mune[5b] has pointed out, an effectively square geometry for the parent cyclobutadiene in a matrix is not incompatible with the distorted structures found in the crystals of derivatives, provided that the potential surface for distortion is flat. Relatively flat potential surfaces for distortion are known in larger molecules with [4*n*]annulene perimeters, which undergo rapid (on the NMR time scale) oscillation between two equivalent bond-alternated forms with energies of activation on the order of 3–5 kcal/mol.[6]

(5) (a) H. Irngartinger and H. Rodewald, *Angew. Chem., Int. Ed. Engl.*, **13**, 740 (1974); (b) L. T. J. Delbaere, M. N. G. James, N. Nakamura, and S. Masamune, *J. Am. Chem. Soc.*, **97**, 1973 (1975).

(6) E. Vogel, H. Konigshofen, K. Mullen, and J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, **13**, 281 (1974); E. Vogel, H. Konigschofen, J. Wassen, K. Mullen, and J. F. M. Oth, *ibid.*, **13**, 732 (1974), and references therein.

(7) (a) W. T. Borden, *Chem. Commun.*, 881 (1969); (b) W. T. Borden and L. Salem, *J. Am. Chem. Soc.*, **95**, 932 (1973); (c) W. T. Borden, *ibid.*, **97**, 2906 (1975); (d) W. T. Borden, "Modern Molecular Orbital Theory for Organic Chemists", Prentice-Hall, Englewood Cliffs, N.J., 1975, pp 208–223.

(8) H. A. Jahn and E. Teller, *Proc. R. Soc. London, Ser. A*, **161**, 220 (1937).

(9) R. G. Pearson, *J. Am. Chem. Soc.*, **91**, 4947 (1969), and references therein.

(10) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

(11) The semiempirical calculations of M. J. S. Dewar, M. C. Kohn, and N. Trinajstic, *J. Am. Chem. Soc.*, **93**, 3437 (1971), also show only a small (2 kcal/mol) energy gain for the lowest singlet on distortion. Although not given explicitly by the authors, this number can be deduced from their calculated difference in energy between the triplet and the rectangular singlet and from the fact that they find the square singlet to be accidentally degenerate with the triplet.

(12) For a discussion, see R. G. Parr, "The Quantum Theory of Molecular Electronic Structure", W. A. Benjamin, New York, N.Y., 1963.

(13) A similar technique for computing multicenter integrals was used by D. P. Craig, *Proc. R. Soc. London, Ser. A*, **202**, 498 (1950), in an early calculation on cyclobutadiene.

(14) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

(15) An earlier treatment of square cyclobutadiene by Craig[13] also showed that the singlet becomes the ground state when CI is included.

(16) See, for instance, ref 7d, pp 265–271.

(17) The correct expression can be obtained by using the lowering operator on (2). It will then be observed that a detailed interpretation of the effect of CI on improving the $m_s = 0$ component seems different than that for $m_s = 1$, as is often the case in triplet states. Although the mixings of the excited configurations into the lowest ones appear to be very different for the $m_s = 1$ and 0 components of the triplet, they of course have the same effect and result in wave functions that have identical energies.

(18) Note Added in Proof. M. J. S. Dewar and H. W. Kollmar, *J. Amer. Chem. Soc.*, **97**, 2933 (1975), have, in contrast to previous results from the Dewar group,[11] found square singlet cyclobutadiene to lie 13 kcal/mol above the triplet. Since, as discussed above, any calculation of the NDO type, in which the zero differential overlap approximation is made, must perforce lead to an accidental degeneracy between the singlet and triplet in the square geometry, this latest result is obviously spurious. It arises from the fact, apparently pointed out by a referee of the Dewar communication (see footnote 19 therein), that in order to obtain the $^1B_{1g}$ state of the square molecule, CI must be included between the two electronic configurations appropriate for describing the two possible rectangularly distorted cyclobutadienes. Dewar's failure to include this minimal CI results in an overestimation of the energy of the square singlet by $\frac{1}{4}(\gamma_{11} - 2\gamma_{12} + \gamma_{13})$. Using Dewar's formula for calculating electron repulsion integrals, the overestimation of the energy of the square singlet in his recent calculation is computed to be 13 kcal/mol. This fact, taken together with the discussion above of the additional stabilization of the singlet relative to the triplet by inclusion of further CI, renders improbable Dewar's assertion that the triplet lies below the singlet in a square geometry. Thus, even if the triplet should ultimately be shown by experiment to be the state observed in the matrix by ir, Dewar's explanation, that this state is metastable because it has a lower energy at its equilibrium square geometry than the singlet ground state, appears highly unlikely.

Ethylene Formation in Carbon Atom Reactions. Mechanism and Isotope Effects[1]

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Abstract: Energetic carbon-11 atoms were allowed to react with specifically deuterated hydrocarbons containing completely deuterated methyl or methylene groups and with mixtures of protonated and perdeuterated hydrocarbons. The doubly labeled ethylenes (^{11}C and D) formed in this process were radio gas chromatographically analyzed. The failure to observe carbon-11 labeled $C_2H_2D_2$ in any of these systems suggests that a mechanism including C_2 formation, e.g., by "high-energy stripping", and subsequent hydrogen abstraction does not significantly contribute to ethylene-^{11}C production. The ratios $^{11}C_2H_3D/^{11}C_2H_4$ and $^{11}C_2D_4/^{11}C_2HD_3$ obtained from reaction in equimolar mixtures of C_2H_6 and C_2D_6 or C_3H_8 and C_3D_8 and in CH_3CD_3 are consistently greater than 1, which provides additional support for the contention that ethylene-^{11}C is formed primarily via methyne insertion into the carbon–hydrogen bonds of methyl groups. The ^{11}C distribution among the various isotopic ethylenes observed in the systems under investigation indicates preferential CD formation and preferred insertion by methyne (^{11}CD or ^{11}CH) into CH_3 relative to CD_3 groups.

The hot-atom chemistry of carbon has been discussed in review articles by Wolf[2] and Wolfgang[3] 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 ($\dot{C}H$:) insertion into C–H bonds of methyl groups being responsible in major part for the production of ethylene-^{11}C 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.[7a] 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. MacKay et al.[7b] subsequently suggested that pentene-*1*-^{11}C resulted from methyne-^{11}C reaction in ethylene. The use of ethylene as a substrate, however, precludes the intermediacy of either the vinyl radical or of methyne in forming ethylene-^{11}C. Thus it is not directly relevant to the results reported in this paper.

Double label techniques will be described which have

Table I. Composition of the Substrate Molecules

Compd	% purity	Probable major impurity[a]	Place of analysis
CD_3CD_3	97.2	CHD_2CD_3	BNL
CH_3CD_3	97.1	CH_3CHD_2	Merck
$CD_3CD_2CD_3$	95.0	$CHD_2CD_2CD_3$	Merck
$CH_3CD_2CH_3$	98.0	CH_3CHDCD_3	Merck
$CD_3CH_2CD_3$	85.7	$CHD_2CH_2CD_3$	Merck
$CH_3CH_2CD_3$	94.0	$CH_3CH_2CHD_2$	Merck

[a] Impurities identified by cracking pattern in the mass spectrum.

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

Evidence will be presented in this paper which further supports the methyne insertion mechanism into methyl groups leading to ethylene-^{11}C formation. It rules out contributions made by the reactions (hydrogen abstraction) of $^{11}C_2$[8] species, possibly formed via "high-energy stripping",[9] to the overall ethylene yield (in oxygen scavenged systems). The observed ^{11}C distribution among the various isotopic ethylenes will be discussed within the framework of the existing "insertion-decomposition"[2,7,10-15] mechanism.

Experimental Section

Deuterated Alkanes. The specifically deuterated $CD_3CH_2CH_3$, $CD_3CH_2CD_3$, $CH_3CD_2CH_3$, CD_3CH_3 and the perdeuterated compounds C_2D_6 and C_3D_8 were obtained from Merck Sharpe and Dohme, 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 pattern of the labeled compounds. The results listed in subsequent tables have been corrected for these compositions. The correction factor was found by assuming no isotope effects to be operative in the system. The ratio of the yield of a particular deuterated product expected in the pure substrate to the yield expected in the impure substrate was used as the correction factor. In the special case where no yield of a given product was expected in the pure substrate, the yield expected in the impure substrate was subtracted from the experimental yield.

Other Compounds. Phillips Research Grade ethane and propane were used without further purification.

Airco Research Grade oxygen was used without further purification. Mass spectrometric assays provided by the supplier indicate 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 $^{12}C(p,pn)^{11}C$ reaction. Typical beam intensities were 1 μA with exposure times ranging from 50 to 200 sec. The radiation dose was 1.74×10^{-4} eV molecule^{-1} μA^{-1} sec^{-1} as determined by acetylene to benzene dosimetry.[16] No change in the total ethylene-^{11}C yields or in the relative ^{11}C distribution among the isotopic ethylenes was observed as a function of varying radiation dose within this range.

The gas composition in all cases was 95.5% organic compound and 4.5% oxygen added as scavenger. The total gas pressure was 700 mm in all cases.

Assay of the Isotopic Ethylenes. The assay of the isotopic ethylenes was carried out in a manner similar to that previously described.[12,13,17] Carrier ethylenes were added to the irradiated mixture and the ethylenes-^{11}C gas chromatographically isolated from the bulk gas. The mixture of the isotopic ethylenes-^{11}C was collected and subsequently separated into its various components $^{11}C_2H_4$, $^{11}C_2H_3D$, $^{11}C_2H_2D_2$, $^{11}C_2HD_3$, and $^{11}C_2D_4$ by a recycling gas chromatographic method[12,17-19] using columns consisting of 30-60 mesh firebrick coated with 25% $AgNO_3$-saturated ethylene glycol.[20]

The radioactivity measurements were made in the usual way by gas effluent counting.[21] The total gaseous ^{11}C activity was determined by counting an aliquot using conventional static gas counting techniques. The relative ^{11}C 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 Du Pont 310 Curve Resolver. The instrument was calibrated for peak shape with standard compounds, e.g., $^{11}C_2H_4$ and $^{11}C_2D_4$ (see Figures 1 and 2).

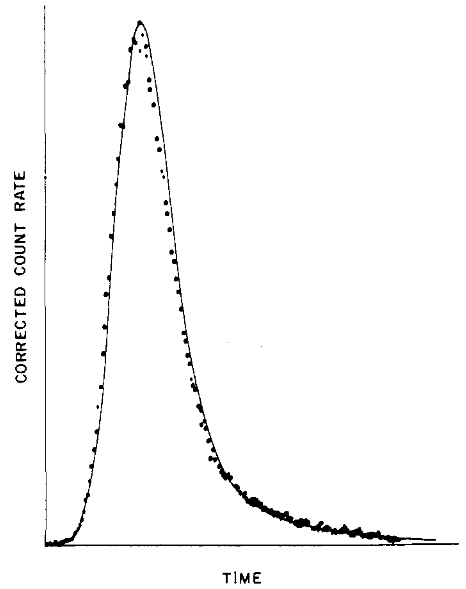


Figure 1. Fit of $^{11}C_2H_4$ peak shape for calibration of Du Pont curve resolver.

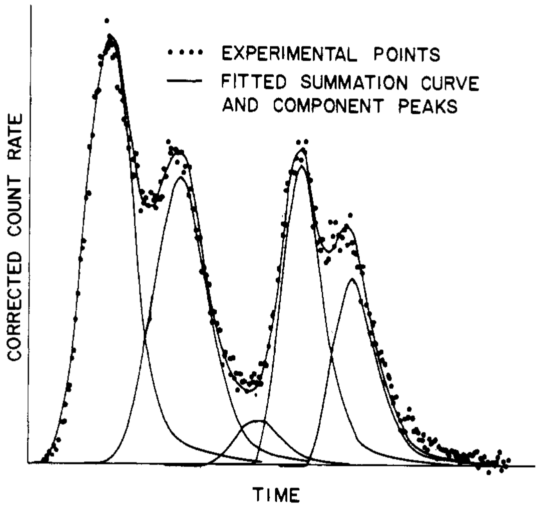


Figure 2. Resolution of a five-component experimental curve.

Results and Discussion

Table II summarizes the relative yields of the various isotopic ethylenes-^{11}C (corrected for isotopic composition of the substrate) obtained following $^{12}C(p,pn)^{11}C$ in equimolar mixtures of C_2H_6-C_2D_6, C_3H_8-C_3D_8, and specifically deuterated compounds containing completely deuterated methyl or methylene groups.

The failure to observe significant amounts of $^{11}C_2H_2D_2$ clearly suggests that an intermolecular mechanism of the type

$$R—CH_3 + {}^{11}C_{hot} \longrightarrow {}^{11}C_2 \xrightarrow{\text{several steps}} {}^{11}C_2H_4 \quad (1)$$

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

Table II. Relative and Total Ethylene-^{11}C Yields from 1:1 Mixtures of Protonated and Perdeuterated Hydrocarbons, and Specifically Deuterated Hydrocarbons[a,b] (Data Corrected for Isotopic Composition of Substrate)

Substrate	% of total ethylene-^{11}C					Absolute yields[c] of ethylene-^{11}C
	$^{11}C_2H_4$	$^{11}C_2H_3D$	$^{11}C_2H_2D_2$	$^{11}C_2HD_3$	$^{11}C_2D_4$	
$C_2H_6 + C_2D_6$	24.2 ± 0.8	33.9 ± 0.6	0.9 ± 0.7	19.4 ± 0.9	21.3 ± 0.5	16.6 ± 2.3
CH_3CD_3	23.4 ± 1.8	32.9 ± 1.3	1.9 ± 0.7	19.3 ± 0.9	22.5 ± 1.7	17.1 ± 1.0
$C_3H_8 + C_3D_8$	25.3 ± 1.7	29.2 ± 0.8	2.8 ± 1.2	19.8 ±1.6	23.0 ± 1.6	14.1 ± 1.0
$CH_3CD_2CH_3$	68.2 ± 0.5	32.0 ± 1.1				13.7 ± 2.0
$CD_3CH_2CD_3$		0.7 ± 0.6	0.4 ± 0.6	26.8 ± 1.3	72.1 ± 1.0	13.2 ± 1.2
$CH_3CH_2CD_3$	34.0 ± 1.8	23.8 ± 0.5	1.3 ± 1.0	26.1 ± 0.9	14.8 ± 0.5	13.8 ± 0.9

[a] Data represent the arithmetic mean of results from three to eight determinations. [b] Errors listed represent one standard deviation. [c] As percent of total gaseous activity.

Table III. Production Ratios (Ethylene-^{11}C from Acyclic Alkanes)[a]

Substrate	$^{11}C_2H_4$/ $^{11}C_2H_3D$	$^{11}C_2HD_3$/ $^{11}C_2D_4$	($^{11}C_2H_4$ + $^{11}C_2HD_3$)/ ($^{11}C_2H_3D$ + $^{11}C_2D_4$)	$^{11}C_2H_4$/ $^{11}C_2HD_3$	$^{11}C_2H_3D$/ $^{11}C_2D_4$	($^{11}C_2H_4$ + $^{11}C_2H_3D$)/ ($^{11}C_2HD_3$ + $^{11}C_2D_4$)
$C_2H_6 + C_2D_6$	0.71 ± 0.04	0.91 ± 0.06	0.79 ± 0.05	1.25 ± 0.10	1.60 ± 0.07	1.43 ± 0.08
CH_3CD_3	0.71 ± 0.08	0.86 ± 0.11	0.77 ± 0.09	1.21 ± 0.15	1.46 ± 0.17	1.34 ± 0.16
$C_3H_8 + C_3D_8$	0.86 ± 0.13	0.87 ± 0.08	0.86 ± 0.10	1.28 ± 0.19	1.27 ± 0.12	1.27 ± 0.16

[a] Errors represent one standard deviation.

Thus in the following the present results shall be considered in view of the "^{11}CH-insertion" mechanism,[2,4-6,10-14] eq 2-4, and "^{11}C-insertion vinyl-radical" mechanism,[7] eq 5-7.

Stöcklin and Wolf[4] were able to show that ethylene-^{11}C formation depends on the presence of methyl groups in the substrate molecule. From this result it can be concluded that ethylene-^{11}C production is preceded by ^{11}CH or ^{11}C insertion into the C-H bond of a methyl group; i.e., ethylene-^{11}C is solely formed via ^{11}CH or ^{11}C insertion into a methyl group.

Thus the two proposed mechanisms may be schematically shown as follows:

CH insertion-decomposition mechanism

$$\mathrm{R{-}H} + {}^{11}\mathrm{C} \longrightarrow {}^{11}\underline{\mathrm{CH}} + \mathrm{R}\cdot \qquad (2)$$

$$\mathrm{R'{-}CH_3} + {}^{11}\mathrm{CH} \longrightarrow [\mathrm{R'{-}CH_2{-}{}^{11}CH_2}] \qquad (3)$$

$$[\mathrm{R'{-}CH_2{-}{}^{11}CH_2}] \longrightarrow \begin{cases} \text{"other products"} \\ \mathrm{R'}\cdot + \mathrm{CH_2{=}{}^{11}CH_2} \end{cases} \qquad (4)$$

Vinyl radical mechanism

$$\mathrm{R'{-}CH_3} + {}^{11}\mathrm{C} \longrightarrow [\mathrm{R{-}CH_2{-}{}^{11}CH}] \qquad (5)$$

$$[\mathrm{R'{-}CH_2{-}{}^{11}CH}] \longrightarrow \begin{cases} \text{"other products"} \\ \mathrm{R'}\cdot + \mathrm{CH_2{-}{}^{11}CH}\cdot \end{cases} \qquad (6)$$

$$\mathrm{CH_2{-}{}^{11}CH}\cdot + \mathrm{R{-}H} \longrightarrow \mathrm{CH_2{=}{}^{11}CH_2} + \mathrm{R}\cdot \qquad (7)$$

An inspection of the results in Table II reveals immediately that the isotopic ethylenes-^{11}C are not formed in the proportions which one would expect if hydrogen abstraction (step 2 or 7) and insertion (step 3 or 5) were to occur at random. As an example consider the results using CD_3CH_3 as substrate. One would predict random distribution yields of 25% for each of the four isotopic ethylenes-^{11}C: $^{11}C_2H_4$, $^{11}C_2H_3D$, $^{11}C_2HD_3$, and $^{11}C_2D_4$. The drastic deviations observed, especially for $^{11}C_2H_3D$ (32.9%) and $^{11}C_2HD_3$ (19.3%) from the value predicted on the basis of random attack (25%), must therefore be the result of isotope effects involved in the various reaction steps leading to the formation of ethylene-^{11}C.

The yields of the isotopic ethylenes-^{11}C in the systems C_2H_6-C_2D_6 (1:1), C_3H_8-C_3D_8 (1:1), and CH_3CD_3, as listed in Table II, show the same trend, namely an enhanced yield of monodeuterated product, $^{11}C_2H_3D$, compared with that of the fully protonated ethylene, $^{11}C_2H_4$, and also a higher yield for the perdeuterated compound, $^{11}C_2D_4$, than for $^{11}C_2D_3H$.

According to the vinyl radical mechanism, $^{11}C_2H_3$ or $^{11}C_2D_3$, would be formed following ^{11}C insertion and subsequent decomposition of the insertion complex. Their relative yields may therefore be subject to isotope effects involved in these reaction steps. The ratio of $^{11}C_2H_4$/$^{11}C_2H_3D$ or $^{11}C_2D_3H$/$^{11}C_2D_4$, however, will be solely the result of their capability to abstract hydrogen or deuterium from surrounding molecules. The observed ratios $^{11}C_2H_4$/$^{11}C_2H_3D$ and $^{11}C_2D_3H$/$^{11}C_2D_4$ (Table III) indicate that D abstraction is favored over H abstraction by a factor of about 1.2, a highly unlikely event in view of the fact that in order to explain this observation one would have to assume preferential breakage of the stronger C-D bond by an abstracting vinyl radical.

Considering (1) the observed deuterium isotope effect in ethylene formation is the opposite of what one would predict if vinyl radicals were the immediate precursor, (2) that little (<1%) or no vinyl chloride is observed from carbon atom reactions in chlorinated hydrocarbons,[22] (3) that drastically reduced yields of ethylene in halocarbons are not consistent with the mechanism given in eq 5-7, (4) that vinyl radicals react readily with oxygen yet no appreciable diminution of ethylene yield is observed in oxygen scavenged systems[23] suggests that the vinyl radical mechanism is not operative or is a minor pathway for ethylene formation. The following discussion will therefore be limited to an interpretation of the observed results in terms of the methyne insertion-decomposition mechanism.[5,6,10,11]

Isotope effects may be operative in all the sequential steps shown in the "methyne mechanism", eq 2-4. An isotope effect can be operative in the formation of methyne (CH or CD) and again in the insertion step (^{11}CH or ^{11}CD insertion into a C-H or C-D bond). Third, the decomposition probability of either insertion complex may be altered by isotopic substitution and this would in addition be reflected in the ratio of the yields of "other products" to ethylene-^{11}C.

Table IV. Calculated Ethylene Distribution[b]

	Calculated yield in %							
	Random abstraction and insertion				Corrected for isotope effect[a]			
Substrate	$(^{11})C_2H_4$	$(^{11})C_2H_3D$	$(^{11})C_2HD_3$	$(^{11})C_2D_4$	$(^{11})C_2H_4$	$(^{11})C_2H_3D$	$(^{11})C_2HD_3$	$(^{11})C_2D_4$
$C_2H_6 + C_2D_6$ (1:1)	25.0	25.0	25.0	25.0	26.5	31.8	18.9	22.7
CH_3CD_3	25.0	25.0	25.0	25.0	26.5	31.8	18.9	22.7
$C_3H_8 + C_3D_8$ (1:1)	25.0	25.0	25.0	25.0	26.5	31.8	18.9	22.7
$CH_3CH_2CD_3$[c]	30.3	19.7	30.3	19.7	35.0	23.3	25.0	16.7

[a] CD/CH = 1.2 taken as formation isotope effect. CH_3/CD_3 = 1.4 taken as insertion isotope effect. [b] For observed yields see Table II. [c] Hydrogen abstraction by ^{11}C atom taken as CH_3/CH_2 = 1/0.8.

It has previously been shown[24] that the ethylene-^{11}C yields in oxygen scavenged C_2H_6 or C_3H_8 are the same as in C_2D_6 or C_3D_8, respectively. This is essentially in agreement with the overall ethylene-^{11}C yields for the various equimolar mixtures of C_2H_6-C_2D_6, C_3H_8-C_3D_8, and specifically deuterated ethanes and propanes observed in the present investigation and listed in Table II.

They agree very well within each group and suggest that the isotopic composition of the substrate has little effect on the total amount of ethylene-^{11}C formed. (It should, however, be pointed out, that due to the experimental errors involved, cf. Table II, small isotope effects in the overall reaction sequence may not be recognized.) If one takes these results at face value, one would have to assume that a more or less complete cancellation of the isotope effects involved in the individual reaction steps, which might oppose each other, occurs; e.g. enhanced CD formation in step 2 may be followed by a more favorable insertion of ^{11}CH into the methyl group (or vice versa), and then be further modified by a possible isotope effect in step 4.

Although the overall ethylene-^{11}C yields are nearly constant within the series of isotopic propanes or ethanes used as substrates, *the presence of isotope effects in the individual reaction steps should be reflected in the relative distribution among the various isotopic ethylenes-^{11}C depending on the isotopic composition of the substrate.*

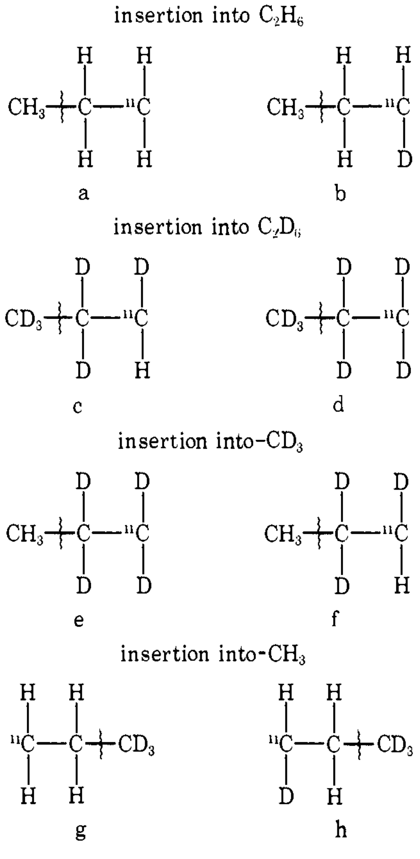
In Table III the ratios of the yields of the isotopic ethylenes, whose formation includes H or D abstraction by ^{11}C atoms and insertion of CH or CD into methyl groups, are listed for various systems; e.g., if CH_3CD_3 is the substrate, the formation of $^{11}C_2H_4$ and $^{11}C_2HD_3$ will involve CH-insertion, whereas $^{11}C_2H_3D$ and $^{11}C_2D_4$ can be considered as the result of CD insertion. In all these cases more carbon-11 is found incorporated in those isotopic ethylenes, whose production involves ^{11}CD insertion.

Another general trend can be recognized in the comparison of the total yields of isotopic ethylenes-^{11}C produced via CH *and* CD insertion into a CH_3 *or* CD_3 group (Table III); e.g., in CH_3CD_3 the products $^{11}C_2H_4$ and $^{11}C_2H_3D$ result from CH and CD insertion into the CH_3 group, whereas $^{11}C_2HD_3$ and $^{11}C_2D_4$ are formed via CH and CD attack at the CD_3 group. In each case the yields of the products resulting from CH and CD insertion into a C-H bond of a CH_3 group are clearly larger than those obtained via CH or CD insertion into a CD_3 group.

These results can best be explained by invoking two different isotope effects, one involving the formation of methyne, with CD favored over CH by a factor of about 1.2, and a second effect which makes CH or CD insertion into a CH_3 group approximately 1.4 times more probable than insertion into a CD_3 group. This is demonstrated in Table IV, where values for the various isotopic ethylenes have been calculated by assuming an isotope effect of 1.2 in favor of CD formation and an insertion isotope effect of 1.4 in favor of methyne insertion into a CH_3 group. (The data shown for $CH_3CH_2CD_3$ have been normalized for a hydrogen abstraction ratio from methyl to methylene group of 1.0/0.8, vide infra.)

The calculated ^{11}C distribution is indeed very close to the observed results. The explanation based on the results in terms of only two isotope effects governing the ethylene formation process implies tacitly that there is no significant isotope effect involved in the decomposition (step 4) of the insertion complex.

The possibility of a decomposition isotope effect in the final step of the methyne mechanism must be considered. The ^{11}CH and ^{11}CD insertion complexes formed in the equimolar mixture of C_2H_6/C_2D_6 and in the specifically deuterated ethane CH_3CD_3 are given as structures a-h. In each case, C-C scission is required to lose a methyl group and form ethylene. Thus the isotope effect, if any, would be secondary at best since a CH or CD bond is not directly involved in the bond-breaking steps. It can be seen there are clear differences in the structures in which C-C bonds are broken, yet the isotopic distributions of the ethylenes from these substrates listed in Table II are identical within experimental error. Thus, any isotope effect due to decomposition of the excited intermediate must be small and within experimental error.



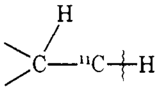
A further test of the "two-isotope effects" hypothesis is possible in the specifically deuterated propane systems:

$CH_3CD_2CH_3$ and $CD_3CH_2CD_3$. In these propanes no significant insertion isotope effect should be present, because the two methyl groups into which CH or CD could insert are identical in each of the two systems, i.e., there are either two CH_3 or two CD_3 groups present. Thus the experimentally observed overall isotope effect must mainly represent the differences in the formation probability between CD and CH, which according to the above hypothesis should be about 1.2 in favor of CD formation.

It is first necessary to calculate the relative likelihood of methyne formation from methyl and methylene groups of a hydrocarbon. This can be done by examining the ethylene yields from $CH_3CD_2CH_3$ and from $CD_3CH_2CD_3$, cf. Table II. The only product of H abstraction from $CH_3CD_2CH_3$ is C_2H_4 which must result from abstraction from a methyl group, just as C_2H_3D must result from abstraction from the methylene group. The same reasoning leads to the conclusion that C_2D_4 is the product of abstraction from the methyl group of $CD_3CH_2CD_3$, and C_2HD_3 results from abstraction from its methylene group. These yields have been altered by isotope effects, but they can be canceled by averaging the yields from methyl and from methylene groups from these two compounds. Therefore, the average yield from a methylene group is $(32.0 + 26.8)/2 = 29.4\%$. Similarly, the average yield from two methyls is $(68.2 + 72.1)/2 = 70.2$. Thus the ratio of abstraction from a methyl to abstraction from a methylene is 1.00:0.84.

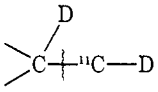
The observed values for $^{11}C_2H_3D$ (31.5%) from $CH_3CD_2CH_3$ and $^{11}C_2D_3H$ (27.3%) from $CD_3CH_2CD_3$ deviate from the average of 29.4% by about 7%. If this is weighted by the factor 2.8/0.8 which considers the fact that hydrogen abstraction from the methylene group occurs only in 0.8 out of 2.8 cases, then the resulting isotope effect is about 20%, i.e., CD formation is favored over CH formation by the factor 1.2.

Preferential formation of ^{11}CD over ^{11}CH may be understood in terms of the "insertion-decomposition" mechanism for methyne formation. The carbene intermediate formed following ^{11}C insertion into a C-H or C-D has various modes of decay:[10,11]



i

or



j

It seems reasonable that in i bond breakage between ^{11}C and H (relative to ^{11}C-C bond breakage) is more likely to occur than breakage between ^{11}C and D (relative to ^{11}C-C bond breakage), thus leading to slightly larger amounts of ^{11}CD than of ^{11}CH.[25]

Conclusion

Evidence is presented to support the hypothesis[5,6] that a multistep mechanism is operative in the formation of ethylene-^{11}C from the reaction of carbon-11 atoms with acyclic alkanes and involving the intermediacy of methyne. A pathway which involves a $^{11}C_2$ species as an intermediate is ruled out on the basis of the absence of doubly labeled products which would necessarily result from the presence of this intermediate.

The relative yields of isotopic ethylenes-^{11}C observed in C_2H_6-C_2D_6, C_3H_8-C_3D_8, CH_3CD_3, $CH_3CH_2CD_3$, $CH_3CD_2CH_3$, and $CD_3CH_2CD_3$ suggest an isotope effect of about 1.2 in favor of deuterium over hydrogen "abstraction" by ^{11}C to form methyne and an insertion isotope effect of about 1.4 in favor of methyne insertion into a CH_3 group over insertion into a CD_3 group.

Intramolecular hydrogen abstraction from a methylene group occurs with a probability of approximately 0.8, if hydrogen abstraction from a methyl group is set equal to unity.

References and Notes

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(8) In the interest of brevity, this form will be used to designate the presence of a single atom of carbon-11 in a molecule or radical; e.g., $^{11}C_2H_3D$ is equivalent to $C_2H_3D^{11}C$.
(9) (a) Cf. R. M. Lambrecht, N. Furukawa, and A. P. Wolf, *J. Phys. Chem.*, **74**, 4605 (1970), for the intermolecular formation of acetylene-^{11}C; (b) cf. T. Rose and C. MacKay, *J. Phys. Chem.*, **77**, 2598 (1973).
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(25) The decomposition shown in i will lead to another or other carbon-11 labeled products. It should be noted that there are numerous products observed in these systems and that we are unable as yet to ascribe a particular yield to this precursor. It should be noted that barring fragmentation and assuming a unique product to be formed, its yield would only be in the 1 to 3% range.