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INSERTION MECHANISMS OF ATOMIC CARBON: DEGRADATION OF ALLENE PRODUCED BY REACTION WITH ETHYLENE

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It has been postulated recently that two major modes of reaction of atomic carbon with hydrocarbons are insertion into C-H and into C=C bonds.1),2) Consequently, it was predicted that allene formed by the reaction of carbon-11 with ethylene should be labeled in both center and terminal positions.2) To test this hypothesis and to obtain a measure of the relative importance of the two insertion mechanisms in ethylene, we have degraded allene formed in this manner. Recoil C^{11} (half life 20.4 minutes) produced by the $C^{12}(\gamma,n)C^{11}$ reaction was reacted with ethylene and the allene separated and degraded by a fast technique. Results are shown in Table I.

The following conclusions are drawn:

1) The hypothesis that both C-H and C=C insertion reactions are important in ethylene is supported.

2) The similarity of liquid and gas phase results shows: a) the absence of a large temperature effect; b) that rapid collisional deactivation of the primary C atom-C_2H_4 adduct does not markedly affect the yield and the C^{11} distribution of the allene produced. This further implies that rearrangement of carbon atoms in the excited adduct (which might cause the C-H insertion adduct to yield some center-labeled product and vice-versa) is not significant.

3) The results in pure ethylene represent reactions of atomic carbon at all possible kinetic energies, while the neon moderated runs represent largely thermal reactions. It is seen that the thermalized carbon atom has a greater specificity for attack at the C=C bond to give allene, but that the effect is not large. This is consistent with the earlier conclusion that the chemical potential of atomic carbon is so high that additional kinetic energy has only a moderate effect on its modes of attack on hydrocarbons.2)

4) The C atom reactions with ethylene can be compared with those of the other insertion reagents, C_2O4),5) and CH_2.6),7) (See Table II.) It is clear that C_2O is the most selective of these reagents. If only the allene product of the C atom reaction is considered the C atom and CH_2 appear to be of comparable selectivity. However, acetylene accounts for 38% of the yield of volatile products arising from the reaction of C atoms with ethylene,3) and it is likely that most of this acetylene arises from a C-H bond insertion.1) This means that the selectivity ratio for attack at the C=C bonds versus attack at the C-H bond to give any product is lower than the selectivity ratio for the formation of allene alone. The recoil carbon atom therefore appears to be the least discriminating of the three insertion reagents.

Further conclusions may be drawn regarding the state of excitation of the reacting carbon atom. These require much more detailed consideration of the available data on reactions in ethylene and will appear in a fuller account of this work.

Outline of Technique. C^{11} was produced by irradiating the reaction mixture with a 40 Mev Bremsstrahlung beam of sufficient intensity to give of the order of 10^8 atoms of C^{11} from the $C^{12}(\gamma,n)C^{11}$ process. Allene-C^{11} was separated by gas chromatography. It was converted to acetone-C^{11} by passage over a silica gel bed impregnated with Ag_2SO_4, H_2SO_4, and H_2O and held at a temperature of 192°C.8) The acetone-C^{11} was mixed with acetone-C^{14}-1,3. The iodoform reaction was carried out and iodoform and acetic acid separated. Extensive precautions were necessary to prevent cross-contamination of products. Acetone, iodoform, and acetic acid fractions were counted for both C^{11} and C^{14}. The C^{14} tracer served to establish chemical yields. Data on C^{11} content of the three fractions provided two independent methods for calculation of the $H_2C{=}C^{11}{=}CH_2/H_2C^{11}{=}C{=}CH_2$ ratio. Attainment of close consistency of results by the two calculations provided a measure of the validity of the procedure.

TABLE I

Results of Allene Degradation under Various Conditions

Reaction Mixture	Yield Allene (% Total Volatile Products)	$\frac{H_2C{=}C^{11}{=}CH_2}{H_2C^{11}{=}C{=}CH_2}$ b)
152 cm. C_2H_4; 25°C.	15.2 ± 1.0 a)	1.8 ± 0.1
Liquid C_2H_4; -130°C.	15.0 ± 2.0 a)	2.0 ± 0.2
Solid C_2H_4; -196°C.	11.5 ± 2.5 a)	2.1 ± 0.2
4 cm. C_2H_4, 76 cm. Neon; 25°C.	12.0 ± 2.5 c)	3.2 ± 0.3
7.6 cm. C_2H_4, 144.4 cm. Neon; -130°C.	-	3.4 ± 0.3

a) These values represent slight revisions of those reported in refernces 2 and 3.

b) All values represent the average of two independent calculations from one degradation run except for the 152 cm. C_2H_4 sample. This represents data from five degradations. Errors for this sample are at the 95% confidence level. Errors for other samples are estimates.

c) Data of H. E. Rosenberg, this Laboratory, private communication.

TABLE II

Comparison of Insertion Reagents (Gas Phase Systems)

Reagent	Source	C=C Attack / C-H Attack
C	Hot atoms from $C^{12}(\gamma,n)C^{11}$ recoil	7.2 a)
C	Thermalized atoms from $C^{12}(\gamma,n)C^{11}$ recoil (Ne moderated)	13.2 a)
CH_2 (ref. 7)	CH_2CO photolysis at 3100 Å	8.9
C_2O (ref. 5)	C_3O_2 photolysis with Hg lamp	46 b)

a) Ratio is for the formation of allene only and is therefore an upper limit. (See Text.)

b) Ratio is for the formation of allene only. A 20% yield of methylacetylene is also reported.

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