Tetrahedron, 1966, Vol. 22, pp. 2967 to 2976. Pergamon Press Ltd. Printed in Northern Ireland

THE REACTIONS OF ATOMIC CARBON WITH BUTENE

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(*Received in U.S.A.* 11 *April* 1966; *accepted for publication* 23 *May* 1966)

Abstract—C^{11} resulting from nuclear transformations has been used to investigate the reactions of free carbon atoms with both *cis* and *trans* 2-butene. Studies were made in both gaseous and condensed systems, and moderator techniques were used to distinguish between hot and thermal processes. As in the case of other hydrocarbons, primary reactions appear to be insertion of the carbon into C—H and C=C bonds. The adducts formed, if not stabilized by rapid removal of their excess internal energy, will then fragment to give either small molecules, or radicals which add to another molecule of 2-butene. Such decomposition is particularly favoured when hot carbon atoms react in the gas phase where collisional de-excitation is slow. Stabilisation of the adduct is maximized when the 2-butene reagent is in a dilute dispersion in a xenon matrix in which thermalization of the carbon atom and de-excitation of the adduct are both efficient. The relative complexity of the 2-butene molecule, which enables it to distribute excitation energy internally, also diminishes fragmentation and promotes stabilization of the adduct. Thus the yield of the fragmentation product normally most prominent, acetylene, becomes very small with 2-butene dispersed in a xenon matrix. Under these conditions, there is also evidence that some cyclic adducts survive sufficiently long to react with a second 2-butene molecule to form spiro compounds.

INTRODUCTION

Recoil C^{11} produced by nuclear techniques has recently been the subject of intensive studies.[2–4] These have resulted in the characterization of some fundamental modes of reaction of free carbon atoms in the ground (^3P) and low excited (^1D) and (^1S) electronic states with hydrocarbon molecules. It appears that most reactions usually proceed in two steps, first an insertion into a C—H or C=C bond, and second, a decomposition or de-excitation of the adduct thus formed.[2–4]

Several factors are of importance in determining the course of reaction. One is the kinetic energy of the carbon atom. In a pure hydrocarbon system, most atoms react while hot; but thermal reactions can be studied by addition of moderator, usually a noble gas. Whether formed by a hot or thermal process, the intermediate adduct will be excited and must dispose of its excess energy. Hence the efficiency of collisional de-excitation in stabilizing the adduct is an important second factor in controlling the course of reaction. This has been studied by variation of the phase of the reaction media; condensed systems being far more effective for de-excitation. The combined effect of thermalizing carbon atoms and also efficiently de-exciting the adduct has recently been investigated using solid xenon and krypton containing a low concentration of ethylene:[5] as expected, products (particularly allene) formed by stabilization of the adduct were enhanced, while products (such as acetylene) resulting from extensive fragmentation were reduced—though not eliminated.

The complexity of the reactant molecule is a third factor which affects the fate of the intermediate adduct. In a larger molecule, the excitation energy can be spread over a greater number of modes of internal vibration. This extends the half life for

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[2] C. MacKay and R. Wolfgang, *Science* **148**, 899 (1965).

[3] A. P. Wolf, *Advances in Physical Organic Chemistry* (Edited by V. Gold) Vol. II; p. 201. Academic Press, N.Y. (1964).

[4] R. Wolfgang, *Progress in Reaction Kinetics* (Edited by G. Porter) Vol. 3; p. 99. Pergamon Press, Oxford (1965).

[5] J. Nicholas, C. MacKay and R. Wolfgang, *J. Amer. Chem. Soc.* **87**, 3008 (1965); and **88**, 1610 (1966).

unimolecular decay and allows more time for collisional stabilization. Isolated studies of larger molecules, such as cyclopentadiene, indicate that the adducts they form with carbon atoms are indeed less likely to undergo extensive fragmentation.[6]

In this paper, we report on systematic experiments in which all three factors tending to stabilize the initial carbon atom adduct were studied separately and in combination: thermalization of the carbon atom, efficient collisional de-excitation, and a large reagent molecule. The systems chosen for this purpose were *cis*- and *trans*-2-butene in gas, liquid and solid, both pure and moderated by noble gas. The choice of 2-butene was made in the expectation that the structural isomerism of some of the likely products might be used as a further indication of the detailed reaction mechanism.

EXPERIMENTAL

The Yale heavy ion and electron accelerators served as sources of C^{11}. The experimental procedures for sample preparation, C^{11} production, and analysis of the products have been discussed elsewhere.[5,7,8]

The materials used in these experiments were Phillips Research Grade *cis*- and *trans*-2-butene; Matheson Research Grade helium and xenon; and Matheson c.p. oxygen. All were used without further purification.

The chromatographic columns principally used in the analysis were: (1) 30′ deactivated alumina at 25° for separating ($CO + CH_4$) and C_2H_4 and C_2H_2; (2) 60′ silicone oil (15% G.E. SF-96 on Anakrom ABS) at 25° for separating C_3H_4 (sum peak of allene and methylacetylene) and oil observed C_4 products from each other; 30′ silicone oil (15% G.E. SF-96 on Anakrom ABS) at 25° for separating the various C_5 products; 20′ silicone oil (15% G.E. SF-96 on Anakrom ABS) at 110°C for separating C_9 molecules from other products.

The identities of most C_5 products were confirmed by addition of appropriate carriers, trapping of the individual peaks from the effluent of the silicone oil column and injection onto a second column with different characteristics, e.g. silver nitrate or $\beta\beta'$-oxydipropionitrile columns. However, 2–3 pentadiene and 2-pentyne were identified only by comparing retention volumes on the silicone oil column with those determined in previous work with C_5H_8 isomers.[7,9] Their identification must thus be considered tentative. For the dimethyl cyclopropanes, carrier gas was available only for the trans form and assignment of the cis isomer is tentative.

No attempt was made to separate the C_9 yield into its various components. However, a chemical procedure was used to estimate what fraction of it was saturated. n-Nonane was added to the product mixture as a marker, and the total C_9 products were separated on a 20′ silicone column. As they eluted, they were passed through an 8′ column packed with glass beads bearing an alkaline permanganate solution. This oxidizes non-aromatic double and triple bonds. The treated mixture was then passed through a short $\beta\beta'$-oxydiproprionitrile column to retard the oxygenated material. Finally, the effluent from this column was counted to determine the activity of the saturated compounds not affected by this procedure. The method was tested by passing the product mixture from reaction of C^{11} with cyclopentadiene[6] through the train. All unsaturates were removed except benzene which, like saturated compounds, is not oxidized by the procedure, and is passed through unaffected and in full yield.

RESULTS

Product yields shown in Tables 1–4 are expressed as percentages of the total volatile activity. They may be converted to absolute yields by multiplying by the fraction of C^{11} recovered in volatile form. By use of appropriate monitoring techniques, this fraction was determined (for gas phase systems only) to be 0·65. The results quoted are the average of several runs in each case. As discussed previously, the main source of error lies in statistical fluctuations in counting. Except for the solid moderated system, errors are of the order of 5% for major products and 10% for minor products. In the highly moderated solid systems, errors were of the order of 10% for major products and up to 30% for the minor products.

[6] T. Rose, C. MacKay and R. Wolfgang, *J. Amer. Chem. Soc.* **88**, 1064 (1966).

[7] J. Dubrin, C. MacKay and R. Wolfgang, *J. Amer. Chem. Soc.* **86**, 4747 (1964).

[8] J. Dubrin, C. MacKay, M. Pandow and R. Wolfgang, *J. Inorg. Nucl. Chem.* **26**, 2113 (1964).

[9] In the work of Ref. 7, all C_5H_8 isomers were determined to be separable on the column described.

TABLE 1. YIELDS OF PRODUCTS IN THE C^{11}-*trans*-2-BUTENE SYSTEM[a]

	Gas	$+2\% O_2$	Liquid	Solid
Carbon monoxide + methane	4·1	13·0	1·9	2·2
Ethylene	7·3	7·7	4·2	3·4
Acetylene	26·1	24·9	11·0	8·6
methyl acetylene + allene	5·9	5·3	5·7	5·7
Vinyl acetylene	9·3	8·5	4·0	3·6
1–3 Butadiene	2·1	1·9	1·6	1·4
1–2 Butadiene	1·8	2·0	1·1	1·7
Isopentane	$<0·5$	$<0·5$	$<0·5$	$<0·5$
1,2 Dimethyl cyclopropane *trans*	3·9	3·3	4·2	5·5
1,2 Dimethyl cyclopropane *cis*	2·0	1·6	$<0·5$	$<0·5$
2 Pentene *trans*	2·5	2·6	7·2	9·9
2 Pentene *cis*	$<0·5$	$<0·5$	$<0·8$	$<0·8$
1–3 Pentadiene *trans*	9·1	8·3	10·6	12·2
1–3 Pentadiene *cis*	4·9	4·3	2·0	1·6
2–3 Pentadiene	1·7	1·5	4·4	3·9
2 Pentyne	1·1	0·8	2·0	1·7
C_9's (total)	3·1	$<1·0$	10·0	10·6
C_9's unoxidized by $KMnO_4$	$<0·3$	$<0·3$	1·0	1·4

[a] Yields are expressed as % total volatile activity. All gaseous samples at total press. of 80 cm Hg.

The hydrocarbon products may be divided into several groups on the basis of their behaviour when the several experimental parameters are varied.

(1) Fragmentation products, whose yield decreases on moderation and in condensed phase. These include ethylene, acetylene, allene and methyl acetylene, 1–3 butadiene, 1–2 butadiene and vinyl acetylene.

(2) C_5H_8 products whose total yield tends to increase in condensed phase and on moderation (though individual yields vary). These include cis and trans 1–3 pentadiene, 2–3 pentadiene and 2-pentyne.

(3) Products formed by reaction involving two butene molecules—C_9's. This group is unresolved, except between those products resistant to alkaline permanganate oxidation (saturates or aromatic compounds) and the larger portion which is oxidized (unsaturated compounds).

(4) C_5H_{10} products, which show a high yield in unthermalized condensed phase systems. These are mainly cis and trans dimethyl cyclopropane and cis and trans 2-pentene: all molecules which would be formed by reaction of a CH_2 intermediate with 2-butene.[10–12]

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[10] The reactions of methylene generated in other ways are reviewed in:
  [a] S. Benson and W. DeMore, *Advances in Photochemistry* (Edited by W. A. Noyes, Jr. and J. N. Pitts) Vol. 2; p. 219. Interscience, New York (1964);
  [b] H. Frey, *Progress in Reaction Kinetics* (Edited by G. Porter) Vol. 2; p. 131. Pergamon Press, Oxford (1964);
  [c] W. Kirmse, *Carbene Chemistry*. Academic Press, New York (1964).

[11] R. Badar and J. Generosa, *Canad. J. Chem.* **43**, 1631 (1965).

[12a] W. von E. Doering and P. La Flamme, *J. Amer. Chem. Soc.* **78**, 5447 (1956);
  [b] R. C. Woodworth and P. S. Skell, *Ibid.* **87**, 3383 (1959);
  [c] H. M. Frey, *Ibid.* **82**, 5947 (1960).

TABLE 2. YIELDS OF PRODUCTS IN THE MODERATED C^{11}-*trans*-2-BUTENE SYSTEM[a]

	+95% He	+90% Xe solid	+99% Xe solid	+99·7% Xe solid
Carbon monoxide + methane	3·0	6·0	10·3	13·6
Ethylene	5·9			
Acetylene	12·5	6·4	1·6	1·1
Methyl acetylene + allene	3·2	2·3	<1·0	<1·5
Vinyl acetylene	8·0	3·4	1·5	1·5
1–3 Butadiene	1·8			
1–2 Butadiene	1·1	1·3	<1·0	<1·5
Isopentane	<0·5	<1·0	<1·5	<2·0
1,2 dimethyl cyclopropane *trans*	1·3	4·4	<1·5	<2·0
1,2 dimethyl cyclopropane *cis*	1·3	<1·0	<1·5	<2·0
2 Pentene *trans*	1·8	9·5	<1·5	<2·0
2 Pentene *cis*	<0·5	<1·0	<1·5	<2·0
1–3 Pentadiene *trans*	9·5	12·2	7·7	6·1
1–3 Pentadiene *cis*	6·2	2·7	1·8	2·0
2–3 Pentadiene	2·9	8·0	23·5	20·1
2-Pentyne	1·6	<1·5	<2·0	<3·0
C_9's (total)	3·0	14·8	16·7	18·2
C_9's unoxidized by $KMnO_4$	<0·3	3·9	4·9	5·0

[a] Yields are expressed as % total volative activity. All gaseous samples at total press. of 80 cm Hg.

DISCUSSION

Intensive studies of the ethylene system have shown that most carbon atoms react by insertion into C—H and C=C bonds to form intermediate adducts. The final product spectrum is then largely determined by the relative importance of the various possible fragmentation, stabilization and addition processes undergone by these adducts.[2,3,5,7]

A smaller fraction of the carbon atoms react with ethylene to form a $C^{11}H_2$ intermediate which then undergoes its characteristic addition and insertion reactions.[2,3,7]

We may postulate a strictly analogous reaction scheme of free carbon atoms in 2-butene. The two primary processes leading to adduct formation are written as (i) C—H bond insertion (e.g. for *cis*-2-butene)

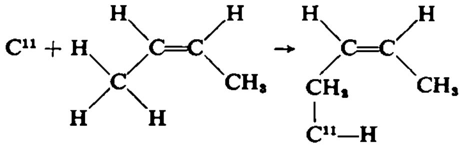
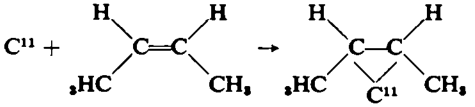


TABLE 3. YIELD OF PRODUCTS IN THE C^{11}-*cis*-2-BUTENE SYSTEM[a]

	gas	+2% O_2	liquid	solid
Carbon monoxide + methane	4·3	10·3	1·8	1·9
Ethylene	7·6	6·7	3·8	3·2
Acetylene	27·6	24·8	11·7	9·3
Methyl acetylene + allene	5·5	5·4	4·9	4·7
Vinyl acetylene	8·9	9·9	3·7	2·6
1–3 Butadiene	2·2	2·1	1·7	1·6
1–2 Butadiene	2·0	2·5	1·6	1·5
Isopentane	<0·5	<0·5	<0·5	<0·5
1,2 Dimethyl cyclopropane *trans*	1·2	<0·5	1·3	1·9
1,2 Dimethyl cyclopropane *cis*	2·3	2·0	1·2	1·2
2-Pentene *trans*	1·1	<0·8	0·8	0·9
2-Pentene *cis*	2·9	1·7	6·4	8·8
1–3 Pentadiene *trans*	9·5	9·8	8·8	8·4
1–3 Pentadiene *cis*	6·1	6·3	8·1	9·7
2–3 Pentadiene	1·8	1·8	4·0	3·7
2-Pentyne	1·4	1·3	1·6	1·5
C_9's (total)	3·0	<1·0	9·5	9·5
C_9's unoxidized by $KMnO_4$	<0·3	<0·3	1·1	1·2

[a] Yields are expressed as % total volatile activity. All gaseous samples at total press. of 80 cm Hg.

(ii) pi bond attack



The reactions of these $C^{11}C_4H_8$ adducts may then be schematically summarized:

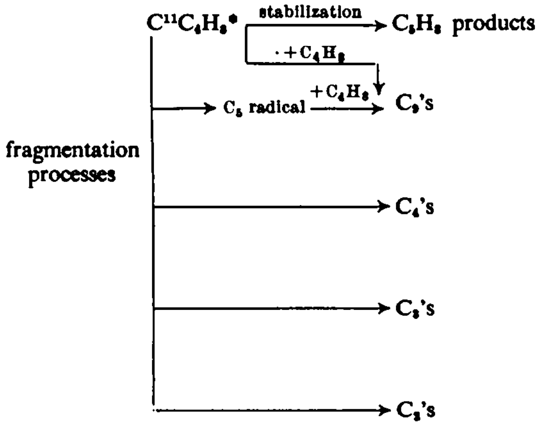


Table 4. Yields of products in the moderated C^{11}-*cis*-2-butene system[a]

	+95% He	+90% Xe solid	+99% Xe solid	+99·7% Xe solid
Carbon monoxide + methane	3·0	7·0	12·1	15·0
Ethylene	4·0			
Acetylene	12·4	6·0	1·4	1·0
Methyl acetylene + allene	2·8	1·5	<1·0	<1·5
Vinyl acetylene	7·7	3·5	1·7	1·5
1–3 Butadiene	2·0			
1–2 Butadiene	1·8	1·5	<1·0	<1·5
Isopentane	<0·5	<1·0	<1·5	<2·0
1,2 Dimethyl cyclopropane *trans*	<0·5	1·8	<1·5	<2·0
1,2 Dimethyl cyclopropane *cis*	2·2	2·0	<1·5	<2·0
2 Pentene *trans*	<0·8	2·8	<1·5	<2·0
2 Pentene *cis*	1·0	6·1	<1·5	<2·0
1–3 Pentadiene *trans*	9·0	8·0	2·8	2·0
1–3 Pentadiene *cis*	7·5	11·0	3·0	2·8
2–3 Pentadiene	2·0	5·5	21·0	22·2
2 Pentyne	1·4	1·5	<2·0	<3·0
C_9's (total)	3·2	13·7	17·7	16·0
C_9's unoxidized by $KMnO_4$	<0·3	3·0	5·8	5·8

[a] Yields are expressed as % total volatile activity. All gaseous samples at total press. of 80 cm Hg.

In addition, there are the processes involving $C^{11}H_2$ and possibly $C^{11}H$ intermediates:

$$\begin{tikzcd}
& C^{11}H \arrow[r, "+C_4H_8"] \arrow[d, dashed] & C_5,\ C_9 \text{ products} \\
C^{11} + C_4H_8 \arrow[ur] \arrow[dr] & & \\
& C^{11}H_2 \arrow[r, "+C_4H_8"] & C_5H_{10} \text{ products}
\end{tikzcd}$$

This mechanistic scheme may be tested and the relative importance of the various competitive paths evaluated by determination of its effect on a number of experimental parameters:

(a) Addition of O_2 at scavenger concentrations. This will reduce the yield of products that have radical precursors which do not react rapidly.

(b) Addition of 95% moderator in gas phase. The energy of the C atom will be reduced before it reacts with 2-butene. The primary adduct should be formed with less excitation energy and high energy fragmentation processes reduced. A secondary, possibly complicating, effect of the inert gas could arise from its low efficiency as a collisional deactivator.

(c) Change of phase. In condensed phases, carbon atoms still react while hot, but collisional deactivation is efficient and unimolecular fragmentation processes should be reduced.

(d) Moderation in the solid phase by dispersion of the 2-butene in a rare gas matrix. Here the carbon atom reacts at low energy in a medium in which collisional deactivation is efficient. Survival of the adduct is optimized and fragmentation processes minimized.

When the results are considered in light of these predictions, a reasonably clear pattern emerges.

1. *Fragmentation products*

The C_2–C_4 fragmentation products arise from bond ruptures in the excited primary adducts discussed above. The actual fragmentation product spectrum is quite specific and is directly related to these primary adducts, those products which can be formed with minimal structural changes, atom and group migration being favoured. For all of this group, the observed effect of varying the experimental parameters described above is as predicted. Specific comments for each product follow.

(a) *Acetylene and ethylene.* Acetylene is formed by fragmentation involving rupture of at least two bonds in the adduct. It is likely that most of this yield derives from the intermediate formed by insertion into C—H bonds,[2,13] e.g.

$$HC^{11}—CH_2—CH{=}CH—CH_3^* \rightarrow HC{\equiv}C^{11}H + CH{=}CH—CH_3 + H$$

Such a process will obviously be favoured by high excitation energy in the adduct. The drop from 27% to 12·5% in yield on moderating gas phase systems by 95% helium is therefore most reasonable. (It should be noted that part of this decrease may also result from a lower relative probability of inserting into a C—H rather than a C=C bond on the part of a thermalized carbon atom.)[14] When the adduct formed by a thermal carbon atom is also efficiently de-excited, as occurs in butene trapped in a xenon matrix, the yield of acetylene drops to only 1%.

The same excited adduct which leads to acetylene formation could account for ethylene formation.

$$HC^{11}—CH_2—CH{=}CH—CH_3 + RH \rightarrow H_2C^{11}{=}CH_2 + CH{=}CH—CH_3 + R$$

Alternatively, this product could also be formed by insertion of a $C^{11}H$ intermediate into a methyl C—H bond followed by appropriate bond rupture.[3]

$$\begin{aligned} C^{11}H + CH_3—CH{=}VH—CH_3 &\rightarrow H_2C^{11}—CH_2—CH{=}CH—CH_3^* \\ &\rightarrow H_2C^{11}{=}CH_2 + CH{=}CH—CH_3 \end{aligned}$$

Both these mechanisms are consistent with results of isotopic mixing experiments in analogous simple systems, such as C_2H_6–C_2D_6.[15,2] As yet, no experiments have been reported which distinguish between these possibilities.

(b) C_3 *Products; allene and methylacetylene.* Decomposition of the adduct formed by insertion into the H atoms bonded to the number 2 and 3 carbon atoms provides a convenient route to methylacetylene.

$$\underset{\displaystyle C^{11}H}{CH_3—\overset{}{C}}{=}CH—CH_3^* \rightarrow CH_3—C{\equiv}C^{11}H + CH_3—CH$$

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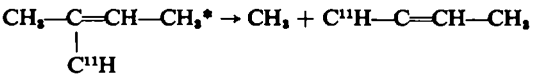
[13] L. J. Stief and V. De Carlo, *J. Chem. Phys.* 43, 2552 (1965) have recently used acetylene formation in the photolysis of C_3O_2–CH_4 mixtures with 1470A quanta as evidence that C atoms were formed from the C_3O_2.

[14] M. Marshall, C. MacKay and R. Wolfgang, *J. Amer. Chem. Soc.* 86, 4741 (1964).

[15] J. Dubrin, C. MacKay and R. Wolfgang, *J. Amer. Chem. Soc.* 86, 959 (1964).

Allene would seem to be a less likely product on this basis. The adduct postulated here results from the insertion into ethylenic C—H bonds, rather than terminal C—H bonds as was suggested above for acetylene production. It is tempting to associate the low ratio of C_3H_4 to C_2H_2 yields with the smaller number of such ethylenic C—H bonds, but a quantitative correlation is probably unjustified since both types of adducts can also give other products (see below).

(c) C_4 *Products; 1–3 and 1–2 butadiene and vinylacetylene.* The same excited adduct which leads to allene and methylacetylene can give rise to a C_4H_5 radical by a different C—C bond rupture.



$$\underset{\displaystyle C^{11}H}{CH_3—\underset{|}{C}}{=}CH—CH_3^{*} \rightarrow CH_3 + C^{11}H—C{=}CH—CH_3$$

Such a radical could either abstract a hydrogen atom to give a butadiene molecule or lose one to another species to give vinylacetylene.

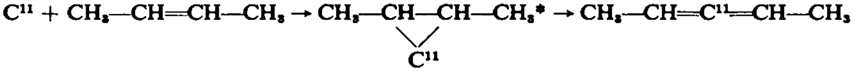
$$C^{11}H—C{=}CH—CH_3 + RH \rightarrow C^{11}H_2{=}C{=}CH—CH_3 + R$$

$$C^{11}H—C{=}CH—CH_3 + R \rightarrow HC^{11}{\equiv}C—CH{=}CH_2 + RH$$

The formation of the C_4H_5 radical seems to require considerable excitation energy as indicated by the low yield of the butadienes and vinylacetylene in the xenon matrix experiments.

2. C_5H_8 *Products*

The nature of the processes giving rise to the C_5H_8 products is most clearly indicated by the xenon matrix experiments. In these systems, not only is fragmentation minimized, but the adducts are most likely to be stabilized without having undergone isomerization. Under these conditions, 2–3 pentadiene is the most important C_5H_8 isomer, showing a yield of ~22% from both cis and trans 2-butene. The formation of this product apparently occurs via the double bond insertion mechanism and is completely analogous to the well-established mechanism for formation of allene from ethylene.[2,14,15]



$$C^{11} + CH_3—CH{=}CH—CH_3 \rightarrow CH_3—\underbrace{CH—CH}_{C^{11}}—CH_3^{*} \rightarrow CH_3—CH{=}C^{11}{=}CH—CH_3$$

An alternate route involving a primary insertion into a methyl C—H bond is a much less likely source of this molecule. Either a methyl group migration or the migration of two H atoms would then be required to form 2–3 pentadiene. An adduct formed by insertion into a methyl C—H bond would be much more likely to give the more stable cis and trans 1–3 pentadienes by migration of a single H atom.

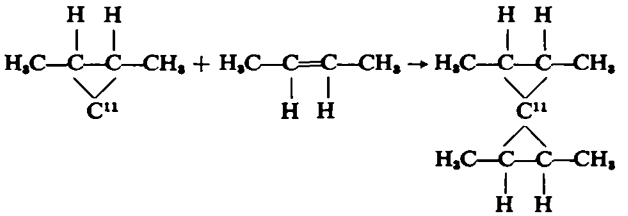
$$C^{11} + CH_3—CH{=}CH—CH_3 \rightarrow H—C^{11}—CH_2—CH{=}CH—CH_3 \rightarrow H_2C^{11}{=}CH—CH{=}CH—CH_3$$

These products are actually found in quite high yield in xenon matrix systems. Under conditions where adducts of minimal excitation energy are formed and can be efficiently de-excited, such a process would tend to preserve the configuration of the double bond. In accord with this, the formation of cis 1–3 pentadiene from cis-2-butene is somewhat favoured in the solid phase and in the xenon matrix experiments, though considerable isomerization does occur. Formation of the more stable trans 1–3 pentadiene from trans 2-butene is favoured by a considerably greater degree.[16]

In the gas phase where de-excitation is less rapid than in condensed phase, the data suggest that 1–3 pentadiene can also be produced by isomerization of 2–3 pentadiene or its precursors. This can account for the lower stereospecificity of the 1–3 pentadiene as produced in the gas phase, as well as the decrease in 2–3 pentadiene. A similar isomerization is probably responsible for the pentyne-2 as found in gas phase and also in unmoderated condensed phase experiments.

3. C_9 *Products*

Formation of C_9 products requires addition of a C_5 radical to 2-butene. In general, such products would be unsaturated, but there is one interesting exception. If the original cyclic C_5 adduct survives reaction with a 2-butene molecule, formation of saturated C_9 bi-cyclic compounds could result.



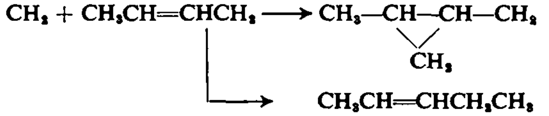
The analogous spiropentane was specifically sought in the ethylene studies but was not found even at high moderation in the solid phase.[5,7] However, 2-butene presents a more favourable case than does ethylene because it forms larger adducts with more internal degrees of freedom. Such adducts will have a longer lifetime before decomposing or isomerizing and therefore have more chance to react while still in their original configuration.

The amount of product non-oxidizable by alkaline permanganate serves to set an upper limit to the yield of bicyclic C_9 compounds. No non-oxidizable C_9 compounds were detected in the gas phase even when helium moderator was used to reduce the energy of the reacting C atoms. Evidently helium cannot de-excite the intermediate cyclic adduct quickly enough to give it chance to survive sufficiently long to react with a second butene molecule. However, a non-oxidizable yield of $\sim 1\%$ is observed in solid and liquid butene. It increases to as much as $5{\cdot}8\%$ in xenon matrix experiments in which conditions favour rapid de-excitation of low energy adducts formed by thermal carbon atoms. Thus the behaviour of this non-oxidizable component is consistent with that expected for formation of C_9 bicyclics.

[16] On the basis of the product assignments given above, the xenon matrix experiments can be used to estimate the relative reactivity of thermal C atoms towards the C═C and methyl C—H bonds in the 2-butenes. This should simply be measured by the ratio of 2,3-pentadiene to the 1,3-pentadienes, corrected by the relative numbers of each type of bond. The result is (reactivity of C═C)/(reactivity of methyl C—H) = 15. This estimate is subject to the validity of the inherent assumption that adducts formed by C—H and C═C insertion will be stabilized to a similar extent to give 1,3 pentadiene and 2–3 pentadiene respectively. The result is to be compared to a value of 10 for the relative efficiency of C═C to C—H insertion by thermal carbon into ethylene to form C_3H_4 molecules.[14] (In the ethylene system, similar assumptions much be made to arrive at such a figure. They will be less accurate because the adduct is smaller, and the experiment was performed in the gas phase. Thus stabilization is less likely and differences in the extent of decomposition of the two types of adducts are likely to be greater.)

4. *Formation and reaction of* CH_2 *intermediate*

Methylene reacts with 2-butene to form 1,2-dimethylcyclopropane and pentene-2.[10,11,12]



$$\begin{aligned} CH_2 + CH_3CH{=}CHCH_3 &\longrightarrow CH_3{-}\underset{CH_2}{\underbrace{CH{-}CH}}{-}CH_3 \\ &\longrightarrow CH_3CH{=}CHCH_2CH_3 \end{aligned}$$

These products are observed in the present work. Their appearance was expected since there is considerable evidence that some CH_2 is formed in reaction of carbon atoms with hydrocarbons.[2,3] Formation of methylene products from 2-butene appears to involve hot reaction since the corresponding products disappear on moderation (Tables 2 and 4). As expected, trans 2-butene yields trans 2-pentene. Correspondingly, cis 2-butene yields predominantly cis 2-pentene, although there is some isomerization to the more stable trans 2-pentene. This isomerization is minimized in the liquid and solid phases where there is good collisional deactivation.

Formation of cis and trans dimethyl cyclopropane is more complex since it can involve different behaviour patterns by singlet and triplet methylenes, as well as cis-trans isomerization. Since our identification of cis-1,2-dimethyl cyclopropane is only tentative, and since this matter is not central to the main theme, we will discuss it only briefly.[17] In general, trans reagent yields mainly trans product and cis reagent, cis product. An unexplained discrepancy in this trend are the yields from cis 2-butene in liquid and solid phase.[12] Oxygen affects these yields in gas phase systems in a manner which may be rationalized by invoking previously postulated reaction mechanisms of triplet methylene.[10c,12c]

Relation between free carbon atoms and vapour deposited carbon

There is considerable interest in the extent to which the reactions of vapour deposited carbon may be attributed to free carbon atoms.[18,19,5] As reactions of 2-butene with carbon vapour have been studied previously,[18] the present work affords an opportunity for making comparisons. Unfortunately, the absence of quantitative data makes such comparisons less definitive than they might otherwise be. Both systems appear to yield spiro compounds as well as allenes. Furthermore, yields of fragmentation products are low, that of acetylene being only about 1% in the present work on thermalized free carbon atoms and apparently below the limits of detectability in the analogous carbon vapour studies.[18] These observations are consistent with the stated predictions of the model for free carbon atom reactions[2,5] but cannot exclude the possibility that the carbon vapour studies involve intermediate complexes acting as carbon atom donors.

Acknowledgement—This work was supported by the Atomic Energy Commission. We wish to thank the staffs of the Yale University Heavy Ion and Electron Accelerators for assistance with irradiations.

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[17] A detailed study of these products has been carried out by A. P. Wolf *et al. Chemical Effects of Nuclear Transformations* Vol. I; p. 145. I.A.E.A., Vienna (1965).

[18] P. S. Skell, L. D. Wescott, J. P. Goldstein and R. R. Engel, *J. Amer. Chem. Soc.* **87**, 2829 (1965).

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