The Reactions of Carbon Atoms and Methyne (CH) with Hydrogen and Ethylene[1]

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Abstract: C^{11} produced by nuclear recoil has been used to examine the reactions of free carbon atoms with hydrogen. Reaction with added ethylene was used to intercept CH, CH_2, and CH_3 intermediates. Product yields were measured as a function of the relative pressures of hydrogen and ethylene at constant total pressure, as a function of total pressure, and in the presence of oxygen and iodine scavengers. Methyne (CH) was found to react with ethylene to give an allyl radical which reacted further to yield pentene-1. This product served as an indicator of the amount of CH formed. CH_2 was estimated through the yields of its reaction products with ethylene, propylene, and cyclopropane. The results obtained serve to outline the complex series of processes in the C–H_2–C_2H_4 system. It is possible to identify an initial reaction involving addition of hot C atoms to H_2 to form excited CH_2 which can either be stabilized by collisional deactivation or can dissociate to CH. This process is considerably less efficient than addition of C to ethylene, possibly because nonlinear CH_2 complexes revert promptly to $C + H_2$. A kinetic analysis allows estimation of the average energy of the reacting hot C atom and also provides a basis for quantitative and semiquantitative estimates of the relative rate constants involved. Both CH_2 and CH show somewhat higher reactivity toward C_2H_4 than toward H_2, but the difference in reactivity is greater for CH. This is consistent with the fact that in these studies, CH_2 must be formed with higher average translational energy than is CH.

Although recently there has been intensive investigation of the reactions of free carbon atoms with hydrocarbons,[4] reaction with H_2, in a sense the simplest alkane, has received relatively little attention. Moll and Thompson have reported a study in an argon matrix,[5] and fragmentary results have been reported elsewhere.[6]

H_2 is an attractive system because of its relative simplicity. Reaction with carbon atoms can yield only two primary products, CH and CH_2. Formation of CH (methyne) represents a particularly intriguing possibility, for, while this radical is well known in flame studies, there are only a few reports of its reactions with molecules.[7-9] Although Braun, McNesby, and Bass[10] have recently reported rate constants for its reaction with CH_4, H_2, and N_2, it still represents a considerable gap in our knowledge of the reactions of electron-deficient species with molecules.

The energetics of the reactions of C with H_2 present some interesting features.[11] It is evident that CH

$$C(^3P) + H_2 \longrightarrow CH(^2\pi) + H \qquad \Delta H = +20 \text{ kcal} \qquad (1)$$

$$C(^1D) + H_2 \longrightarrow CH(^2\pi) + H \qquad \Delta H = -6.6 \text{ kcal} \qquad (2)$$

$$C(^3P) + H_2 \longrightarrow CH_2(^3\Sigma_{g-}) \qquad \Delta H = -88 \text{ kcal} \qquad (3)$$

$$C(^1D) + H_2 \longrightarrow CH_2(^1A_1) \qquad \Delta H = -115 \text{ kcal} \qquad (4)$$

can be produced by a $C(^3P)$ atom only if that atom possesses excess translational energy, *i.e.*, is hot. This is particularly relevant since it is likely that the bulk of the reacting C atoms are in the ground (^3P) state.[16] On the other hand, if CH_2 is formed by reaction of a hot carbon atom, the excess energy will tend to promote decomposition back to $C + H_2$ before collisional deactivation can occur. Therefore the reaction of hot C atoms with H_2 to give CH_2 may well be quite inefficient. Finally, the principle of conservation of

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(1) A communication on certain aspects of this work has appeared: J. Nicholas, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, **88**, 1065 (1966).

(2) Haverford College, Haverford, Pa.

(3) Author to whom inquiries should be addressed.

(4) Much of this work is summarized in three recent reviews: (a) C. MacKay and R. Wolfgang, *Science*, 148, 899 (1965); (b) A. P. Wolf, *Advan. Phys. Org. Chem.*, 3, 210 (1964); (c) R. Wolfgang, *Progr. Reaction Kinetics*, 3, 97 (1965).

(5) N. G. Moll and W. E. Thompson, *J. Chem. Phys.*, **44**, 2684 (1966).

(6) In addition to ref 1, a brief mention of the reactions of $C + H_2$ is made in (a) C. MacKay, M. L. Pandow, P. Polak, and R. Wolfgang in "Chemical Effects of Nuclear Transformations," Vol. I, International Atomic Energy Association, Vienna, 1961, p 38; and (b) H. Ache and A. P. Wolf, *ibid.*, p 107.

(7) CH reactions with C_2H_2 to give C_3H_3* have been postulated by G. P. Glass, G. B. Kistiakowsky, J. V. Michael, and H. Niki, "Tenth Symposium on Combustion," The Combustion Institute, Pittsburgh, Pa., 1965, p 513; A. Fontyn, W. J. Miller, and J. M. Hogan, *ibid.*, p 545; H. F. Calcotte, S. C. Kurzius, and W. J. Miller, *ibid.*, p 605.

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

(9) The formation of ethylene in the reaction of free C atoms with alkanes has been attributed to an insertion by CH into the CH bond of a CH_3 group followed by decomposition of the resulting adduct.

$$RCH_3 + CH \longrightarrow RCH_2CH_2 \longrightarrow R\cdot + CH_2{=}CH_2$$

See A. P. Wolf and G. Stöcklin, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 32C; and ref 4b. Recently this has been supported by D. E. Clark and A. F. Voigt, *J. Am. Chem. Soc.*, 87, 5558 (1965).

(10) W. Braun, J. R. McNesby, and A. M. Bass, *J. Chem. Phys.*, **46**, 2071 (1967).

(11) We give here the energetics for $C(^3P)$ and $C(^1D)$ atoms. CH and CH_2 could also be produced by atoms in the (^1S) state. However, reactions of $C(^1S)$ should be more exothermic than those for $C(^1D)$ by 34 kcal. The resulting CH_2 would be so excited that little of it could survive under our conditions. As discussed earlier[1] our evidence points to CH_2 being formed in an addition reaction.

In writing these equations, we have assumed that $CH(^2\pi)$ is the ground state for the C-H radical. The other possibility, the $CH(^4\Sigma)$ state, has not been observed experimentally. The calculated separation of the ($^2\pi$) and ($^4\Sigma$) states varies. See, for example, ref 12.

The CH bond energies in C-H, CH_2 and CH_3 are from ref 13, the H-H bond energy from ref 14, and the energies of the various C atom states is from ref 15.

(12) P. C. H. Jordan and H. C. Longuet-Higgens, *Mol. Phys.*, **5**, 121 (1962); F. O. Ellison, *J. Chem. Phys.*, **36**, 3112 (1962).

(13) G. Bell and G. Kistiakowsky, *J. Am. Chem. Soc.*, 84, 3417 (1962).

(14) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(15) G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, N. Y., 1944.

(16) M. Marshall, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4741 (1964).

momentum requires that most of the translational energy brought to reactions 3 and 4 by hot C atoms appear as translational energy of the CH_2 products. Any subsequent CH_2 reactions may then be those of a translationally hot species.

The general technique used in this work involves the production of a trace of C^{11} (20.5-min half-life) atoms by nuclear techniques. These atoms are formed in low-lying (^3P, ^1D, ^1S) electronic states[4a,16] but initially possess a high excess translational energy. They may react while hot or after thermalization by successive collisions. The fraction of thermal processes may be increased by addition of inert moderators such as neon. After reaction, products containing C^{11} are separated and assayed by radio-gas chromatography.

Since this technique is limited to assay of stable molecules, intermediates such as CH and CH_2 can be identified only by addition of a molecule with which they will react to give identifiable products. Ethylene is suitable for this purpose. It combines with CH_2,[17] with C,[4] and with CH_3[18] to give known end products. Under these circumstances, it seems reasonable to expect that products of its reaction with CH can also be characterized.

Experimental Section

The techniques used in studies of this kind have been described in detail elsewhere[16,19,20] and will only be reviewed briefly here. C^{11} was produced by use of either the Yale heavy ion accelerator (HILAC) or the Yale electron accelerator. With the HILAC, C^{11} is produced as a beam of high enough energy so that it can be injected into the sample vessel through a thin wall. The electron accelerator produces a bremsstrahlung beam of 40–50 Mev maximum energy. This beam enters the sample vessel and produces C^{11} *in situ* by the $C^{12}(\gamma,n)C^{11}$ reaction. Radiation delivered to the sample was below 0.04 ev/molecule in the HILAC runs[21] and below 0.01 ev/molecule in electron accelerator runs, as measured using acetylene production from benzene as a crude dosimeter. Both irradiation techniques gave similar results.

Sample containers and procedures for preparing samples have been discussed elsewhere.[20] All compounds used as reagents were Phillips and Matheson research grade and were used without further purification. After irradiation at room temperature, radio-gas chromatography was used for analysis. In this method, a thermal conductivity detector and counter are connected in series to the outlet of a gas chromatographic column so that mass and activity analysis can be performed simultaneously. Aliquots of each sample are passed through the counter without prior separation on the column in order to determine total volatile activity. A separation of larger aliquots on appropriate columns is then carried out and results are recorded as per cent total volatile activity. Columns used in the analyses are listed in Table I. The identities of most compounds found had previously been established in studies on ethylene.[16,19]

It is possible to convert relative yields from gas-phase experiments to an absolute basis. For the experiments using the heavy ion accelerator, an O_2 sample having the same stopping power as the reagent sample was irradiated for the same period under similar beam conditions. It was assumed on the basis of earlier work[20] that all of the C^{11} stopped reacts with O_2 to give $C^{11}O$ and $C^{11}O_2$. Thus after normalization to equal integrated beam intensities, the total volatile activity in this O_2 monitor represents the number of C^{11} atoms delivered to the reagent gas. Absolute yields are then obtained by dividing this total activity into the observed activity of any product.

Table I. Columns Used for Analysis of Various Compounds

Compound	Column
CO, CH_4	5-ft activated charcoal
Allene, methylacetylene, C_2H_2	20-ft dimethylformamide (25%) on Firebrick at 0°
C_3H_8, propylene, cyclopropane	25-ft dimethylformamide (40%) on Firebrick at 0°
C_4H_4, *n*-C_5H_{12}, pentene-1, pentyne-1, ethylallene	30-ft GESF 96 silicone oil (15%) on Anakrom ABS (Analabs, Inc.) at room temperature

On the electron accelerator, the yield of C^{11} is directly proportional to the number of C^{12} atoms in the sample. A monitor sample of ethane was irradiated simultaneously and under identical conditions with the hydrogen sample. The fraction of C^{11} yielding volatile products in ethane is known[23] and measurement of the total volatile activity in the monitor could thus provide a basis for determining absolute yields.

By these methods it was found that with both accelerators, over the complete range of reagent mixture compositions and total pressures, the total volatile activity of the samples represents 83 ± 6% of the total number of available C^{11} atoms. Thus when yields are expressed as per cent total volatile activity, they may be converted to an absolute basis by multiplying by a factor of 0.83. The unobserved activity may be attributed to the formation of involatile products, such as polymeric hydrocarbon species.

Results

Results are summarized in Figures 1–4 and Tables II–V and are expressed in per cent of total volatile activity. (As discussed above, total volatile activity represents 83% of the total C^{11} delivered to these systems.) Figure 1 shows the effect of increasing the H_2/C_2H_4 ratio in the gas phase on those products previously assigned as resulting directly from the reaction of C atoms with ethylene.[16,19] With the exception of the two C_5's, the yield of each of these products decreases as hydrogen is added, as does their sum yield. Ethylallene remains constant, while pentyne-1 may increase slightly. The general trends are very similar to those previously reported for dilution of ethylene by neon.[24]

Figure 2 shows the effect of increasing mole per cent H_2 on products with the stoichiometry $CH_2 \cdot nC_2H_4$ where $n = 1$ or 2. It is significant that the yield curves for cyclopropane and propylene show maxima, while that for pentene-1 increases steadily over the whole range studied.

Figure 3 shows yield curves for products of $CH_4 \cdot nC_2H_4$ stoichiometry with $n = 0$–2. These are products not found in pure C_2H_4 and are those expected to result from reaction of $CH_3\cdot$ in H_2–C_2H_4 systems. Each increases steadily as mole per cent H_2 is increased.

Moderator Effects. Results on thermalization of hot C and other effects of moderation are reported in Table II. This compares the effects of neon on pure C_2H_4 with those of helium on mixtures for which the

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(17) Reactions of CH_2 with hydrocarbons are summarized in (a) W. Kirmse, "Carbenes," Academic Press Inc., New York, N. Y., 1964, p 26 ff; (b) W. B. De More and S. W. Benson, *Advan. Photochem.*, 2, 129 (1964); (c) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1962, p 20 ff.

(18) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, p 175 ff.

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

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

(21) In an earlier paper,[20] the radiation dosage at the HILAC was cited as <0.01 ev/molecule. The value given here results from (1) a new targeting arrangement, and (2) use of a *G* value of 5[22] rather than 10 for acetylene production from benzene.

(22) J H. Futrell and L. W. Sieck, *J. Phys. Chem.*, **69**, 892 (1965); F. H. Field, *ibid.*, **68**, 1039 (1964).

(23) G. Stöcklin and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 229 (1963).

(24) J. Dubrin, H. Rosenberg, R. Wolfgang, and C. MacKay in "Chemical Effects of Nuclear Transformation," Vol. I, International Atomic Energy Association, Vienna, 1964, p 133.

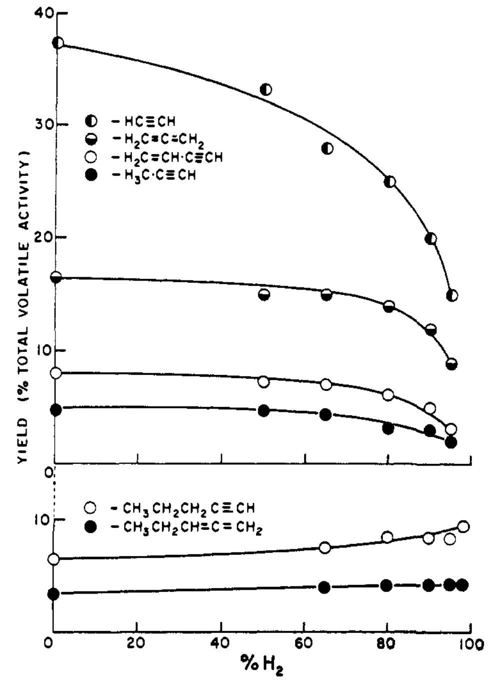

Figure 1. Yields of products of the direct reaction of C with C_2H_4 as a function of % H_2 in H_2–C_2H_4 mixtures at 77 cm pressure.

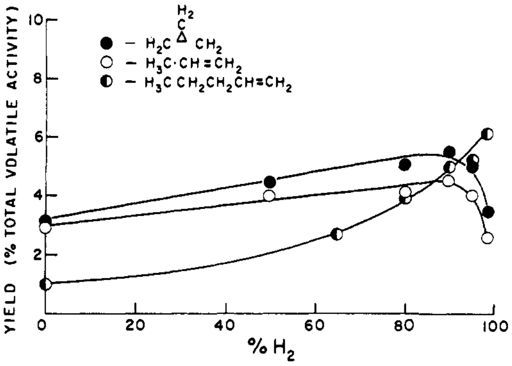

Figure 2. Yields of cyclopropane, propylene, and pentene-1 in various H_2–C_2H_4 mixtures at 77 cm pressure.

H_2/C_2H_4 ratio is 4:1.[25] Since the ratio of neon moderator to reactant is 19:1 while that of helium moderator to reactant is 4:1, one might expect that the pure C_2H_4 is more highly moderated than the mixture.[26] Despite this, yields of products arising from the C + C_2H_4 reaction in the helium-moderated H_2–C_2H_4 system are surprisingly similar to those found in the neon-moderated C_2H_4 system. Significantly, the sum yield of products of direct C atom reaction with C_2H_4 remains almost constant on addition of helium as moderator, while there is a reduction from 12.5 to 7.5% in the sum yield of CH_4, C_3H_8, and n-C_5H_{12}, products found only in the presence of H_2. It therefore appears that thermalization of C atoms favors reaction with C_2H_4 over reaction with H_2.

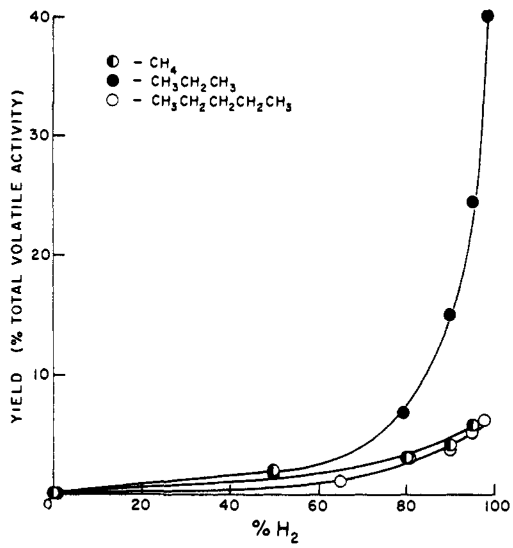

Figure 3. Yields of methane, propane, and n-pentane as a function of % H_2 in H_2–C_2H_4 mixtures at 77 cm pressure.

Scavenger Effects. Effects of the addition of scavenger quantities of oxygen and iodine are reported in Tables III and IV. Oxygen (Table III) eliminates methane, propane, and all C_5's. The yields of propylene and cyclopropane are reduced, with the cyclopropane being more affected. Finally both CO and CO_2 are formed in substantial yields. In the iodine scavenged samples (Table IV), methane, propane, and n-pentane are replaced by an equivalent yield of methyl iodide.

Table II. Products in C_2H_4 Mixtures under Various Conditions[a]

Product	C_2H_4[b]	0.95 Ne, 0.05 C_2H_4	0.80 H_2, 0.20 C_2H_4	0.80 He, 0.16 H_2, 0.04 C_2H_4
Carbon monoxide	1.2	4.6	1.4	2.5
Methane			2.6	1.5
Ethane	<0.2	<0.5	<0.5	<1.0
Ethylene	1.1	<2.0	<1.0	<1.0
Acetylene	38.5	17.5	25.0	17.0
Propane	<0.1	<0.5	7.0	4.8
Cyclopropane	3.2	1.0	5.3	1.6
Propylene	2.9	1.0	3.9	2.9
Allene	16.5	10.0	14.0	12.0
Methylacetylene	4.5	5.0	3.0	3.0
Vinylacetylene	7.0	3.5	5.7	3.5
n-Pentane	<0.5	<0.5	3.0	1.2
Pentene-1	1.0	<0.5	3.8	2.0
Pentyne-1	6.6	28.0	8.8	20.0
Ethylallene	3.3	13.5	3.9	5.9

[a] All samples are at 77 cm total pressure. Yields are per cent total volatile activity. [b] Taken from ref 19.

Pressure Variations. In Figure 4, the pressure dependence of $CH_2 \cdot nC_2H_4$ products at an H_2/C_2H_4 ratio of 4:1 is examined over the range from 18 to 150 mm. The sum yield (propylene + cyclopropane) decreases with decreasing pressure, and, within experimental error, this decrease is balanced by an increase in pentene-1 yield.

In pure C_2H_4, a decrease in pressure from 77 to 7.7 cm results in a substantial decrease in the sum yield (cyclopropane + propylene) and a change in the cyclopropane/propylene yield ratio (Table V). There is no

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(25) The resonance rule which we use as a guide toward determining the extent of neutralization of any C^+ before it can react[40,16] does not exclude the possibility of some C^+ reactions in Ne and He mixtures.

(26) The different moderations reported result from the fact that, for the C_2H_4 experiments, the heavy ion accelerator was used, while for the H_2–C_2H_4 experiments only the electron accelerator was available. Helium was used rather than neon to ensure isotopic purity. Higher moderations than 80% were barred by the fact that C_2H_4 served as the source of C^{11}.

Table III. Effect of O_2 Scavenger on Some Yields

Products	Yields[a] 0.950 H_2, 0.050 C_2H_4	 0.945 H_2, 0.050 C_2H_4, 0.005 O_2
Carbon monoxide	2.0	36.5
Carbon dioxide	0.5	20.0
Propylene	5.1	3.4
Cyclopropane	4.0	1.0
Methane	6.0	<0.5
Propane	24.0	<0.5
n-Pentane	4.9	<0.5
Pentene-1	5.1	<0.5
Pentyne-1	8.5	<0.5
Ethylallene	4.2	<0.5

[a] All samples at 77 cm total pressure. Yields are per cent total volatile activity. Uncertainties are ~10% of values given.

Table IV. Effect of I_2 Scavenger on C_1, C_3, and C_5 Saturate Yields

Products	Yields[a] 0.80 H_2, 0.20 C_2H_4	 0.80 H_2, 0.20 C_2H_4 + $I_2(s)$[b]	 0.95 H_2, 0.05 C_2H_4	 0.95 H_2, 0.05 C_2H_4 + $I_2(s)$[b]
Methane (C_1)	2.9	<0.5	6.0	<0.5
Propane (C_3)	7.0	<0.5	24.0	<0.5
n-Pentane (C_5)	3.1	<0.5	4.9	<0.5
$C_1 + C_3 + C_5$	13.0	<1.5	34.9	<1.5
CH_3I	0.0	15.2	0.0	34.0

[a] All samples at 77 cm total pressure. Yields are per cent total volatile activity. [b] I_2 crystals were added to give the vapor pressure of I_2 at room temperature (~0.7 mm).

Table V. Effect of Pressure Variation on Products of Reaction of C Atoms with C_2H_4

Products[a]	Yields[b] 77 cm	 7.7 cm
Cyclopropane	3.2 ± 0.3	0.5 ± 0.1
Propylene	2.9 ± 0.3	1.7 ± 0.2
Allene	16.5 ± 1.7	13.0 ± 1.3
Pentene-1	1.0 ± 0.1	1.0 ± 0.1

[a] With the exception of pentene-1, only those products are reported here whose yields show some variation with pressure. See ref 19 for complete listing of all identified products. [b] Yields are per cent total volatile activity.

compensating increase in pentene-1 yield in marked contrast to the 4:1 H_2/C_2H_4 mixtures discussed above.

Summary. These results can be briefly summed up as showing a general experimental distinction between several groups of products: (I) products known to be formed in high yield by the reaction of C atoms with ethylene itself (this group includes allene, methylacetylene, acetylene, vinylacetylene, pentyne-1, and ethylallene (Figure 1)); (II) cyclopropane and propylene, whose yields peak at a moderate H_2 fraction (Figure 2) (the total yield of these products and their ratio to each other shows a marked dependence on total pressure (Figure 4)); (III) pentene-1, whose yield shows a steady rise up to the highest H_2 fraction studied and is dependent on total pressure (Figures 2 and 4); (IV) methane, *n*-propane, and *n*-pentane, whose yields increase markedly up to the highest H_2 fractions studied (Figure 3).

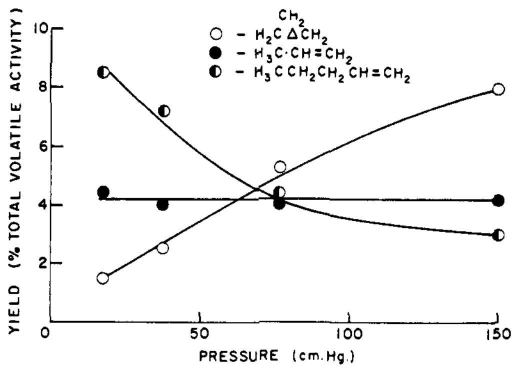

Figure 4. Pressure dependence of cyclopropane, propylene, and pentene-1 yields for a 4:1 $[H_2]/[C_2H_4]$ mixture.

Discussion

1. C + C_2H_4 Reaction. Group I Products. Before considering the reactions of C atoms with hydrogen, it is worthwhile to examine the behavior of the group I products, those assigned to the C + C_2H_4 reaction, in order to be certain that this behavior is consistent with the model previously presented.[16,19] Briefly, this model assumes the two primary reactions of C–H insertion and π-bond attack by the C atom to form excited C^{11} C_2H_4 intermediates. The fate of these adducts is decided by (1) their initial excitation energy, and (2) the rate at which this energy is transferred to the surrounding medium. These factors have been studied extensively in moderator experiments in gas[4,24] and condensed phases.[27] This work has shown that in the gas phase with the exception of vinylacetylene, all group I products can be formed by both hot and thermal carbon atoms. However, the yields of fragmentation products (primarily C_2H_2) decrease, and the yields of five-carbon products increase markedly as the fraction of moderator in the system is increased.[28]

Correlation with Present Data. In applying the above model to the products of C atom reactions with C_2H_4 in the H_2–C_2H_4 system, two factors must be kept in mind. (1) As the fraction of H_2 increases, more C atoms will react with it, reducing the number available to react with C_2H_4. This effect leads to the observed reduction in group I products on dilution with H_2. (2) As the fraction of H_2 increases, the average energy of the C atoms surviving to react with ethylene may change, modifying the relative yields of these products.

This second effect is clearly apparent in the change of relative yields of group I on hydrogen dilution (Figure 1). Those products deriving from lower energy paths are relatively favored, the sum yield of pentyne-1 and ethylallene actually increasing. High-energy products, such as acetylene, decrease sharply. This behavior indicates that hydrogen shows a moderator effect qualitatively similar to that observed on dilution by neon[24] (see Table II). Such a net moderator effect is only observed if the diluent added, in this case hydrogen, is appreciably more inert toward high-energy reaction than the original reactant, in this case ethylene.

We conclude, therefore, that behavior of group I products is entirely consistent with their formation

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(27) J. E. Nicholas, C. F. MacKay, and R. L. Wolfgang, *J. Am. Chem. Soc.*, 88, 1610 (1966).

(28) As might be expected, the efficient energy transfer in the condensed phase leads to very low yields of fragmentation products.[27]

from direct C + C_2H_4 reaction, and, furthermore, that H_2 is substantially less reactive toward hot carbon atoms than is ethylene. As will be seen subsequently, this latter conclusion can be quantitatively verified, using other aspects of the results.

2. Reactions of Intermediates Formed by C + H_2 Reactions. Group II, III, and IV Products. We turn now to examine those products formed by reaction of ethylene and hydrogen with CH, CH_2, and CH_3 intermediates.[29]

Methyl Radical. CH_3 can give methane by H atom abstraction, and propyl radical by addition to ethylene.[18] The propyl radical can abstract hydrogen to form propane or react further to yield eventually *n*-pentane.[30] Further addition products in a pentyl radical sequence would not be detected by our analysis.

$$C^{11}H_3\cdot + RH \longrightarrow C^{11}H_4 + R$$

$$\begin{tikzcd} C^{11}H_3\cdot + C_2H_4 \arrow[r] & H_3C^{11}CH_2CH_2\cdot \arrow[r, "+RH"] \arrow[d, "+C_2H_4"] & H_3C^{11}CH_2CH_3 \\ & H_3C^{11}(CH_2)_3CH_2\cdot \arrow[r, "+RH"] & H_3C^{11}(CH_2)_3CH_3 \end{tikzcd}$$

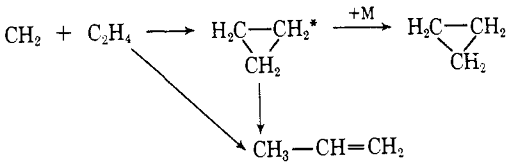
$C^{11}H_3$ will react rapidly with O_2 and I_2

$$C^{11}H_3 + O_2 \longrightarrow \text{unobserved products}$$

$$C^{11}H_3 + I_2 \longrightarrow C^{11}H_3I$$

The elimination of saturated hydrocarbon products by addition of these scavengers is therefore consistent with this scheme. A more specific confirmation is the appearance of an approximately equivalent yield of methyl iodide in the presence of iodine as reported in Table IV.

Methylene. The C–H insertion and π-bond addition reactions of methylene are well established,[17] the principal products being cyclopropane and propylene



Small yields of cyclopropane and propylene resulting from the reaction of carbon atoms in pure ethylene have previously been attributed to a CH_2 intermediate.[19] This hypothesis is supported by the increase in the propylene/cyclopropane ratio with decreasing ethylene pressure reported in Table V which is consistent with that observed previously for photochemically generated CH_2.[17,32] A similar pressure dependence of the cyclopropane/propylene ratio is also found in H_2–C_2H_4 mixtures (Figure 4). The yields of these products can thus be taken as a rough measure of the relative importance of CH_2 in the system.[33]

Methylene has also been shown to insert into the H–H bond in H_2 to give CH_4.[13] Such a reaction probably involves a singlet CH_2, since triplet CH_4 should be unstable, and the spin conservation rule usually holds in reactions involving elements of low atomic weight. We find no evidence for the direct insertion reaction, since O_2 and I_2 both reduce the yield of CH_4 below the limits of detection, indicating that the bulk of the methane we observe is formed in a radical process. This finding can be interpreted in a variety of ways. (1) The CH_2 in our system is incapable of insertion because of its unusually high translational energy. Arguing against this is the fact that the C atom with an even higher translational energy does insert, as discussed below. (2) Under our conditions, the excited methane insertion product largely decomposes. (3) The chief CH_2 species in our system is the triplet which is incapable of insertion into an H–H bond. Supporting interpretation 3 is the observation (Table III) that the propylene and cyclopropane products of the reaction of CH_2 with ethylene are both significantly reduced by addition of oxygen. Indeed, the reduction of the propylene yield is greater than that found in pure ethylene.[19,35] It would seem then that interpretation 3 best accounts for our findings, but diagnosis 2 certainly is not rigorously excluded.

Methyne. The only observed product which we have not assigned to reaction of C, CH_2, or CH_3 with gaseous ethylene is pentene-1. Addition of CH to an ethylene molecule should result in an allyl radical. This in turn is known to react with the ethyl radical to give pentene-1 as a preferred product.[36]

$$CH + C_2H_4 \longrightarrow CH_2{=}CHCH_2\cdot$$

$$CH_2{=}CHCH_2\cdot + C_2H_5\cdot \longrightarrow CH_2{=}CH(CH_2)_2CH_3$$

Alternately, an allyl radical may add ethylene to give a pentenyl radical, which then abstracts hydrogen from another molecule or radical.[37]

$$CH + C_2H_4 \longrightarrow CH_2{=}CHCH_2\cdot$$

$$CH_2{=}CHCH_2\cdot + C_2H_4 \longrightarrow CH_2{=}CH(CH_2)_2CH_2\cdot$$

$$CH_2{=}CH(CH_2)_2CH_2\cdot + RH \longrightarrow CH_2{=}CH(CH_2)_2CH_3 + R$$

Both mechanisms probably contribute. At any rate, whatever the details of its mode of formation, pentene-1 is certainly a plausible end product of a reaction initiated by CH attack on ethylene.[30,38]

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[29] The explanation of the group II, III, and IV products that we offer here is based on CH, CH_2, and CH_3 intermediates. An alternative explanation postulating that these products arise from reduction of the various unsaturates formed in the direct C + C_2H_4 reaction seems much less likely. The high concentration of ethylene, an efficient H atom scavenger, works against this. Moreover, the data are inconsistent with this explanation since large yields of highly unsaturated C_3 and C_4 products are found, while their reduction products are not detected.

[30] The mechanism for propane formation probably varies with the C_2H_4/H_2 ratio. Estimates based on our radiation dosage data and on rate constants for reactions involving CH_3, C_2H_4, and C_2H_5[31] indicate that at high C_2H_4 concentrations CH_3 addition to C_2H_4 predominates. However, at high H_2 concentrations, CH_3 reaction with C_2H_5 becomes more important. This is in agreement with our observation (Figure 3) that as the H_2/C_2H_4 ratio increases, propane becomes an increasingly more important product than methane and pentane.

[31] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 119 (1961).

[32] H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957).

[33] Formation of CH_3 and CH_4 by reaction of CH_2 with hydrogen competes with the reactions with ethylene.[13] Thus cyclopropane and propylene measure only a fraction of the CH_2 yield, and this fraction will diminish as the H_2/C_2H_4 ratio increases. A further complication arises when the different spin states of CH_2 are considered. Recent work[34] indicates that triplet CH_2 may abstract H atoms with an efficiency comparable to that with which singlet CH_2 inserts into C–H bonds. Thus the propylene–cyclopropane yields represent only a lower limit to the yield of CH_2 in our system.

[34] R. W. Carr, Jr., *J. Phys. Chem.*, **70**, 1970 (1966).

[35] The reduction is probably higher than indicated by Table III. Yields there are computed on a total volatile activity basis. In a system such as H_2 where radical reactions are extremely important, O_2 should reduce the total volatile activity. For the same reasons, the yields of CO and CO_2 are probably exaggerated in Table III. However, the high yield of CO_2 relative to CO seems characteristic of saturated systems.

[36] D. G. L. James and G. E. Troughton, *Chem. Commun.*, 94 (1965). As discussed earlier,[30] at high H_2/C_2H_4 ratios radical reactions with $C_2H_5\cdot$ probably predominate over reactions with C_2H_4.

[37] This is discussed in some detail with references to the pertinent literature in ref 19.

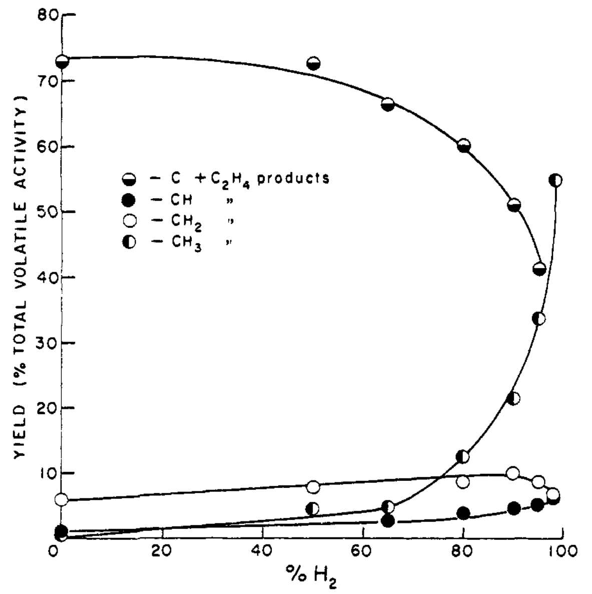

Figure 5. Yields of products from addition of C, CH, CH_2, and CH_3 to ethylene.

On the basis of the product assignments given above, one may estimate the percentages of C^{11} adding to ethylene as C (atomic), CH, CH_2, or CH_3 to give observed products under any set of experimental conditions, and these are plotted in Figure 5 as a function of H_2 concentration. (It should be kept in mind that this plot does not include in the amount of any intermediate CH_n that portion which reacts to give more highly hydrogenated intermediates, CH_{n+x}.)

3. C + H_2 Reactions. The principal experimental data on which any model of reaction of C with H_2 must be based can be summarized as follows: (1) the change in product spectrum on increasing the fraction of H_2 at constant pressure as shown in Figures 1–3 and 5; (2) the effect of changing pressure at constant H_2/C_2H_4 ratio. In particular, the products derived from CH_3 show little pressure dependence in the region studied, while those derived from CH and CH_2 vary as shown in Figure 4.

CH and CH_2 must be formed in a series of reactions which begin either with an insertion of the C atom into the H_2 molecule, or abstraction of an H atom by the C atom. For an initial insertion, the reaction sequence (3a–c) follows. (All ΔH values are given for ground state (^{3}P) C atoms unless otherwise indicated.[11])

$$C^{11} + H_2 \longrightarrow C^{11}H_2^* \qquad \Delta H = -88 \text{ kcal mole}^{-1} \quad (3a)$$

$$C^{11}H_2^* + M \longrightarrow C^{11}H_2 + M^* \quad (3b)$$

$$C^{11}H_2^* \longrightarrow C^{11}H + H \qquad \Delta H = +108 \text{ kcal mole}^{-1} \quad (3c)$$

For an initial abstraction, sequence 1, 5–6c is possible.

$$C^{11} + H_2 \longrightarrow C^{11}H + H \qquad \Delta H = 20 \text{ kcal mole}^{-1} \quad (1)$$

$$C^{11}H + H_2 \longrightarrow C^{11}H_2 + H \qquad \Delta H -5 \text{ kcal mole}^{-1} \quad (5)$$

$$C^{11}H + H_2 \longrightarrow C^{11}H_3^* \qquad \Delta H = -110 \text{ kcal mole}^{-1} \quad (6a)$$

$$C^{11}H_3^* + M \longrightarrow C^{11}H_3 + M^* \quad (6b)$$

$$C^{11}H_3^* \longrightarrow C^{11}H_2 + H \qquad \Delta H = +105 \text{ kcal mole}^{-1} \quad (6c)$$

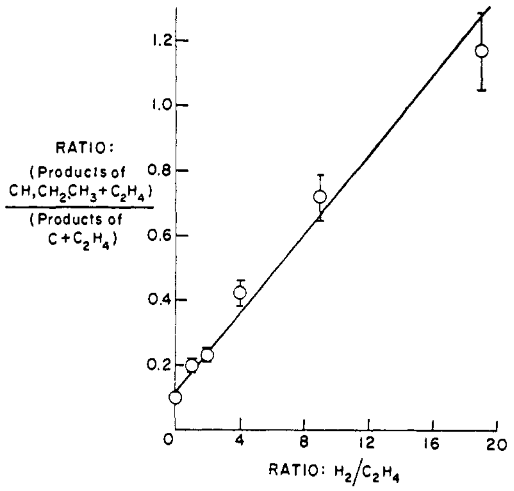

Figure 6. Σ[CH, CH_2, CH_3 + C_2H_4 products]/[C + C_2H_4 products] *vs.* $[H_2]/[C_2H_4]$ ratio.

Both sequence 3a–c and sequence 1, 5–6c predict the constant sum yield of products derived from CH and CH_2 reaction with ethylene as pressure is varied. However, only sequence 3a–c is consistent with the variation of relative yields of CH and CH_2 products with pressure

4. Relative Reactivity of C with H_2 and C_2H_4. As described in section 1, carbon atoms will react with ethylene by addition to form C_3H_4* intermediates and ultimately a variety of products. They may also form cyclopropane, propylene, and pentene-1, possibly *via* CH and CH_2 intermediates, but these seem to be less important reaction modes. These same products plus methane, propane, and *n*-pentane, products characteristic of the CH_3 radical, are found in the C–H_2–C_2H_4 system. Thus we can write

$$C + C_2H_4 \longrightarrow C_3H_4^* \longrightarrow \text{products M} \quad (7)$$

$$C + C_2H_4 \longrightarrow CH, CH_2 \longrightarrow \text{products N} \quad (8)$$

$$C + H_2 \longrightarrow CH, CH_2, CH_3 \longrightarrow \text{products N} \quad (9)$$

This scheme leads to the relation

$$\frac{\text{yield M}}{\text{yield N}} = \frac{k_8}{k_7} + \frac{k_9[H_2]}{k_7[C_2H_4]} \quad (A)$$

The corresponding data plot shown in Figure 6 gives an intercept, $k_8/k_7 = 0.1$, and a slope, $k_9/k_7 = 0.055$. Thus for the mixture of hot and thermal C atoms in our system

$$\frac{\text{reactivity of C with } H_2}{\text{reactivity of C with} C_2H_4} = k_9/(k_7 + k_8) = 0.05$$

This figure provides a quantitative verification of the statement made earlier that hot C atoms will react less efficiently with H_2 than with C_2H_4. Thus H_2 acts somewhat like a relatively inert moderator for C atoms.

5. Detailed Kinetic Considerations. Because of the simplicity of the primary C + H_2 reaction, this system provides a unique opportunity to estimate the average energy of a hot C atom reaction. In order to do this the data presented above must be fitted to a kinetic scheme and estimates of the relative reactivities of methyne and methylene toward H_2 and C_2H_4 must be made. A simplified scheme consistent with the known properties of the species involved is[39]

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(38) Some allene and propylene are also possible products of allyl radical reactions. These are probably much less important than pentene-1. James and Troughton[36] found 85% pentene-1, 10% propylene, and 4% allene to result from the allyl + ethyl radical reaction. If allyl is reacting with ethylene, hydrogen-abstraction reactions should be even less favored relative to addition to ethylene.

$$\mathrm{C} + \mathrm{H_2} \longrightarrow \mathrm{CH_2^*} \qquad (3a)$$

$$\mathrm{CH_2^*} + \mathrm{M} \longrightarrow \mathrm{CH_2'} + \mathrm{M^*} \qquad (3b)$$

$$\mathrm{CH_2^*} \longrightarrow \mathrm{CH} + \mathrm{H} \qquad (3c)$$

$$\mathrm{CH} + \mathrm{H_2} \longrightarrow \mathrm{CH_2'} + \mathrm{H}^{40} \qquad (5)$$

$$\mathrm{CH_2'} + \mathrm{H_2} \longrightarrow \mathrm{CH_3} + \mathrm{H}^{40} \qquad (10)$$

$$\mathrm{CH} + \mathrm{C_2H_4} \longrightarrow \mathrm{C_3H_5}\ \text{(trapped as pentene-1)}^{41} \qquad (11)$$

$$\mathrm{CH_3} + \mathrm{C_2H_4} \longrightarrow \mathrm{C_3H_7}\ \text{(trapped as } \mathrm{C_3H_8} \text{ and } n\text{-}\mathrm{C_5H_{12}}) \qquad (12)$$

$$\mathrm{CH_2'} + \mathrm{C_2H_4} \longrightarrow \text{cyclopropane} + \text{propylene} \qquad (13)$$

$$\mathrm{C} + \mathrm{C_2H_4} \longrightarrow \mathrm{C_3H_4^*} \longrightarrow \mathrm{CH_2} + \mathrm{C_2H_2} \qquad (14)$$

$$\mathrm{CH_2} + \mathrm{C_2H_4} \longrightarrow \text{cyclopropane} + \text{propylene} \qquad (15)$$

Reactions 14 and 15 require brief comment. (14) assumes that CH_2 is formed from C_2H_4 without a CH precursor. Some such reaction seems to be required since the ratio of (cyclopropane + propylene)/(pentene-1) is 6:1 in pure ethylene, substantially higher than in hydrogen-rich mixtures. If CH were indeed the precursor of CH_2 in ethylene, then in order to explain this 6:1 ratio it would be necessary to assume that CH has a higher efficiency for H abstraction from ethylene than for addition, and this seems unlikely. Methylene formed by reactions 3 and 5 appears to differ in reactivity from that produced in reaction 14. This is probably because the CH_2' formed from H_2 possesses a higher average translational and vibrational energy than the CH_2 formed from C_2H_4. The energy of the CH_2' is derived from the parent CH_2^*, which in addition to the usual vibrational excitation resulting from bond formation must have a translational energy almost as high as that of the original high-velocity C atom according to the momentum conservation principle.

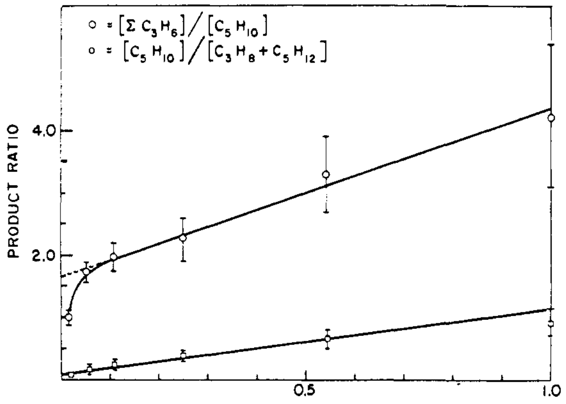

Figure 7. Plots of kinetic eq C and D.

From the reaction scheme given above we write

$$\frac{\Sigma[\mathrm{C_3H_6}]}{[\mathrm{C_5H_{10}}]} = \frac{k_{13}[\mathrm{CH_2'}]}{k_{11}[\mathrm{CH}]} + \frac{k_{15}[\mathrm{CH_2}]}{k_{11}[\mathrm{CH}]} \qquad (B)$$

Using the steady-state assumptions $[CH_2]/[CH]$ can be expressed in terms of $[C_2H_4]/[H_2]$ giving

$$\frac{\Sigma[\mathrm{C_3H_6}]}{[\mathrm{C_5H_{10}}]} = \left\{\frac{k_{13}[\mathrm{CH_2'}]}{k_{11}[\mathrm{CH}]} + \frac{k_{14}k_5}{k_{11}k_3k_{3a}}\right\} + \frac{k_{14}}{k_3k_{3a}}\frac{[\mathrm{C_2H_4}]}{[\mathrm{H_2}]} \qquad (C)$$

where $k_3 = k_{3c}/(k_{3c} + k_{3b}[M])$. Expressing CH_3 in terms of CH_2' we also find

$$\frac{[\mathrm{C_5H_{10}}]}{[\mathrm{C_3H_8} + \mathrm{C_5H_{12}}]} = \frac{k_{11}[\mathrm{CH}][\mathrm{C_2H_4}]}{k_{10}[\mathrm{CH_2'}][\mathrm{H_2}]} \qquad (D)$$

In regions where the ratio $[CH]/[CH_2']$ is constant, both (C) and (D) should be straight lines, with (C) showing a finite intercept and (D) passing through the origin. As Figure 7 shows, only at high H_2 values does (C) begin to show curvature. The plot corresponding to (D) shows a small finite intercept. Since (D) depends on $[CH]/[CH_2']$ while (C) depends on $[CH_2']/[CH]$, this intercept may result from a slight upward curvature at high H_2 concentrations.

Using the slopes and intercepts of (C) and (D) we arrive at

$$\frac{k_{13}}{3.2k_{10}} + \frac{k_5}{k_{11}} = 0.6 \qquad (E)$$

Pressure Variation. Proceeding in a manner similar to that outlined above, we arrive at an equation for the variation of the ratio $\Sigma[C_3H_6]/[C_5H_{10}]$ with pressure at compositions of the system at which methylene is largely derived from H_2.

$$\frac{\Sigma[\mathrm{C_3H_6}]}{[\mathrm{C_5H_{10}}]} = \frac{k_{13}k_5a}{k_{11}(k_{10}a + k_{13})} + \frac{k_{13}k_{3b}(k_5a + k_{11})[\mathrm{M}]}{k_{3c}k_{11}(k_{10}a + k_{13})} \qquad (F)$$

where $a = [H_2]/[C_2H_4]$. This equation is plotted in Figure 8 for $a = 4$. From a least-squares fit of the data

$$(\text{intercept}) = \frac{k_{13}k_5a}{k_{11}(k_{10}a + k_{13})} = 0.9 \qquad (G)$$

$$(\text{slope})/(\text{intercept}) = \frac{k_{3b}(k_5a + k_{11})}{k_{3c}k_5a} = 9 \times 10^{-19}\ \mathrm{cm^3\ molecule^{-1}} \qquad (H)$$

Estimation of Rate Constant Ratios. From (E) and (G) we find $k_{11}/k_5 = 14$ and $k_{13}/k_{10} = 2$. Then using (H), $k_{3b}/k_{3c} = 2 \times 10^{-19}$ cm^3 molecule^{-1}. The value of k_{13}/k_{10} is of the same order of magnitude as the 6 reported by Bell and Kistiakowsky[13] as the ratio of attack at the double bond of ethylene to attack on H_2 for methylene generated by photolysis. That the methylene observed in these experiments might be less discriminating is expected in view of its unusually high translational energy as discussed below. The ratio k_{11}/k_5 refers to the relative reactivity of CH toward C_2H_4 and H_2 and is about as expected for a typical insertion reagent.[17]

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(39) We use the symbol (3) to stand for sum reactions of (^{3}P) and (^{1}D) atoms in the rest of the discussion. Previously (4) was used for reactions of (^{1}D) atoms.

(40) This reaction is kinetically indistinguishable from the insertion–decomposition sequence of the type 6a–c if the rate of decomposition is greater than the rate of stabilization. This seems to be likely for such a small species, particularly in H_2-rich mixtures since H_2 would be expected to be an inefficient deactivating agent. The fact that we assume that most of the excited CH_4^* and CH_3^* from the insertion reactions of CH_2 and CH into H_2 decomposes may seem strange at first sight since so much of the excited CH_2 from the C + H_2 reaction is stabilized. However, as discussed later, CH_2 from this reaction must have a very high translational energy, and thus its time of flight before collision is unusually short.

(41) We do not distinguish between radical reactions with C_2H_4 and C_2H_5 since this distinction is not essential to our treatment. We also neglect products of carbon number greater than 5. This neglect is probably not critical for hydrogen-rich systems since, as pointed out earlier, the ratio of propane to n-pentane increases with the $[H_2]/[C_2H_4]$ ratio indicating that radical chains are of reduced importance.

Average Energy of the Reacting C Atom. Knowledge of the ratio k_{3b}/k_{3c} allows an estimate of the average energy of the reacting C atom.[42] Since CH_2^* cannot be too highly excited if it is to survive at the pressures of these experiments, we assume that a single collision will be sufficient to deexcite it.[43] Therefore k_{3b} can be approximated by $\pi\sigma_{12}^2 v$, where σ_{12} is the collision diameter and v the relative velocity of the colliding partners, essentially equal to the velocity of the hot atom. k_{3c} can be calculated from a simple Kassel model for unimolecular decay[44] as a function of the internal energy of the CH_2^*, and hence as a function of the velocity v taking proper account of momentum conservation. Thus we have essentially two equations for k_{3c} and two unknowns (k_{3b} and v). This calculation is subject to several uncertainties.

(1) In the $C + H_2 \rightarrow CH_2^*$ reaction, momentum conservation requires that 85% of the translational energy of the hot atom appear as translational energy of the newly formed CH_2^*. In subsequent collisions, part of this translational energy may be converted to internal energy. In other words, for a translationally hot species, collision may actually promote bond rupture rather than leading to deexcitation. Thus the relation between the excitation energy of CH_2^* and the energy of the reacting hot atom is ambiguous.

(2) Kassel theory requires that some assumption must be made about the number of degrees of freedom involved for CH_2^*. Since we do not know whether the CH_2^* observed is linear or bent, we do not know how many vibrational modes to assign. Moreover, we cannot exclude participation by rotational modes.

(3) Theories of unimolecular decay have not been tested for molecules as simple as CH_2^*. Their applicability here is therefore an unproven assumption.

(4) We will assume that most of the CH_2^* precursor of CH is formed by $C(^3P)$ atoms. This is reasonable, since formation of CH is endoergic by 20 kcal (eq 1), and our results show that CH and methylene formation are decreased by addition of moderator (Table II). In contrast, the formation of CH from a $C(^1D)$ atom is exothermic. (CH_2^* formed from a $C(^1D)$ atom would be so highly excited that it could survive only if linear.)

With the reservations listed above, we proceed. To compute σ_{12}, we use the gas viscosity cross section for H_2,[45] and the value of 1.8 A for C.[46] Using the value $k_{3b}/k_{3c} = 2 \times 10^{-19}$ cm^3 molecule^{-1}, we find the values summarized in Table VI for k_{3b}, k_{3c}, and the energy of the reacting C atom (E_C). Since the threshold for CH formation *via* a CH_2^* intermediate is $E_C = 5.7$ ev, the calculation indicates that this process can occur only in a relatively narrow energy range and should thus be relatively inefficient (particularly if the CH_2^* is bent and has only three vibrational degrees of freedom).

Table VI

Degrees of freedom	k_{3b}, cm^3 molecule^{-1} sec^{-1}	k_{3c}, sec^{-1}	E_C, ev
4	1.8×10^{-9}	8.6×10^9	9.0
3	1.5×10^{-9}	7.3×10^9	6.6

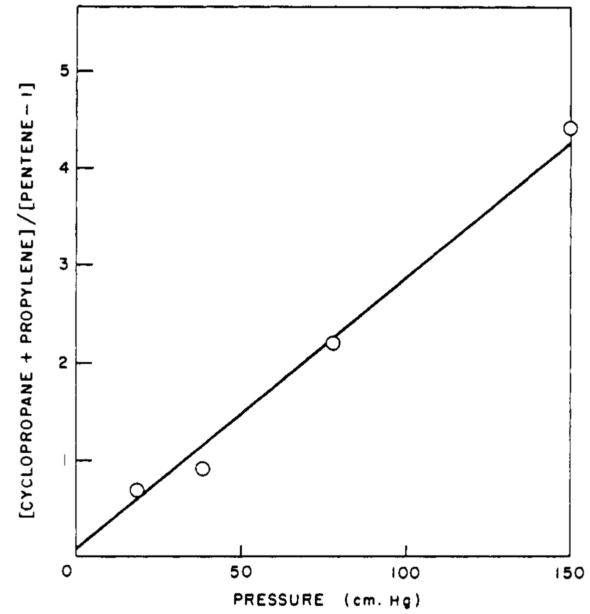

Figure 8. $\Sigma[C_3H_6$ products$]/[C_5H_{10}]$ as a function of pressure (eq F).

Because of the assumptions involved, the above calculations are very approximate, but they are probably correct as to order of magnitude. Now we have previously remarked that the reactivity of C with H_2 is very likely low because of a rapid back-reaction to re-form the reagents. Yet this back reaction of CH_2^* does not appear to be competitive with its decomposition to CH despite the fact that it has a lower energy requirement. If in fact it did compete, the total amounts of CH and methylene scavenged by ethylene should decline with pressure rather than be constant as observed (see Figure 4). (Expressed more formally, eq F seems to hold although the back-reaction was not included in the kinetic treatment used to derive it.)

The following model, consistent with all data, may account for this apparent paradox. At low carbon atom energies, the CH_2^* complex formed has such a short lifetime at all pressures used here that its chance of surviving long enough to undergo a collision, and hence be stabilized or react, is negligible. Possibly such a complex is bent, allowing the H atoms to recombine readily. At higher carbon atom energies, another distinct CH_2^* complex is formed—one which cannot revert easily to $C + H_2$ and thus has a lifetime long enough to allow further reaction. It would be plausible that this complex is formed by insertion into the H–H bond to form a linear H–C–H complex. In such a structure, it would be more difficult for the H atoms to meet to recombine, and unimolecular decomposition to CH + H might predominate.[47]

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(42) E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 897 (1963), have used the pressure dependence of the T + cyclobutane reaction to calculate the average energy of the reacting T.

(43) A change of an order of magnitude in the value of k_{3b} will halve the difference between the threshold and average energy of reaction for an intermediate with four degrees of freedom and cut this difference to one-third the value calculated below for an intermediate with three degrees of freedom.

(44) For example, see p 218 of ref 14.

(45) See p 155 of ref 14.

(46) This point is discussed by J. W. Nicholas, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, **88**, 1610 (1966).

(47) At still higher C atom energies, presumably all CH_2 complexes revert to $C + H_2$.

Summary

This study shows that C atoms react with H_2 to form CH, CH_2, and CH_3. The reactions of these intermediates with ethylene have been identified and the stable products resulting provide an indication of the yields of the primary processes. The latter are shown in Figure 5 as a function of the relative amounts of hydrogen and ethylene. A quantitative treatment of this system is quite complex but becomes possible by making certain simplifying assumptions. Good fits are obtained to the equations derived implying that the general kinetic framework has validity.

The more detailed conclusions of the work are summarized as follows. (1) Hot C atoms may react with H_2 to give CH_2 or CH but with an efficiency of only 0.05 that of hot C atom reaction with ethylene. The efficiency of this process for thermal carbon is even lower. The probable reason for the low yield is that in most cases the $CH_2{}^*$ complex immediately reverts to $C + H_2$.

(2) Some of the $CH_2{}^*$, particularly that formed by hot carbon, does not revert to $C + H_2$, possibly because it has a linear H–C–H structure making the back-reaction sterically unlikely. Instead, it must be collisionally deactivated to CH_2 or decompose to CH + H. The rates for these processes appear comparable at ordinary pressures. This may be surprising in view of the simplicity of CH_2, which would indicate a very short lifetime with respect to decomposition, particularly if it contains the excitation corresponding to a 9-ev C atom. It becomes quantitatively reasonable, however, when it is realized that most of the energy of the hot atom appears as translational energy of the $CH_2{}^*$ and that the resulting high velocity shortens the time elapsed before $CH_2{}^*$ undergoes a deactivating collision.

(3) Reaction of C to abstract H from H_2 and thus directly form CH appears to be less rapid than its insertion to give $CH_2{}^*$ which then decomposes to CH.

(4) The CH radical adds to ethylene to give allyl radical. In these systems, this then reacts further to give pentene-1. CH will also react with H_2 to form CH_2. This reaction may proceed *via* insertion to give $CH_3{}^*$ which then decomposes to CH + H, or it may involve direct abstraction.

(5) Both CH_2 and CH, as formed in this work, have a somewhat higher reactivity toward ethylene than toward H_2. This difference in reactivity is less for methylene, which may be largely due to its reacting with a higher translational energy.

Acknowledgment. We wish to thank the directors and staffs of the Yale HILAC and electron accelerator for aid in performing the irradiations. This work was supported by the U. S. Atomic Energy Commission.

One-Electron Oxidation of Aromatic Hydrocarbons

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Abstract: The electrochemical oxidation of aromatic hydrocarbons has been studied in nitrobenzene as a solvent. The hydrocarbons fall experimentally into two classes. The first class consists of compounds for which unequivocal electrochemical and electron paramagnetic resonance evidence shows a one-electron oxidation to the stable cation radical. The other class of compounds involves rapid follow-up chemical reaction after the initial electron transfer, and the total number of electrons involved varies with compound, solvent, etc.

The confirmed existence of the cation radicals of several aromatic hydrocarbons produced by chemical oxidation[1,2] would seem to imply that an initial one-electron (1-e) step should be observed when these compounds are oxidized electrochemically. The first electrochemical investigation[3] and several subsequent studies[4–6] of the oxidation of these compounds indicated an initial two-electron (2-e) step. Hoijtink tacitly assumed a 1-e mechanism in correlating oxidation potentials and molecular orbital parameters.[7]

Recently 1-e oxidations have been demonstrated for certain hydrocarbons of interest in electrochemiluminescence,[8] and well-resolved epr spectra have been obtained for a few electrochemically generated cation radicals.[2,9] Friend and Ohnesorge[10] on the basis of product isolation have advocated a 1-e process for anthracene. Most recently Peover and co-workers have shown by cyclic voltammetry that in acetonitrile these compounds first undergo a 1-e oxidation which in many cases is followed by rapid irreversible chemical reactions.[11–13] Bard and co-workers[14] have also drawn

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(1) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, 43, 2712 (1965), and references contained therein.

(2) P. A. Malachesky, L. S. Marcoux, and R. N. Adams, *J. Phys. Chem.*, 70, 2064 (1966).

(3) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

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