Of the order of 10^8 atoms of C^{11} were produced in each run. Analysis of those products incorporating C^{11} atoms was by the usual radio gas chromatographic methods.[1,2] Results are shown in Table I. It is seen that a relatively few specific products plus polymer make up the bulk of the yield. None of ten other volatile products found has an individual yield greater than 0.3%. It is interesting to note that this system presents a method for relatively efficient aromatic synthesis of benzene.

The major mechanisms of reaction of atomic carbon with hydrocarbons have been shown to be insertion into C—H and C═C bonds.[1,3,5] The adducts expected on this basis are I, II, III, and IV in Figure 1. They may be either triplet or singlet depending on the multiplicity of the carbon forming them; however, for the sake of brevity and because it does not affect our primary conclusions, we do not make this distinction here.

These adducts may form final products by isomerization involving an H-atom shift. However, even when formed by thermal carbon, they will be quite excited and unless rapidly deactivated will tend to decompose. The path of such decomposition is then predicted by the usual criteria. Modes in which there is a stable "leaving group" are favored, this being equivalent to the requirement that the over-all reactions have high exoergicity, thus tending to maximize the number of states in product phase space which are available. Furthermore, reactions requiring extensive or unusual internal rearrangements are excluded.

It is seen that there is a remarkable correspondence between the results in Table I and the expectations of the model as summarized in Figure 1. Not a single product of appreciable yield is expected but not observed, or observed but not expected.[6] Furthermore, the trends in yield with changes of experimental parameters are as expected. For instance, on going from hot to thermalized carbon atoms and thus to less-excited adducts, the total yields of products formed by extensive fragmentation, acetylene, diacetylene, and vinylacetylene, drop from two-thirds to one-third of the volatile activity. Simultaneously, there is noted a corresponding increase in the total yield of products of relatively low-energy processes, such as benzene and 1,3-hexadien-5-ynes.

Other experimental parameters, such as dependence on phase and oxygen scavenger, provide further detail on the reaction model. This discussion will be provided in the full paper to follow. For the present, however, it is clear that the previously postulated mechanisms are a successful and specific description of the present system.

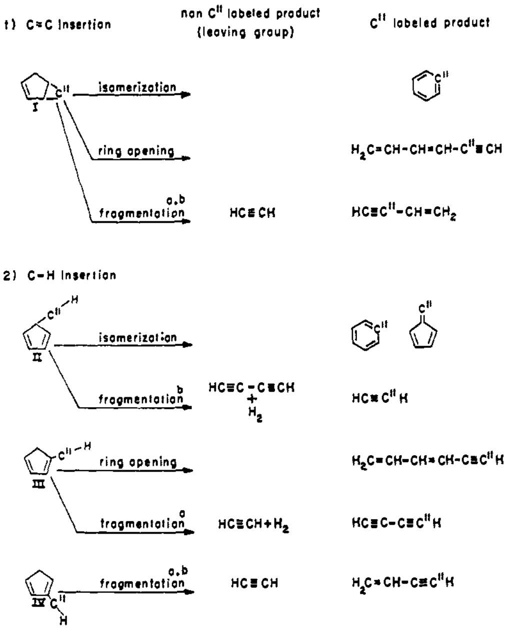

Figure 1. Expected major mechanism of reaction of postulated adducts formed by C-atom insertion into C═C and C—H bonds of cyclopentadiene. For reasons of space, not all possible mechanisms fulfilling the criteria given in the text can be included, but these also lead to the same products. (a) Other fragmentation processes accompanied by H-atom shifts can lead to acetylene-C^{11}. (b) Other fragmentation processes accompanied by H_2 elimination can lead to diacetylene-C^{11}.

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of the major fragmentation products is 8% as compared to 25% in an unmoderated system. Even more significant is the behavior on going from 95 to 99% moderation. Over this range, the amount of reactant, and, to a first approximation, the number of hot collisions and reaction, are reduced fivefold. Yet the sum yield of fragmentation products decreases by only 10%. Hence it would appear that even at 95% neon moderation, the results are little perturbed by hot reaction. The yields of benzene actually drop as one proceeds from 95 to 99% moderation. However, since the yield passes through a maximum as the neon concentration is increased, other effects in addition to translational energy moderation must be important.

(5) J. Dubrin, C. MacKay, and R. L. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4747 (1964).

(6) The mechanism of polymer formation is not explicitly discussed here. There are are many plausible modes by which the adducts can react with further molecules of cyclopentadiene. In the absence of specific information on the makeup of the polymer, it is not appropriate to examine such addition modes in detail.

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Evidence for the Formation and Reaction of Methyne

Sir:

We wish to report on the apparent production of methyne (CH) by reaction of free carbon atoms with hydrogen, and on its reaction with ethylene.[1] Atomic carbon in the form of translationally excited (hot) C^{11} was produced in mixtures of H_2 and C_2H_4 employing nuclear techniques now standard.[5,6] Analysis of products was by radio gas chromatography using the 20.5-min activity to assay the yield of each C^{11}-labeled

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(1) The reaction with ammonia of CH produced in flames has been reported.[2] Methyne has been postulated as a possible intermediate accounting for the formation of ethylene in the reaction of atomic carbon with saturated hydrocarbons.[3,4] This product can also be accounted for by direct reaction of C atoms, and, as yet, it is uncertain which species is actually involved.

(2) D. R. Safrany, R. R. Reeves, and P. Harteck, *J. Am. Chem. Soc.*, **86**, 3160 (1964).

(3) (a) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 210 (1964); (b) A. P. Wolf and G. Stöcklin, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 32C.

(4) D. E. Clark and A. F. Voigt, *J. Am. Chem. Soc.*, **87**, 5558 (1965).

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

(6) J. Dubrin, C. MacKay, and R. L. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4747 (1964).

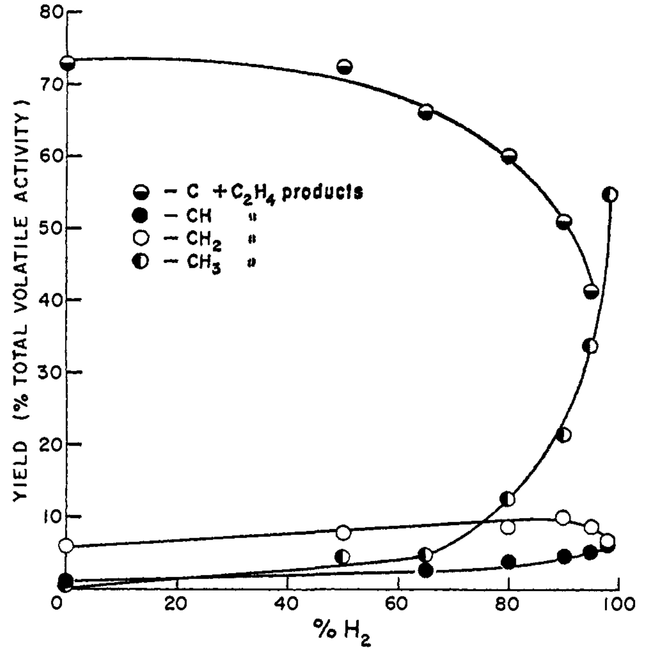

Figure 1. Yields of C, CH, CH_2, and CH_3 products as a function of per cent H_2. Yields are per cent total volatile activity.

molecule. Identifications were made by comparisons with elution times of unlabeled carriers on at least two and usually three columns having different characteristics. These procedures have been fully described elsewhere.[5,6]

The volatile products of reaction of hot carbon atoms with ethylene are well known.[6] They are acetylene, allene, vinylacetylene, pentyne-1, ethylallene, propylene, cyclopropane, and a number of minor products. As ethylene is diluted with hydrogen, the yield of these products is diminished (see Table I). Propylene and cyclopropane, however, increase. These products have previously been postulated[7] to result from reaction of a methylene intermediate with ethylene.

Table I. Products Resulting from Reaction of C^{11} with Three Representative H_2–C_2H_4 Mixtures[a]

Indicated precursor	Product	C_2H_4	80% H_2–20% C_2H_4	95% H_2–5% C_2H_4
C	*b*	75	60	40
CH_2	Propylene + cyclopropane	6	9	9
CH_3	Methane	<0.5	3	6
CH_3	Propane	<0.5	6.5	24
CH_3	Pentane	<0.5	3	5
CH	Pentene-1	1	4	5

[a] Yields are per cent total volatile activity. All samples are at 76 cm pressure. [b] Acetylene, allene, methylacetylene, vinylacetylene, pentene-1, ethylallene, and others as discussed in ref 6.

$$C^{11}H_2 + C_2H_4 \longrightarrow CH_3CH{=}CH_2(C^{11}),\ \overline{C^{11}H_2CH_2CH_2}$$

Evidently CH_2 is also produced, and in greater yield, by reaction of C^{11} with H_2.

Four new products appear. Of these, methane, propane, and pentane would be expected to result from reaction of a CH_3 intermediate with ethylene and radiation-produced radicals. This origin for these products is confirmed by the addition of I_2 to the system. They then do not appear, but an approximately equivalent yield of $C^{11}H_3I$ is found.[8]

The fourth new product, pentene-1, is difficult to assign to C, CH_2, or CH_3 as precursors. It appears to derive from methyne formed by reaction of C with H_2. This three-electron-deficient species can apparently react by insertion either into the π or C–H bonds in a manner analogous to known two- and four-electron-deficient species (CH_2[9] and C[7]).

$$C^{11}H + C_2H_4 \longrightarrow CH_2CHCH_2(C^{11})$$

Allyl radical is thus formed. This has been shown to react with ethylene by addition.[10]

$$C_2H_4 + CH_2CHCH_2(C^{11}) \longrightarrow CH_2{=}CH(CH_2)_3(C^{11})$$

Pentene-1 may then be produced by hydrogen abstraction or a disproportionation reaction with a radical.[10,11]

With such an assignment of intermediates, the relative yields[12] of C, CH, CH_2, CH_3, and CH_4 produced by reaction of C with H_2 in various mixtures of C with C_2H_4 can be evaluated (Figure 1). From this result, and measured pressure dependences, detailed kinetics and relative reaction rates involved in the complex reaction sequence

$$C + H_2 \longrightarrow CH, CH_2, CH_3, CH_4$$

can be quantitatively estimated. These will be reported in a more detailed article.

Acknowledgment. This work was supported by the Atomic Energy Commission. The help of the operating staffs of the Yale heavy ion linear accelerator and the Yale electron accelerator is gratefully acknowledged.

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[7] For references, see C. MacKay and R. Wolfgang, *Science*, **148**, 899 (1965), and ref 3a.

[8] For a $H_2:C_2H_4$ ratio of 4 at 76 cm, a total yield of 15% $C^{11}H_3I$ is found in place of the total of 13% for $C^{11}H_4$, $C^{11}H_3C_2H_5$, and $C^{11}H_3C_4H_9$. An exact equivalence is not to be expected since some $C^{11}H_4$ is apparently formed by combination of $C^{11}H_2$ with H_2, and since in the absence of I_2, there may also be some yield of higher alkanes not detected by the analytical procedure.

[9] Reviewed by W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

[10] References and discussion relating this reaction to the present work are given in ref 6.

[11] Observed product yield dependences on total pressure support these assignments. Methane, propane, and pentane are pressure independent over the range studied (18–150 cm). The sum of the cyclopropane and propylene yields decreases from 12 to 5.5%, while that of pentene-1 increases from 3 to 8.5%. Pressure dependences in this range are consistent with the following reaction scheme

$$C + H_2 \longrightarrow CH_2^*$$

$$CH_2^* \longrightarrow CH + H$$

On the other hand, the data are not consistent with other conceivable mechanisms for formation of pentene-1. For instance, a disproportionation reaction of pentyl radical would be pressure independent. Unimolecular decomposition of pentyl or other large radicals or molecules would be pressure dependent but would not show such a strong dependence in this pressure range.

[12] For this purpose, "yield" is defined by the amount of product which is stable (in the case of CH_4), or which reacts further with C_2H_4. Without this definition, part of the CH_3 yield should also appear as CH yield, since it appears that some CH_3 is formed by reaction of CH with H_2.

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