. For example, ${}^{11}C_2H_4$ yield as 1% in CH₃Cl,²³ 25% in CH₄, but 7% in C₄H₉Cl to be contrasted with 12% in C₄H₁₀. However the ratio of ¹¹CH products to ¹¹CD products is almost independent of chain length. Moreover, the experiments with CCl_4 and ethane indicate that the chlorine does not have to be on the molecule from which the methyne insertion complex is formed for the chlorine to cause this inversion in the ratio of products from CH and CD.

We can gain insight into the reactions of carbon atoms in alkyl chlorides by comparing them to the behavior of a more familiar carbene, CH_2 , which also reacts in two

TABLE III: Ethylene-11C Production Ratios

substrate	$\frac{{}^{11}C_2H_4}{{}^{11}C_2H_3D}$	$\frac{{}^{11}\text{C}_2\text{HD}_3}{{}^{11}\text{C}_2\text{D}_4}$	$\frac{{}^{11}C_2H_4 + {}^{11}C_2H_3D}{{}^{11}C_2HD_3 + {}^{11}C_2D_4}$
$\overline{C_2H_2Cl} + C_2D_2Cl$	1.03 ± 0.03	1.16 ± 0.05	1.36 ± 0.09
$n - C_4 H_0 C_1 + \frac{1}{2}$ $n - C_1 H_0 C_1$	1.11 ± 0.12	1.21 ± 0.18	1.52 ± 0.25
14% CCl ₄ +	1.04 ± 0.04	1.22 ± 0.18	1.57 ± 0.15
$(C_2H_6 + C_2D_6)$ 50% Xe + $(C_2H_4 + C_2D_6)$	0.78 ± 0.04	0.87 ± 0.03	1.36 ± 0.16

different electronic states. Roth²⁴ and Setser²⁵ have shown that, when reacting with CH₂Cl₂ and other chlorinated molecules, singlet methylene selectively abstracts chlorine atoms, and triplet methylene abstracts hydrogen. They also found that the reaction of ${}^{1}CH_{2}$ with chlorine is faster than the intersystem crossing to ${}^{3}CH_{2}$.

These facts suggest the following: In alkanes, both singlet and triplet carbon atoms are present, and both contribute to the ethylene yield by abstraction of hydrogen to form methyne. However, in the presence of an alkyl chloride, some singlet carbon is diverted to form chloromethyne, which then further reacts with oxygen to form carbon- ^{11}C monoxide:

$${}^{11}C({}^{3}P) + RCH_2Cl \rightarrow {}^{11}CH + RCHCl$$

$$^{11}C(^{1}D) + RCH_2Cl \rightarrow ^{11}CCl + RCH_2$$
.

 $^{11}CCl + O_2 \rightarrow ^{11}CO + OCl$

This diversion of a large fraction of methyne sharply reduces the ethylene- ${}^{11}C$ yield and contributes to the very high yield of carbon monoxide in these systems. The reaction of C(³P) is not influenced by the presence of chlorine in the medium. This is consistent with assuming that the acetylene yield in a typical alkyl chloride is identical with the acetylene yield in the analogous alkane.²³

Now we can understand why the isotope effect apparently is different in alkyl chlorides. It has been demonstrated previously that C(¹D) may produce methyne with a ratio of CH/CD < 1 by the insertion–decomposition mechanism.^{8,26} The production of methyne by hydrogen abstraction would be expected to result in a ratio of CH/CD > 1. The overall isotope effect we observe in alkanes is the result of two competing reactions.

insertion-decomposition pathway

$$C(^{1}D) + RH \rightarrow CH + R \qquad CH/CD < 1$$

abstraction pathway

$$C(^{1}D) + C(^{3}P) + RH \rightarrow CH + R \qquad CH/CD > 1$$

In alkyl chlorides C(1D) atoms undergoing abstraction reactions, which are presumably those at near thermal

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

An attempt was made to alter the ratio of CH products to CD products in an ethane/ethane- d_6 mixture by addition of 50% xenon as spin converter. Xenon should have depleted the singlet carbons, enhanced the concentration of triplet carbons, and increased the relative amount of methyne formed by abstraction. This should have increased the ratio of CH/CD products as compared to that found in the neat mixture (~ 0.8). The results in Table II, however, indicate no noticeable effect. One possible reason for the absence of an effect is that not enough xenon was present to alter significantly the ${}^{3}P/{}^{1}D$ ratio.

References and Notes

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