Chemistry and the Carbon Arc

Philip S. Skell,* James J. Havel, and Michael J. McGlinchey

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

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The composition and physical properties of carbon vapor have been widely investigated, but until the last decade its chemical properties had been largely neglected. This is true not only for carbon vapor but also for most other high-boiling elements (and compounds). Only recently have the techniques developed for studying the chemistry of carbon vapor been extended to other elements of the periodic table. This unexplored territory of 10 years ago has now been demonstrated to be a fruitful area of investigation.

High boiling point implies strong bonding between atoms. These strong bonds must be overcome for reactions to occur in which an atom is detached from its condensed-phase form. Only reagents which can engage the atom in a reaction sufficiently exothermic to overcome these forces can react. When the substance is vaporized these forces are overcome, and an atom unreactive in condensed phase becomes highly reactive. The higher the boiling point, the less will the chemical properties of the bulk material serve as a useful guide for the behavior of the free atoms.

Apparatus

The carbon arc is used as a source of carbon vapor which is produced as a result of the high temperature attained by the arc. Using the apparatus shown in Figure 1, carbon vapor is produced at low pressure (*ca.* 5×10^{-5} Torr) by intermittent arcing (16 V ac) between two graphite electrodes and cocondensed on the liquid nitrogen cooled walls with a large excess of substrate.[1] The high vacuums employed insulate the high-temperature zone from the low-temperature zone, and the carbon vapor travels one mean free path or less to the reactor walls, thus eliminating gas-phase reactions. The high dilution of carbon species in the condensed phase is such that the thermodynamically favored association of carbon atoms to elemental carbon is minimized. Although it is difficult to know at which temperature the reactions occur, it is noteworthy that deoxygenation of ketones produces CO during the codeposition at −196° rather than upon warm-up.

Composition of Carbon Vapor

The arc produces a multitude of species, and the chemistry of C_1, C_2, C_3, and C_4 has been investigated. The relative abundances of the carbon species have been determined mass spectrometrically, but it was desirable for us to have a chemical determination also. The relative concentrations are obtained by analysis of the products from the reaction with chlorine. Thus, atomic carbon makes CCl_4, diatomic carbon yields C_2Cl_4 and C_2Cl_6, and C_3 produces perchloropropene and perchloropropane. The ratios change noticeably when the vapor is produced by Langmuir type of vaporization (resistive heating of graphite) as shown in Table I.[2,3] Because of the geometry of our system, only 82% of the carbon emitted from the arc actually reaches the reaction zone. The remainder is deposited on mechanical obstructions in the reactor system. Thus yields are based on 82% of the weight lost from the carbon electrodes.

The carbon species produced in an arc are bombarded by free electrons such that there is a greater preponderance of excited species than would be expected for a Boltzmann distribution of species at arc temperatures (~2500°). The ^1S and ^1D excited states of atomic carbon are sufficiently long-lived to undergo collisionless flight to the walls (in *ca.* 10^{-5} sec) so that their chemistry, together with that of the ^3P ground-state species, can be investigated.[4-6] Higher excited states are lost during the flight; allowed optical transitions to one of the three states

Table I

	Relative molar concentrations[a]	
Species	Arced carbon[2]	Thermally vaporized carbon[3]
C_1	100	100
C_2	35–48	20
C_3	7–10	61
C_4	0.6–1.0	

[a] These concentration ranges are determined from experiments in which at least 75% of the vaporized carbon is accounted for as products.

Philip S. Skell was born in New York City in 1918, obtained the B.Sc. from the City College of New York, the M.A. from Columbia, and the Ph.D. degree at Duke (with C. R. Hauser), did postdoctoral work with H. E. Carter and M. S. Kharasch and was awarded an honorary L.L.D. degree by Lewis College. He joined the faculty at the Pennsylvania State University in 1952. His research interests mainly center around the reactions of reactive intermediates: radicals, carbonium ions, carbenes, silenes, and atomic species from high-boiling elements, with some early contributions to elimination reaction theory.

James J. Havel was born in Urbana, Ill., in 1947, received his B.A. degree from Lewis College, and his Ph.D. degree from The Pennsylvania State University, and has recently joined the faculty of Rice University.

Michael J. McGlinchey was born in Manchester, England, in 1944. He received his B.Sc. and Ph.D. degrees from the University of Manchester. After postdoctoral work with F. G. A. Stone at the University of Bristol and P. S. Skell at Penn State, he recently joined the faculty of McMaster University.

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(1) P. S. Skell, L. D. Wescott, Jr., J.-P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, 87, 2829 (1965).

(2) R. F. Harris, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1968.

(3) J. J. Havel, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1972.

(4) H. Yilmaz, *Phys. Rev.*, 100, 1148 (1955).

(5) L. Ornstein, H. Brinkman, and A. Buenes, *Z. Phys.*, 77, 72 (1932).

(6) R. C. Mason, *Physica*, 5, 777 (1938).

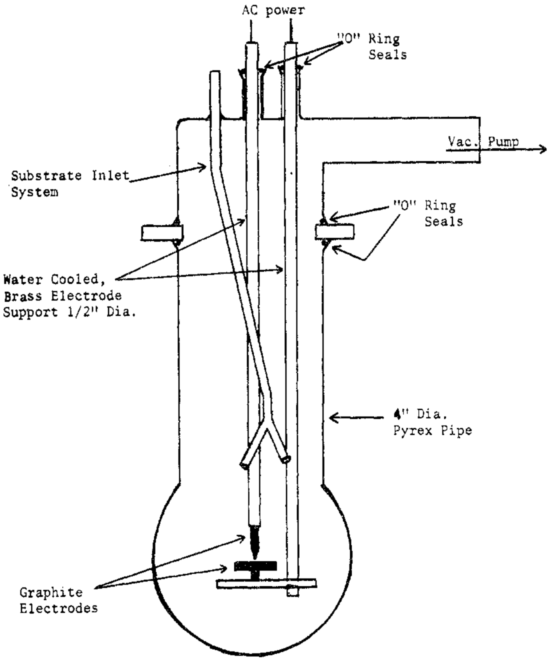


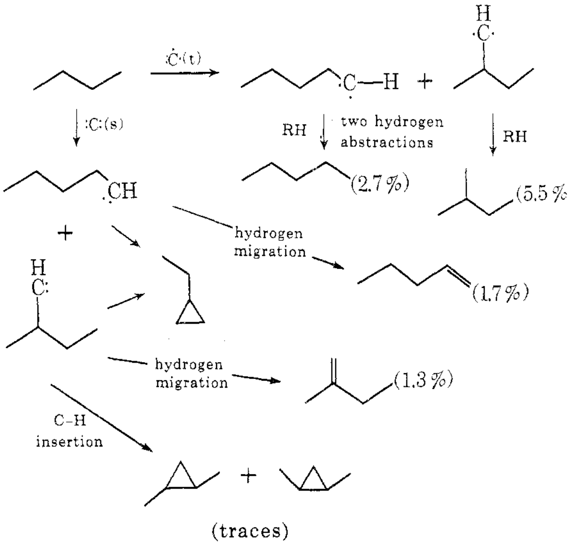
Figure 1. Reaction chamber (immersed in liquid nitrogen).

are available. It is interesting to note that no current theory makes a satisfactory prediction of the proportions of ground state and metastable states which result from allowed decays from upper states.

Reactions of Atomic Carbon

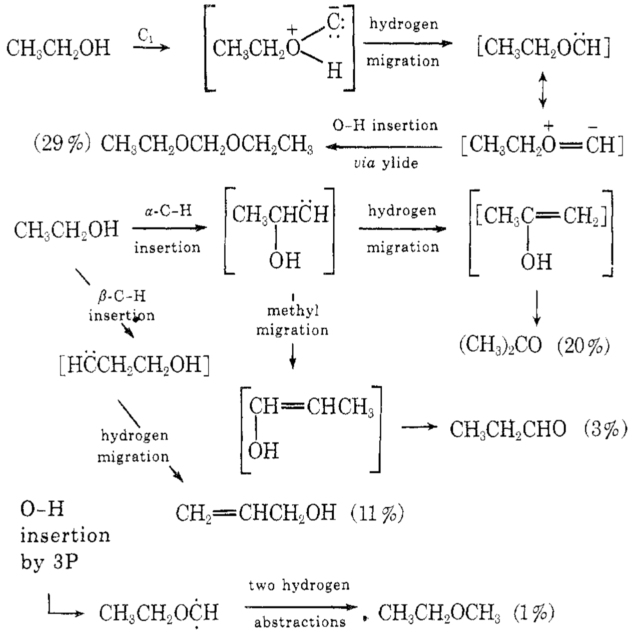
Saturated hydrocarbons react with atomic carbon in low yields, giving a variety of products containing an extra carbon atom. Both triplet (ground state) and singlet (excited state) atoms insert into carbon-hydrogen bonds to make respectively triplet and singlet carbenes. Triplet carbenes abstract two hydrogens to form a methyl group, whereas singlet carbenes react by migration of hydrogen atoms or alkyl groups to give olefins, and also by intramolecular insertions to produce cyclopropanes.[7] Similar behavior has been noted for alkyl carbenes generated in other ways such as diazoalkane thermolyses.[8] Scheme I illustrates the mode of product formation in the reaction of carbon atoms with *n*-butane.[9] (Yields are based on C_1 produced by the arc, about 40% by weight of the carbon vaporized.)

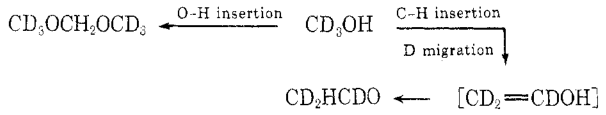
Scheme I



Alcohols react with atomic carbon by insertion into C–H and O–H bonds and by abstraction of oxygen to make CO.[10] All three possibilities occur when EtOH is the substrate; Scheme II outlines the probable pathways. (Yields are based on C_1 produced.) Further evidence for the proposed mechanisms is provided by the use of CD_3OH which yields products labeled as predicted for these pathways

Scheme II





CO (36%) and olefins are also observed, but the mechanism for their origin is still obscure.

With all alcohols studied, O–H insertion occurred five to eight times faster than C–H insertion per bond. The order of decreasing reactivity towards C–H insertion of C_1 is CH_3–O > –CH_2–O > –CH_2–~ –CH_3.

Formation of C–CH_3 groups from C–H groups is attributable solely to insertion by ground-state (^3P) carbon atoms followed by two hydrogen abstractions. Excited-state singlet carbon atoms insert to form singlet carbenes which can undergo rearrangements. Thus acetone yields methyl vinyl ketone (2.5%) and 2-butanone (3%), but when a radical trap such as butadiene is present the methyl vinyl ketone yield is unaltered but the 2-butanone decreases markedly. In contrast, when methanol, a singlet carbene trap, is present the CH_3-producing reaction to make 2-butanone is unaltered.[11]

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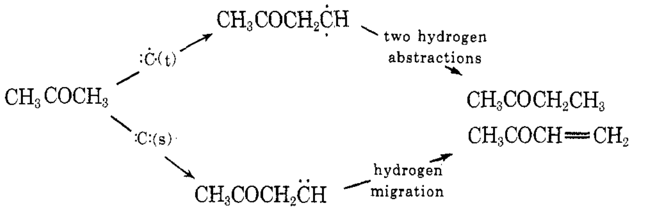
[7] P. S. Skell and R. R. Engel, *J. Amer. Chem. Soc.*, 88, 4883 (1966).

[8] W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

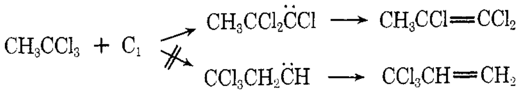
[9] J. H. Plonka, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1970.

[10] P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, 91, 4440 (1969).

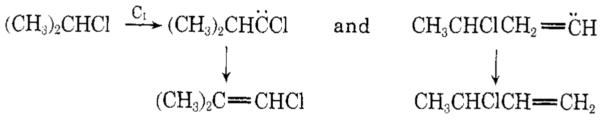
[11] P. S. Skell, J. H. Plonka, and L. S. Wood, *Chem. Commun*, 710 (1970).



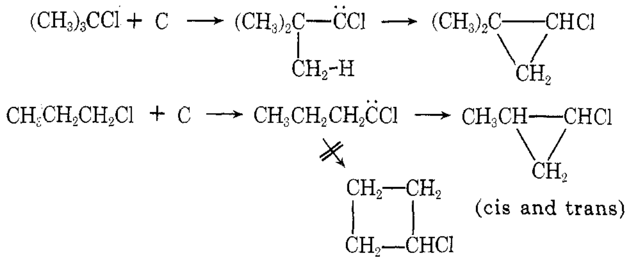
Alkyl halides react with atomic carbon to make olefins, cyclopropanes, and fragmentation products. CH_2Cl_2 and atomic carbon yields 1,1-dichloroethylene. This reaction could occur either *via* C–Cl insertion followed by Cl migration or *via* C–H insertion and then H migration.[12] This dichotomy is unresolvable except where each mechanism yields a unique product such as with 1,1,1-trichloroethane



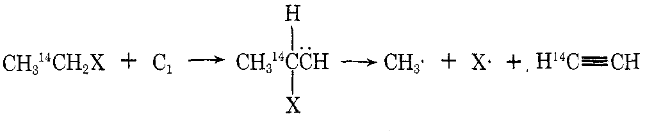
Experimentally, 1,1,2-trichloropropene is produced while 3,3,3-trichloropropene is not, indicating that C–Cl insertion is the predominant process. The less favored C–H insertion products are isolable from the 2-chloropropane reaction whereby not only the expected 1-chloro-2-methylpropene but also 3-chloro-1-butene is produced.[12]



Substrates possessing C–H bonds β to the halogen undergo cyclizations to cyclopropanes;[13] γ insertion to yield cyclobutanes is not observed.



The acetylene yields from ethyl halides are much too high to be attributed solely to hydrogen abstractions by C_2 from the arc (*vide infra*); another precursor is clearly indicated. An insertion–fragmentation mechanism whereby the C_2H_2 comprises monoatomic carbon from the arc and the α carbon of the substrate is supported by labeling studies.[12]

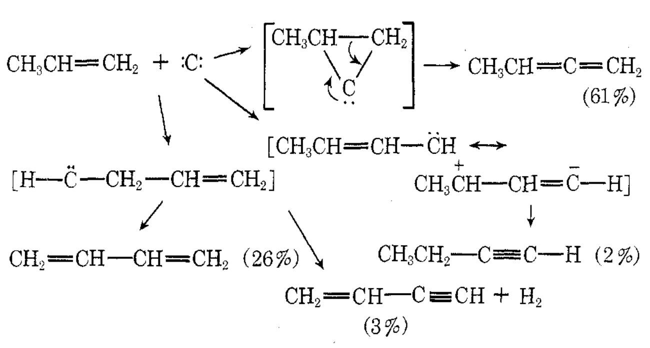


$$CH_3{}^{14}CH_2X + C_1 \longrightarrow CH_3{}^{14}\underset{X}{\overset{H}{C}}\ddot{C}H \longrightarrow CH_3\cdot + X\cdot + H^{14}C{\equiv}CH$$

Labeling of the β carbon produces essentially nonradioactive C_2H_2. This contrasts with the results using atomic carbon produced by nuclear recoil whereby 52% of the C_2H_2 was derived from the β carbon and 48% from the α carbon.[14] The fragmentation processes exhibit a dependency on the dissociation energies of the bonds being cleaved and become increasingly important as the bonds decrease in strength; thus, C_2H_2 yields increase in the series EtCl < EtBr < EtI.[12]

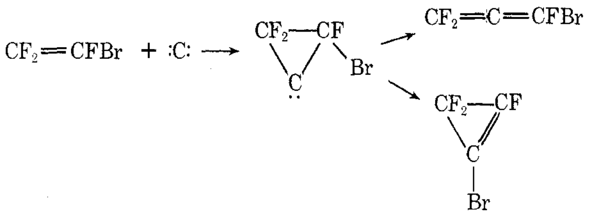
Olefins. Ethylene reacts with atomic carbon to form allene (25%) and propyne (8.8%);[15] but these are also products of hydrogen abstraction by C_3.[16] Enrichment of the arced carbon with radioactive ^{14}C showed that C_3 is the precursor of one-fifth of the allene and one-eleventh of the propyne and the remainder is derived from C_1. These figures are obtained by comparing the relative molar activities of the products with that of 1-pentyne whose relative molar activity is taken as 3.0 since it is derived solely from C_3 and so contains three carbon atoms from the arc.[15]

The major products from the propene reaction are explicable by (a) addition to the double bond forming a cyclopropylidene carbene which collapses to an allene or (b) C–H insertion followed by either rearrangement or dehydrogenation.



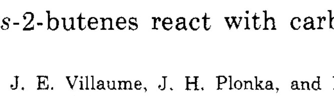
(probably a "hot" reaction)

As further evidence of the cyclopropylidene carbene intermediate, bromotrifluoroethylene yields not only the expected allene but also 1-bromo-2,3,3-trifluorocyclopropene[17]



The products containing one extra carbon atom are thought to be derived from excited-state carbon atoms (^1S or ^1D) since they are not formed when resistively heated graphite (a source of predominantly ground state atoms) is used.

Isobutylene reacts with carbon atoms, producing 1,1-dimethylallene and isoprene in 50 and 31% yields; an adduct consisting of one carbon atom and two olefin molecules is isolable in 3% yield.



cis- and *trans*-2-butenes react with carbon atoms

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[12] L. Eng, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1970.

[13] P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, 87, 5807 (1965).

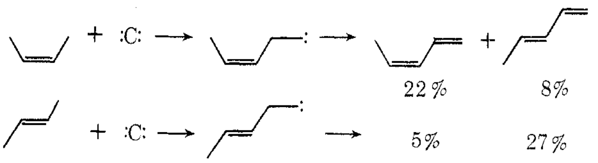
[14] H. J. Ache and A. P. Wolf, *J. Amer. Chem. Soc.*, 88, 888 (1966).

[15] P. S. Skell, J. E. Villaume, J. H. Plonka, and F. A. Fagone, *J. Amer. Chem. Soc.*, 93, 2699 (1971).

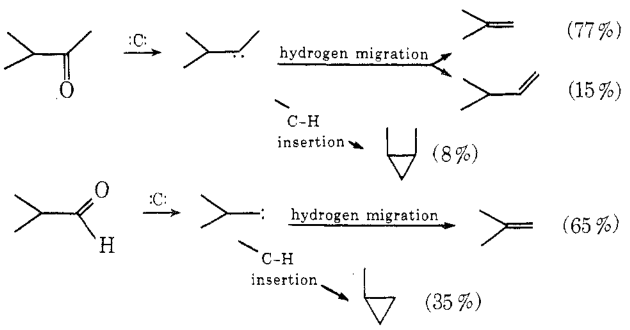
[16] P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, 91, 699 (1969).

[17] M. J. McGlinchey, T. Reynoldson, and F. G. A. Stone, *Chem. Commun.*, 1264 (1970).

to give 2,3-pentadiene (50–60%) and also a mixture of the 1,3-pentadienes. The latter are formed with predominant retention of stereochemistry about the double bond, but some cis–trans interconversion does occur. The intermediates leading to isomerization of the double bonds are thought to be vibrationally excited crotylcarbenes.[15]

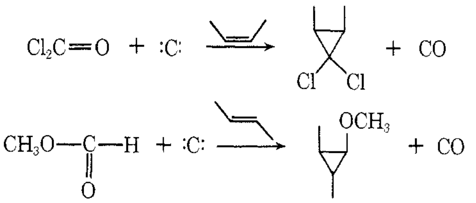


Oxygen- or sulfur-containing compounds react with atomic carbon by abstraction to form carbon monoxide[18] or carbon monosulfide;[19] the active species in this process is the metastable singlet carbon atom since thermally vaporized carbon, which contains ground-state C_1, C_2, and C_3, gives no deoxygenation. Deoxygenation of aldehydes or ketones of formula $C_nH_{2n}O$ produces carbenes which can isomerize to olefins or cycloalkanes, C_nH_{2n}, as typified.[18]

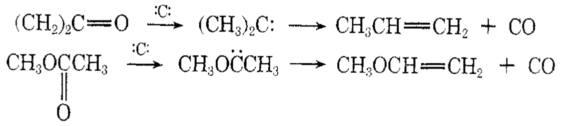


In these deoxygenation reactions in which the carbon monoxide and carbenes are produced at −196°, the product distributions are nearly identical with those from alkylcarbenes made at 160° by diazo thermolyses.[20]

The intermediacy of carbenes in deoxygenations is demonstrable by olefin trapping in some cases. Phosgene and methyl formate react with carbon atoms to yield dichlorocarbene and methoxycarbene, respectively, and these may be trapped *via* stereospecific additions to olefins at −196°.[21]

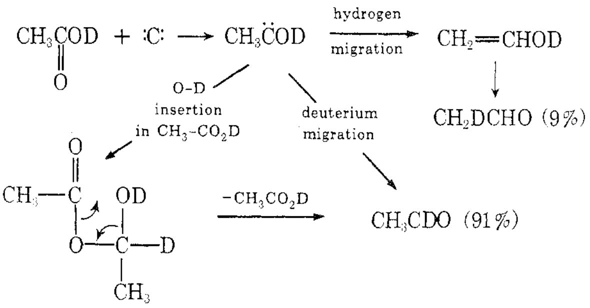


In contrast, dimethylcarbene (from acetone) and methylmethoxycarbene (from methyl acetate) rearrange intramolecularly too fast for intermolecular addition to occur.[22]

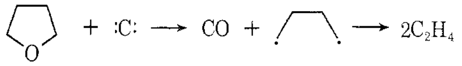


$$(CH_2)_2C{=}O \xrightarrow{:C:} (CH_3)_2C: \longrightarrow CH_3CH{=}CH_2 + CO$$
$$CH_3O\underset{\overset{\|}{O}}{C}CH_3 \xrightarrow{:C:} CH_3O\ddot{C}CH_3 \longrightarrow CH_3OCH{=}CH_2 + CO$$

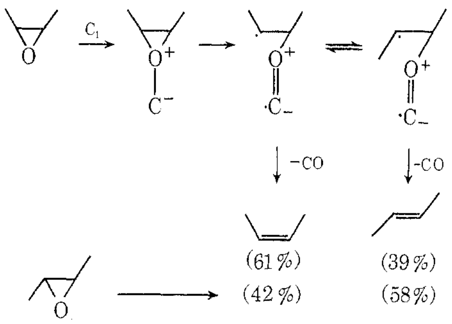
Deoxygenation of acetic acid produces hydroxycarbene; this unique carbene yields acetaldehyde. The mechanism of acetaldehyde formation has been elucidated using $CH_3\text{-}CO_2D$.[22]



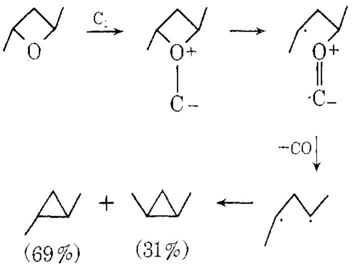
Atomic carbon also deoxygenates ethers. Diethyl ether gives CO, C_2H_4 (40%), C_2H_6 (35%), and traces of $n\text{-}C_4H_{10}$ presumably, *via* formation and disproportionation of two ethyl radicals from each ether molecule. Tetrahydrofuran gives ethylene (27%, based on 2 mol of C_2H_4 per mol of C_1 reacted).[18]



Epoxides are deoxygenated in a nonstereospecific fashion, possibly *via* the formation and ring opening of an ylide.[23]



A similar rationale can account for the nonstereospecificity of the deoxygenation of oxetanes to cyclopropanes whereby the intermediate diradical(s) is free to rotate before ring closure occurs.[24]



On the basis of bond energies, deoxygenation is a highly exothermic process (∼85–100 kcal/mol),

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[18] P. S. Skell, J. H. Plonka, and R. R. Engel, *J. Amer. Chem. Soc.*, **89**, 1748 (1967).

[19] P. S. Skell and K. J. Klabunde, *J. Amer. Chem. Soc.*, **93**, 3807 (1971).

[20] L. Friedman and H. Shecter, *J. Amer. Chem. Soc.*, **81**, 5512 (1959).

[21] P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, **92**, 2160 (1970).

[22] J. H. Plonka and P. S. Skell, *Tetrahedron Lett.*, 4557 (1970).

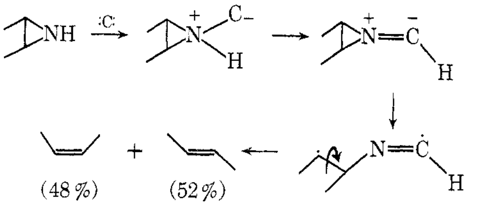
[23] P. S. Skell and J. H. Plonka, *Chem. Commun.*, 1108 (1970).

[24] P. S. Skell, J. H. Plonka, and K. J. Klabunde, *Chem. Commun.*, 1109 (1970).

whereas desulfurization is much less so (~45 kcal/mol).[25] One would thus anticipate less energetic intermediates in the latter process, and this is reflected in the increased stereospecificity of desulfurization of episulfides.[19] Thus *cis*-1,2-dimethylethylene episulfide gives both *cis*- and *trans*-2-butene with a cis:trans ratio of 4.5; the corresponding epoxide deoxygenates, yielding both 2-butenes but with a cis:trans ratio of 1.5.[23] Furthermore, desulfurization of tetrahydrothiophene produces not only ethylene (91%) but also cyclobutane (9%).[19] Deoxygenation of tetrahydrofuran presumably generates an energy-rich diradical which fragments rather than cyclizes. The intermediacy of carbon monosulfide in desulfurizations is demonstrable by trapping it with oxygen at −196° to form carbonyl sulfide.[19]

$$S{=}C{=}S + {:}C{:} \longrightarrow 2CS \xrightarrow{O_2} O{=}C{=}S$$

Singlet carbon atoms bring about decomposition of aziridines to olefins and HCN.[26] A scheme which accounts for the nonstereospecificity of the reaction is presented below.

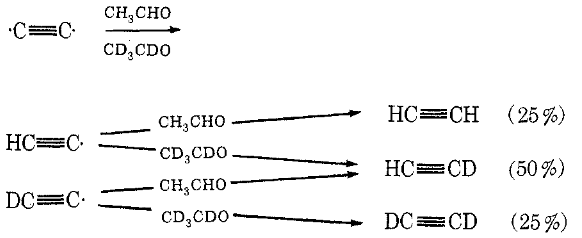


(1)

Reactions of Diatomic Carbon

Mechanism of Acetylene Formation. Acetylene is a product from the reaction of arced carbon with most hydrogen-containing compounds. As was shown earlier,[12] acetylene can arise by an insertion–fragmentation reaction of atomic carbon with alkyl halides. For that case, using an arc enriched with ^{14}C, it was shown that only one carbon in the acetylene was derived from the arc. However, cocondensation of ^{14}C-enriched carbon vapor with a variety of hydrocarbons, alcohols, aldehydes, or ketones reveals that the acetylene (and also ethylene) has a relative molar activity of ~2 compared to that of a product unambiguously derived from C_1.[27] Conversely, reaction of carbon vapor with ^{14}C-enriched substrates produces acetylene and ethylene of low relative molar activity.[2] In these cases, both carbon atoms of the acetylene are arc derived.

The ground state of gaseous C_2 is the singlet x $^1\Sigma_g^+$ with a metastable triplex x′ $^3\Pi_u$ state lying only 1.74 kcal higher than the singlet ground state.[28,29] The reaction of C_2 with an equimolar mixture of CH_3CHO and CD_3CDO gives C_2H_2 (46%), C_2HD (14%), and C_2D_2 (40%). If abstraction of hydrogen (or deuterium) occurred randomly in a two-step intermolecular process, one would expect C_2H_2, C_2HD, and C_2D_2 in a 1:2:1 ratio (eq 2).



(2)

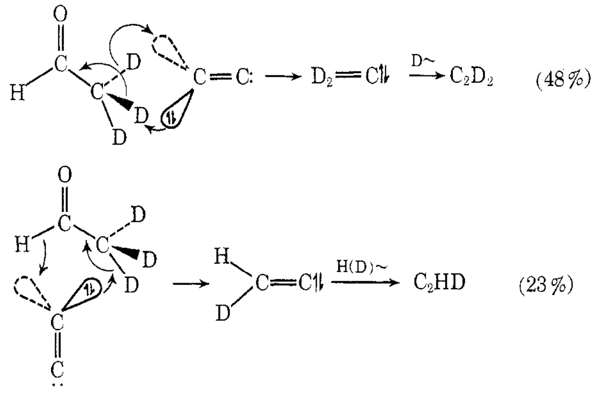
The C_2HD (14%) is attributed to such an intermolecular reaction; thus, 28% of the acetylene is produced by an intermolecular process. The remaining high yields of C_2H_2 and C_2D_2 clearly indicate that most of the acetylene (72%) is formed by an intramolecular diabstraction process.

Radicals are known to selectively abstract the acyl hydrogen from acetaldehyde.[30] Triplet C_2 would be expected to behave as a diradical, and thus the intermolecular reaction is attributed to this form of C_2. Determination of the intermolecularity of reactions of C_2 with a variety of labeled substrates shows that 25–30% of the C_2 derived from the 16-V ac arc is in the metastable triplet state.[9,31]

CD_3CHO yields acetylene of the following composition: C_2H_2 (28%), C_2HD (23%), and C_2D_2 (49%). C_2H_2 arises solely by successive abstraction of acyl hydrogens by triplet C_2 in a manner characteristic of a radical species (eq 3).

$$\begin{aligned}&\cdot C{\equiv}C\cdot\ (t) + CD_3CHO \longrightarrow CD_3\dot{C}{=}O + HC{\equiv}C\cdot\\&\cdot C{\equiv}CH + CD_3CHO \longrightarrow CD_3\dot{C}{=}O + HC{\equiv}CH\ (28\%)\end{aligned} \qquad (3)$$

The singlet C_2 is shown to react by two intramolecular pathways, C_2D_2 (49%) is made by a 1,1-diabstraction while C_2HD is generated by a 1,2-diabstraction process. Similar conclusions may be drawn from the results using using the inversely labeled acetaldehyde-*1-d*.[32]



The duality of mechanism for acetylene formation has also been demonstrated in the reaction of C_2 with CH_3COCD_3, which produces C_2H_2 (42%), C_2HD (18%), and C_2D_2 (40%).[32] The 1,1 diabstrac-

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[25] Required bond dissociation energies were taken from B. deB. Darwent, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 31 (1970).

[26] J. E. Villaume, Ph.D. Thesis, The Pennsylvania State University, University Park, Pa., 1971.

[27] P. S. Skell and R. F. Harris, *J. Amer. Chem. Soc.*, **88**, 5933 (1966).

[28] E. A. Ballik and D. A. Ramsay, *J. Chem. Phys.*, **29**, 1418 (1958).

[29] E. A. Ballik and D. A. Ramsay, *Astrophys. J.*, **137**, 61, 84 (1963).

[30] C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 279.

[31] P. S. Skell, J. H. Plonka, and R. F. Harris, *Chem. Commun.*, 689 (1970).

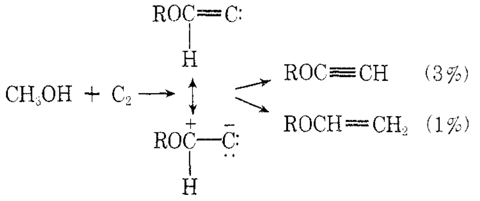
[32] P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, **92**, 5620 (1970).

tion of hydrogen from acetone by singlet C_2 produces acetylcarbene, which readily undergoes Wolff rearrangement to form methylketene. This ketene is trapped by methanol to make methyl propionate. Singlet acetylcarbene generated by photolysis of diazoacetone at −196° in a methanol matrix is known to yield only methyl propionate.[11]

$$CH_3COCH_3 + :C{=}C: \longrightarrow C_2H_2 + CH_3CO\ddot{C}H$$

$$CH_3CO\ddot{C}H \longrightarrow CH_3CH{=}C{=}O \xrightarrow{CH_3OH} CH_3CH_2CO_2CH_3$$

Addition and Insertion Reactions. Although formation of acetylene is the major reaction of C_2 with most substrates, a number of addition reactions are known to occur in low yields. Alcohols yield ethynyl and vinyl ethers as well as small quantities of ethyl ethers; all were shown to contain two carbon atoms from a ^{14}C-enriched arc.[2] The reaction probably proceeds *via* initial attack on the oxygen followed by either hydrogen migration or abstraction.



C_2 undergoes insertion reactions with hydrogen-containing substrates to produce allenes and acetylenes.[33] Typically, isobutane gives 4-methyl-1,2-pentadiene, dimethyl ether yields methoxyallene and 3-methoxypropyne,[33] and propane produces a mixture of allenes.

$$(CH_3)_3CH + C_2 \longrightarrow (CH_3)_2CHCH{=}C{=}CH_2 \quad (10\%)$$

$$CH_3OCH_3 + C_2 \longrightarrow CH_3OCH{=}C{=}CH_2 \quad (30\%)$$

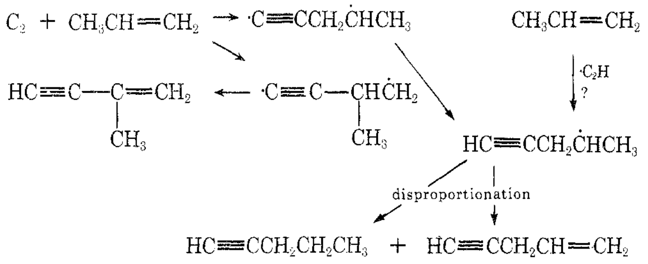
$$CH_3CH_2CH_3 + C_2 \longrightarrow CH_3CH_2CH{=}C{=}CH_2\ (5\%) + (CH_3)_2C{=}C{=}CH_2 \quad (1\%)$$

Reaction of C_2 with a mixture of C_3H_8 and C_3D_8 showed that the allenes are formed intramolecularly,[33] and the postulated mechanism involves a 1,1 diabstraction of hydrogen by C_2 to produce an alkylcarbene and vinylidene. The latter can rearrange to acetylene or rotate through 180° (rate $\sim 10^{11}$ sec^{-1}) and couple to produce the allenes. It is noteworthy that only by this fast-trapping method have carbenes with β hydrogens been trapped; in the presence of all other reagents they rearrange to olefins.

$$RCH_3 + C_2 \longrightarrow [R\ddot{C}H + H_2C{=}C:] \longrightarrow [R\ddot{C}H + :C{=}CH_2] \longrightarrow RCH{=}C{=}CH_2$$

Labeling experiments with ^{14}C show that C_2 adds to olefins, the course of the addition being largely dependent on the presence of allylic hydrogens in the substrate. Although the major C_2 product with propene is C_2H_2, low yields of other products derived from C_2 and one olefin molecule are found, and a possible mechanistic rationale is shown in Scheme III. Ethylene, in contrast, having no readily abstractable hydrogens, yields 1-butane, 1,2-butadiene, and 1-buten-3-yne in nearly equal amounts and a trace of methylenecyclopropane. Other products isolated are 1,5-hexadiyne, 1,2-hexadien-5-yne, and 1,2,4,5-hexatetraene, which all contain four atoms from the arc.

Scheme III



However, the yields are too high to be attributable to C_4, and it is postulated that they are derived from one molecule of ethylene and two C_2 moieties.[26]

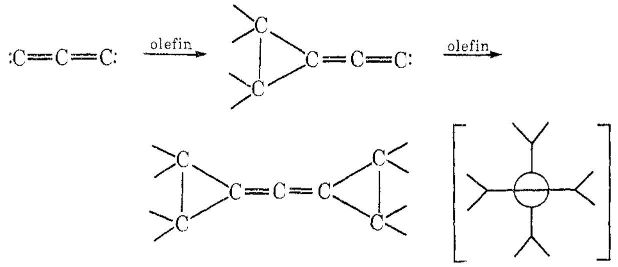
Reactions of Triatomic Carbon

Triatomic carbon was first recognized in the tail of a comet.[34] The ${}^1\Sigma_g{}^+$ ground state of C_3 has been calculated to be a linear, symmetrical singlet;[35] an excited singlet state, ${}^1\Sigma_u{}^-$, and several metastable triplet states, ${}^3\Delta_u$, ${}^3\Sigma_u{}^+$, ${}^3\Pi_u$, and ${}^3\Sigma_u{}^-$, have been postulated,[36] but none have been correlated with any of the known spectroscopic bands. The C_3 emitted from the 16-V ac arc is 10–14% by weight of the carbon vapor, a mixture of ground-state singlet, triplet, and probably some metastable singlet,[2] but thermally vaporized carbon contains more than 33% C_3, exclusively ground-state singlet.[3]

C_3 reacts with organic compounds in three ways: addition to carbon–carbon multiple bonds, insertion into O–H bonds, and hydrogen abstraction.

Bisethanoallenes from Olefins. Triatomic carbon adds to carbon–carbon multiple bonds as a dicarbene;[37] the product of the addition of one C_3 molecule to two olefin molecules is a bisethanoallene. Bisethanoallenes have two cyclopropane rings lying in orthogonal planes, so that, when viewed along the long axis of the molecule, the planes of the rings are represented by perpendicular lines and the substituents lie to either side of these lines (Scheme IV). For

Scheme IV



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(33) P. S. Skell, F. A. Fagone, and K. J. Klabunde, *J. Amer. Chem. Soc.*, **94**, 7862 (1972).

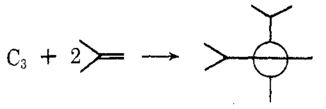
(34) A. E. Douglas, *Astrophys., J.*, **114**, 466 (1951).

(35) K. Clusius and A. E. Douglas, *Can. J. Phys.*, **32**, 319 (1954).

(36) K. S. Pitzer and E. Clementi, *J. Amer. Chem. Soc.*, **81**, 4477 (1959).

(37) P. S. Skell and L. D. Wescott, Jr., *J. Amer. Chem. Soc.*, **85**, 1023 (1963).

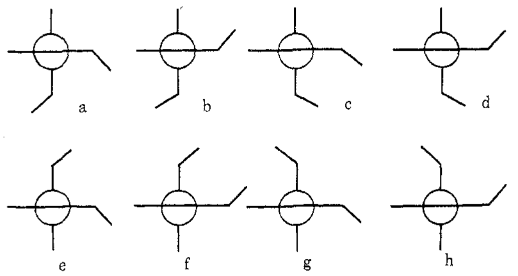
example, 1,1,1′,1′-tetramethylbisethanoallene, the product from the reaction of C_3 with two molecules of isobutylene, is shown in eq 4.



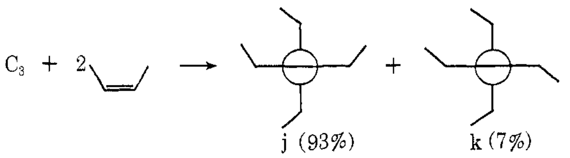
(4)

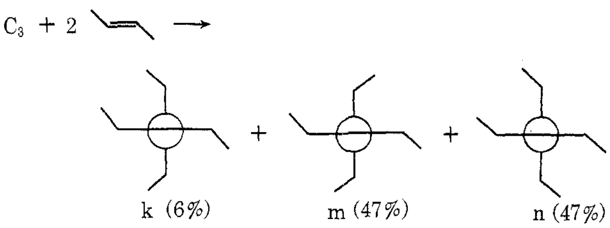
The reaction of C_3 with propene produces three diastereomers of 1,1′-dimethylbisethanoallene, which have the ratio 1:2:1.[1] The eight possible configurations of this product are shown in Scheme V. Configurations a ≡ d and e ≡ h are an enantiomeric pair, b and g are a second enantiomeric pair, and c and f are a third such pair. Random additions account for the ratios of the three diastereomers observed, 1:2:1.

Scheme V

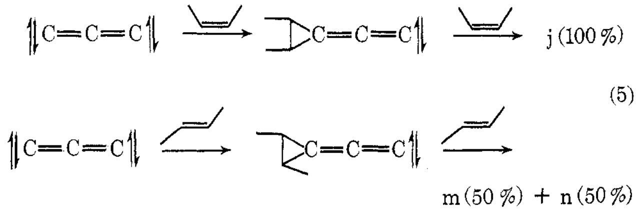


The reaction of C_3 from arced graphite (11 V ac) with *cis*-2-butene produces two bisethanoallenes, j and k, in the ratio 93:7.[1] *trans*-2-Butene makes three diastereomers, k, m, and n, in the ratio 6:47:47. When the triatomic carbon is obtained from thermally vaporized graphite, product k is not found in the reaction of either *cis*- or *trans*-2-butene. Compound k is the only diastereomer which has one pair of methyl groups cis and the other trans.

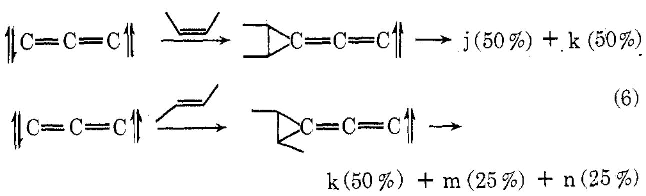




Ground-state singlet C_3, which is obtained from thermally vaporized graphite, adds stereospecifically to both *cis*- and *trans*-2-butene (eq 5). On the other hand, the mixed bisethanoallene can only arise from addition of the metastable triplet C_3, which adds nonstereospecifically in its second addition step (eq 6). The amount of triplet C_3 is twice the percentage of mixed bisethanoallene, k. The fraction of triplet C_3 from arced carbon increases from 14 to 60% as the arc voltage is increased from 11 to 14 V.

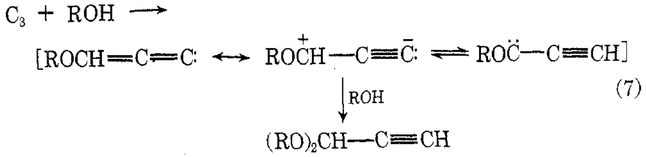


(5)



(6)

Alcohols react with C_3 to give as a major product the 3,3-dialkoxypropynes.[16] The C_3 insertion probably takes the course shown in eq 7. None of the 1,3-dialkoxyallenes are detected, but lack of an authentic sample precluded demonstration that these compounds would survive work-up conditions.



$$C_3 + ROH \longrightarrow [ROCH{=}C{=}C{:} \longleftrightarrow RO\overset{+}{C}H{-}C{\equiv}\bar{C}{:} \rightleftharpoons RO\ddot{C}{-}C{\equiv}CH] \xrightarrow{ROH} (RO)_2CH{-}C{\equiv}CH \quad (7)$$

Hydrogen Abstraction by C_3. Products formed from arc-generated C_3 by hydrogen abstraction are mostly propyne, allene, propene, and traces of propane.[16] These products are not found with thermally produced carbon vapor; this suggests a metastable excited-state C_3 as the precursor. Use of ^{14}C-labeled electrodes using alcohols as substrates shows that nearly all of the propyne and allene and much of the propene is derived from C_3. The hydrogen abstraction reactions may be further elucidated by the results of the reaction of C_3 with a 1:1 mixture of cyclohexane-d_0 and -d_{12}.[2] The major products are allene (43% d_0; 3% d_1; 1% d_2; 5% d_3; 48% d_4) and propyne (40% d_0; 12% d_1; 7% d_2; 20% d_3; 21% d_4). Similar deuterium distributions are found when 1:1 mixtures of other non- and perdeuterated substrates are used. For both allene and propyne, three hydrogen atoms (and to a large extent, a fourth) are abstracted from the same substrate molecule—an unexpected result. The possible precursor of allene is the metastable singlet, $^1\Sigma_u^-$, whereas a metastable triplet state could account for propyne formation.

Reactions of Tetraatomic Carbon

Tetraatomic carbon is predicted to have a triplet ground state with several excited singlet and triplet states.[38] The amount of C_4 produced by the 16-V arc is less than 2% by weight.[2] Tetraatomic carbon reacts with hydrogen-containing substrates to make ethylacetylene, methylallene, 1,3-butadiene, and vinylacetylene, with trace amounts of diacetylene.[39] These products were shown to originate from tetraatomic carbon by radioactive labeling experiments with carbon-14 vapor. Carbon vapor from thermally

(38) E. Clementi, *J. Amer. Chem. Soc.*, **83**, 4501 (1961).

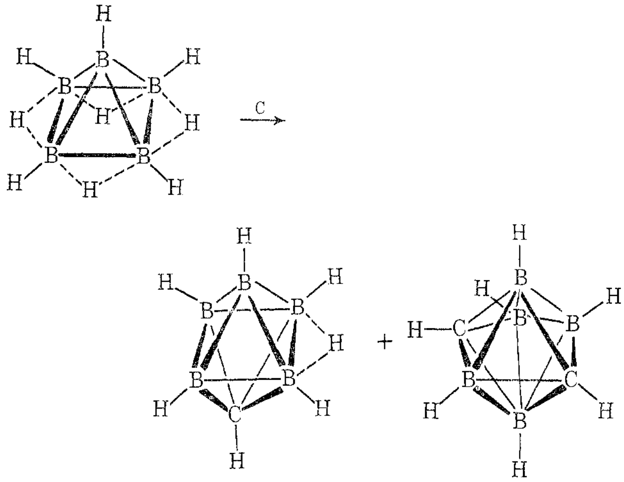
(39) R. F. Harris and P. S. Skell, *J. Amer. Chem. Soc.*, **90**, 4172 (1968).

vaporized graphite produces none of these C_4 hydrocarbons.

Use of Inorganic Substrates

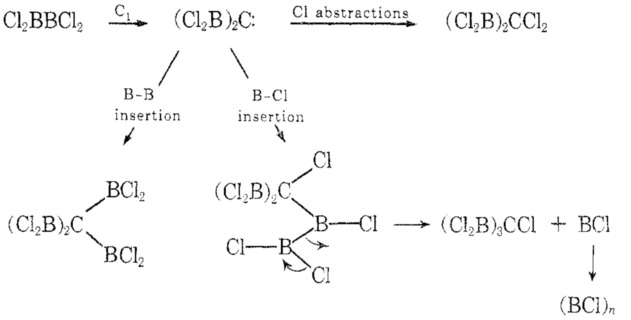
A number of laboratories, notably those of Schaeffer (Indiana) and Stone (Bristol), have extended the scope of carbon vaporizations to include reactions with inorganic substrates; in these cases, emphasis was placed more on synthetic utility than on elucidation of mechanisms.

Boron. Pentaborane-9 reacts with carbon vapor to yield carbahexaborane-7, B_5CH_7, together with traces of $B_5C_2H_7$.[40] The yield of B_5CH_7 (3% based on substrate consumed) is more than 20 times greater than the yield by the previous synthesis.[41]



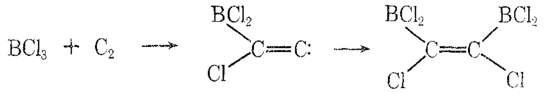
(lines drawn between central atoms C-B are not meant to indicate localized two-electron bonds, but are only to indicate the structure)

Reaction of carbon vapor with diboron tetrachloride produces mainly involatile polymers, but three moisture- and temperature-sensitive dichloroboryl derivatives of methane are isolable.[42] They probably arise *via* insertion of carbon into a B-B bond to give a bis(dichloroboryl) carbene intermediate which can either abstract chlorines or further insert into B-B or B-Cl bonds as indicated.

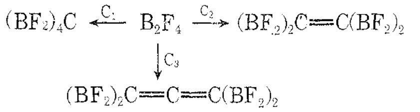


Boron trichloride reacts with C_1 to give dichlorobis(dichloroboryl)methane, $(BCl_2)_2CCl_2$, by successive insertions into B-Cl bonds. BCl_3 is known to decompose to B_2Cl_4, and this may account for the isolation of $(BCl_2)_3CCl$ and B_2Cl_4 from this reaction.

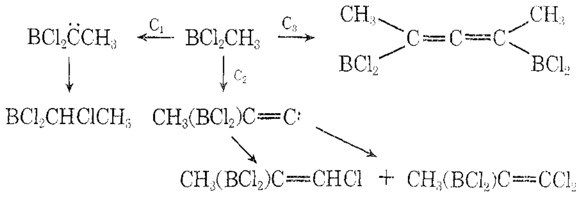
C_2 also reacts with BCl_3 to give 1,2-dichloro-1,2-dichloroborylethylene.



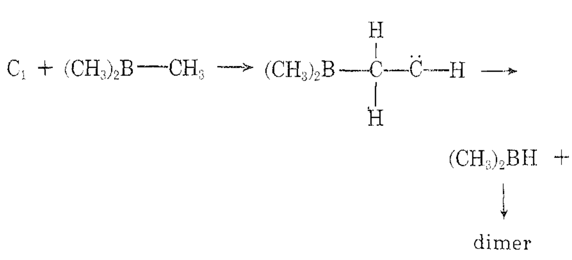
In contrast, diboron tetrafluoride shows products derived solely from insertion into the B-B bond.[42] This reflects the difference in bond dissociation energies in B_2Cl_4 (D_{B-B} = 59 kcal/mol) and in B_2F_4 (D_{B-B} = 36 kcal/mol).[25] Thus, products are isolable from reaction of C_1, C_2, and C_3 with two molecules of B_2F_4. Analogous compounds of C_2 and C_3 are presumably formed in the B_2Cl_4 reaction, but their involatility precludes their isolation.



The major products from the reaction with methylboron dichloride are C_2H_2, CH_3Cl, and $CH_2{=}CHCl$ which are formed by abstraction processes. However, 2,2-bis(dichloroboryl)propane, $(CH_3)_2C(BCl_2)_2$, is formed in good yield, indicating that the B-C bond is attacked in preference to the B-Cl bond.[42] A scheme showing the formation of some of the minor products is presented



Carbon vapor abstracts hydrogens from trimethylboron to give acetylene, ethylene, ethane, and diacetylene.[42] Tetramethyldiborane is also formed and is thought to arise by an insertion-fragmentation process similar to that previously demonstrated for alkyl halides.[12]



Silicon. Silane and carbon vapor give the usual hydrogen abstraction products, and also methylsilane, disilane, and benzene. Methylsilane arises by Si-H insertion followed by hydrogen abstraction; disilane and benzene may be formed in gas-phase reactions since the high volatility of SiH_4 causes high pressures during arcing.[43]

The major C_1 product from trimethylsilane is

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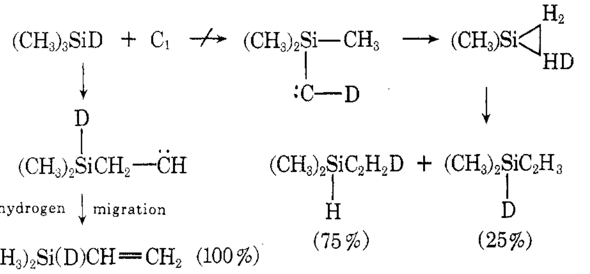
(40) S. R. Prince and R. Schaeffer, *Chem. Commun.*, 451 (1968).

(41) T. Onak, R. Drake, and G. Dunks, *J. Amer. Chem. Soc.*, 87, 2505 (1965).

(42) J. E. Dobson, P. M. Tucker, R. Schaeffer, and F. G. A. Stone, *J. Chem. Soc. A*, 1882 (1969).

(43) J. Binenboym and R. Schaeffer, *Inorg. Chem.*, 9, 1578 (1970).

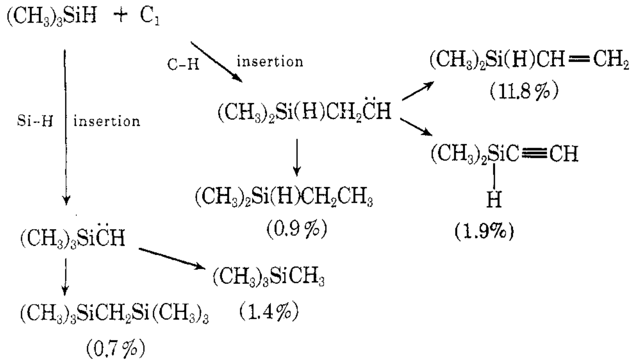
vinyldimethylsilane (11.8%); this could be formed *via* two mechanisms, silicon-hydrogen insertion followed by formation and rearrangement of a silacyclopropane or carbon-hydrogen insertion followed by hydrogen migration. Use of $(CH_3)_3SiD$ as substrate enables one to differentiate between these possibilities, since, in the former case, 25% of the deuterium label ends up on the silicon, and in the latter case, 100% of the deuterium label remains on the silicon.

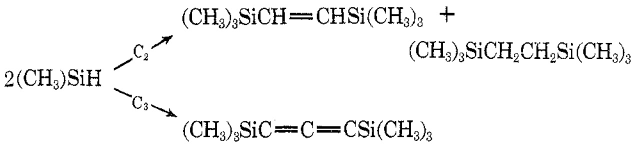


Experimentally, over 98% of the deuterium was still attached to silicon. Therefore, most of the vinyldimethylsilane is produced by C-H insertion.[44] Trimethylsilane and carbon yield minor products from both C-H and Si-H insertion as shown in Scheme VI.

C_2 reacts with a methyl group of trimethylsilane to produce dimethylsilylallene in a similar manner to that previously discussed[33] for alkanes. Ethynyl-, vinyl-, and ethyltrimethyl-silanes are also formed. Also, di-insertion products of C_2 and C_3 have been observed.

Scheme VI





Tetrachlorosilane reacts with C_2 to produce the novel compound chlorotrichlorosilylacetylene.[43]

$$Cl_4Si + C_2 \longrightarrow Cl_3SiC(Cl){=}C\colon \longrightarrow Cl_3SiC{\equiv}CCl$$

Miscellaneous. Germanium tetrachloride and phosphorus trichloride react in a similar manner with carbon vapor. Monoatomic carbon inserts into the metalloid-chlorine bond to form an intermediate carbene which can abstract chlorines or reinsert into another substrate molecule.[45]

$$GeCl_4 + C_1 \longrightarrow Cl_3Ge\ddot{C}Cl \longrightarrow Cl_3GeCCl_3\ (1\%) + (Cl_3Ge)_2CCl_2\ (10\%)$$

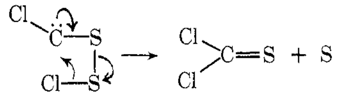
$$PCl_3 + C_1 \longrightarrow Cl_2P\ddot{C}Cl \longrightarrow Cl_2PCCl_3\ (5\%) + (Cl_2P)_2CCl_2\ (1\%)$$

Products from C_2 and $GeCl_4$ or parallel those previously described for BCl_3.[42]

$$GeCl_4 + C_2 \longrightarrow Cl_3GeC(Cl){=}C\colon \longrightarrow Cl_3GeC(Cl){=}CCl_2$$

Carbon atoms insert into an S-Cl bond of sulfur monochloride and can then either abstract chlorines or undergo intramolecular rearrangement with subsequent extrusion of sulfur to form thiophosgene.[45]

$$ClSSCl + C_1 \longrightarrow Cl\ddot{C}SSCl \longrightarrow Cl_3CSSCl\ (4\%)$$



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(44) P. S. Skell and P. W. Owen, *J. Amer. Chem. Soc.*, **94**, 1578 (1972).

(45) M. J. McGlinchey, J. D. Odom, T. Reynoldson, and F. G. A. Stone, *J. Chem. Soc. A*, 31 (1970).