14 May 1965, Volume 148, Number 3672 SCIENCE

Free Carbon Atom Chemistry

The elusive carbon atom, simplest of organic species, can now be studied with new techniques.

Colin MacKay and Richard Wolfgang

It is a fascinating paradox that, although the chemistry of carbon compounds has been most extensively explored, the chemistry of the free carbon atom itself has remained virtually unknown until very recently. Now however, an outline of the properties of atomic carbon is beginning to emerge.

The free carbon atom is the last in a series of simple species with increasing electron deficiency and increasing chemical reactivity; this series can be formally derived from methane, CH_4, by successive removal of hydrogen atoms. In methane, of course, the carbon atom has a full valence shell of eight electrons, and the molecule is therefore quite inert. Methyl radical, $\cdot CH_3$, has only seven electrons, and its two characteristic reactions with hydrocarbon molecules may be thought of as arising from the necessity for its carbon atom to complete an electron octet. These two reactions are (i) abstraction of a hydrogen atom, such as

$$\cdot CH_3 + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2\cdot \quad (1)$$

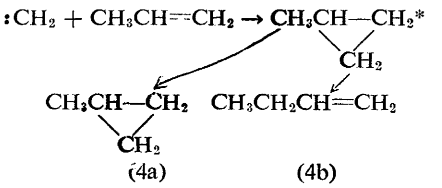
and (ii) addition to the double bond of an unsaturated compound, such as

$$\cdot CH_3 + CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2\cdot \quad (2)$$

The next species in the series, methylene, CH_2, lacks two hydrogen atoms and is therefore "two-electron deficient." It can exist in two electronic spin states: as the singlet, $:CH_2$, in which the two nonbonding electrons are paired; and as the triplet, $\cdot\dot{C}H_2$, in which they are unpaired. The properties of methylene have been intensively investigated. Methylene is considerably more reactive than the methyl radical, and in reactions with hydrocarbons its valence shell is completed in two unusual ways (*1*): (i) by insertion into the C—H bond, such as

$$:CH_2 + CH_3CH_3 \rightarrow CH_3CH_2CH_3 \quad (3)$$

and (ii) by attack at the double bond of olefins which may lead either to ring formation or to a new olefin as a result of isomerization of the initially formed excited cyclic, such as



(4a) (4b)

After methyne, CH, which is little known, the free carbon atom lacking four electrons should be at the apex of such a pyramid of increasing reactivity. Before discussing what has been learned about the free carbon atom, we will discuss the reasons for the long delay in the investigation of this fundamentally important species and point out the developments that have finally made some progress possible.

Because it is necessary to remove four valence electrons, production of a free carbon atom from a carbon compound requires extremely high energy; for this reason carbon atoms have never appeared as products of conventional chemical procedures. While it would be possible to produce free carbon atoms in an environment of very high temperature, such as that of a plasma arc, study of their chemistry under such conditions would be difficult.

However, free carbon atoms can be made by nuclear reactions such as

$$N^{14} + n \rightarrow C^{14} + p \quad (5)$$

$$C^{12} + \gamma \rightarrow C^{11} + n \quad (6)$$

where n is a neutron; p, a proton; and γ, a high-energy photon. Under properly controlled conditions, relatively few free carbon atoms are produced. If these are either of the radioactive isotopes C^{14} or C^{11}, their reactions may be traced by radiochemical methods. This has indeed been done, and atomic carbon is the first chemical species whose chemical properties have been investigated almost entirely by nuclear techniques (*1a*).

After the discovery of radiocarbon (*2*), many investigators exposed solid and liquid nitrogenous compounds to reactor neutrons. Such experiments were often aimed at the direct labeling of complex organic compounds with the long-lived C^{14} (5760 years) that was generated. No clear picture of the chemistry of the carbon atom itself emerged from this work, although a number of interesting suggestions concerning the mechanism of reaction were advanced (*3*).

In view of the seeming complexity of carbon-atom chemistry revealed by this early work, the reactions of C^{14} with a number of simple inorganic and organic gases were studied. Nitrogen was mixed with these gases, and C^{14} was generated by irradiation with neutrons. These experiments were largely unsuccessful. Owing to its long half-life C^{14} can be produced in sufficient quantities for detection only by long and intense irradiation. Under these conditions radiation so damaged and modified the products of the primary reaction of the carbon atoms that they could be identified only with great difficulty or not at all (*4*, *5*).

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Once this problem was recognized, the solution was clear. Another radioactive isotope of carbon, C^{11}, has a half-life of only 20.5 minutes. As a result the number of carbon atoms providing sufficient radioactivity for detection is a factor of 10^8 less for C^{11} than for C^{14}. Only 10^7 atoms of C^{11}, providing 10^5 to 10^6 disintegrations per minute, are required for many types of experiments; this quantity can be produced by a short, mild irradiation under conditions in which the products of C atom reaction can survive.

A half-life of 20.5 minutes puts some severe requirements on the method of analysis, since not more than about five half-lives—100 minutes—are available. In this short time a complex mixture of about 10^{-17} moles of C^{11}-labeled organic molecules must be separated into its components, which must be assayed and identified. This is made possible by the speed and versatility of radio-gas-chromatography. The mixture, carried by a stream of helium, is separated on a suitable column, and emerging products are directly assayed by passage through a very efficient proportional counter (*6*).

There is another remarkable aspect of this general technique. The carbon atoms are produced at very high initial kinetic energy ($\gtrsim 10^5$ ev) which is lost in successive collisions. The atoms may react while still having some of this energy ($\sim$10 ev), or after reaching ordinary "thermal" energies (10^{-2} to 10^{-1} ev). Such hot and thermal reactions can be distinguished by the use of inert gas moderators. If a system is diluted with neon, the carbon atom is less likely to collide with and react with a reagent molecule while it is still hot. Thus thermal reactions are favored, and it is possible to determine the effect of excess kinetic energy on reaction mechanisms.

Our survey only outlines the chemistry of free carbon atoms in some simple organic and inorganic systems. More detailed and technical reviews provide a complete guide to the literature (*7*, *8*).

Production of Carbon-11 Atoms

Several nuclear reactions can produce high-energy C^{11} atoms with minimum complications due to accompanying radiation. There are two distinct classes of methods (*7*, *8*). In the more common type the C^{11} atom is generated by a nuclear reaction occurring within the sample. The C$^{12}(\gamma, n)$C^{11} process is an example (Eq. 6). A glass vessel filled with a carbon-containing compound is exposed to an intense high-energy γ-ray beam such as that provided by the Yale University electron accelerator, which produces a beam whose peak energy, 40 to 50 million ev, is considerably above the threshold energy ($\sim$20 million ev) for converting C^{12} to C^{11} (Eq. 6). Operation at this high peak energy has a considerable advantage: side reactions induced by low-energy γ-radiation are minimized.

In the second method, C^{11} is generated outside the sample and introduced into the sample as a beam. In this method a pulsed beam of 120 million ev C^{12} ions provided by the Yale University heavy-ion accelerator is focused on a target (Fig. 1) consisting of gold and platinum foils which strip a neutron from some of the C^{12} ions converting them into C^{11}. The newly formed C^{11} retains most of the velocity of the incident C^{12}, but is scattered away from the axis of the main beam. A part of the scattered C^{11} can enter the sample vessel (Fig. 1) and react there. The main undeflected beam of C^{12} ions does not reach the sample vessel but is intercepted by a Faraday cup. Monitoring the resulting current due to C^{12} provides a measure of the amount of C^{11} delivered to the sample (*9*).

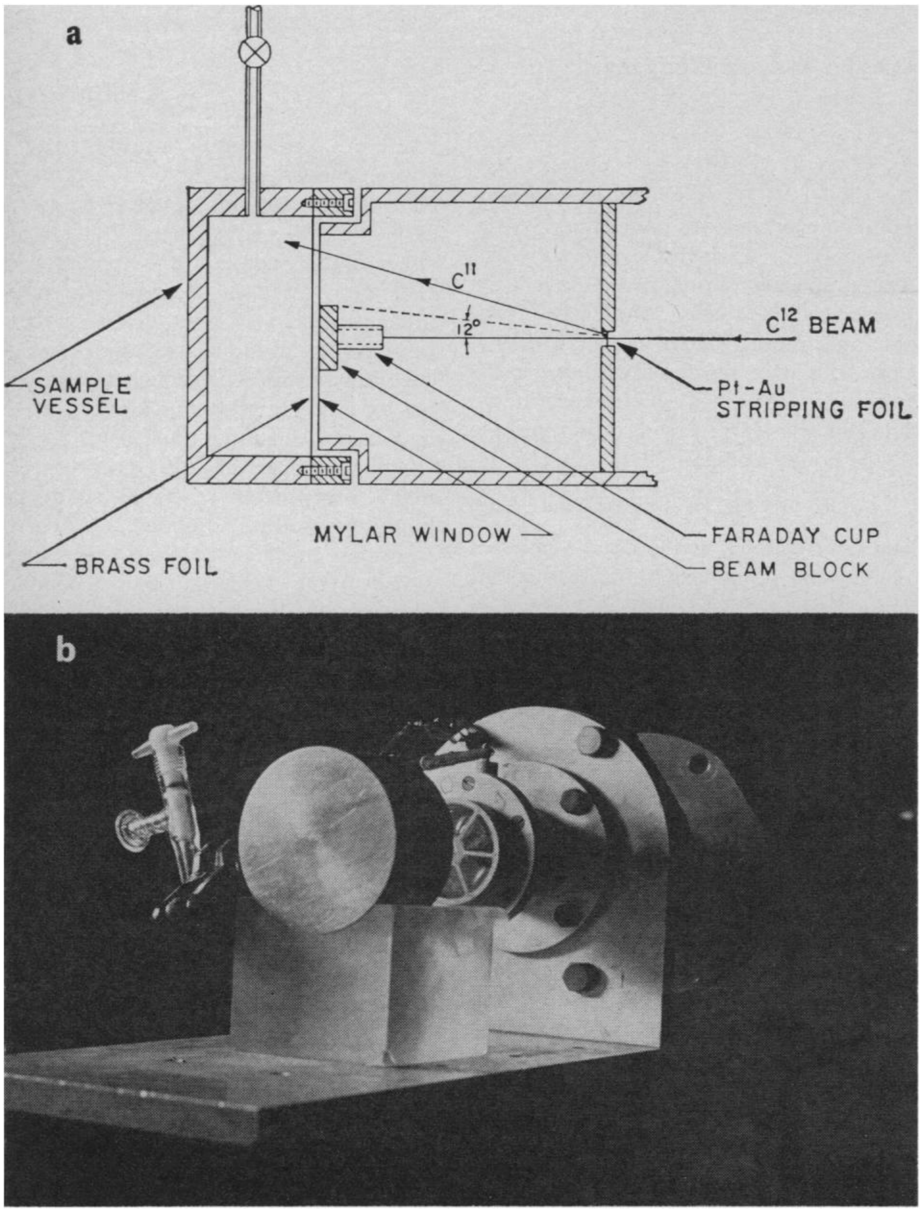


Fig. 1. (*a*) Diagram and (*b*) photograph of apparatus for producing free C^{11} atoms with Yale Heavy Ion Accelerator.

Analytical Techniques

Since only from 10^4 to 10^8 molecules of any given product are produced, none of the standard techniques of product identification, such as mass spectrometry, infrared spectroscopy, and nuclear magnetic resonance, are sensitive enough to be useful. Fortunately radio-gas-chroma-

Table 1. Acetylene yields from various hydrocarbons expressed as percentages of total volatile products.

Hydrocarbon	Yield	Ref.
Methane	30.0	*14*
Ethane	32.7	*14*
Ethylene	38.5	*24*
Ethylene oxide	40.0	*30*
Propane	29.5	*14*
Propylene	31.0	*14*
Cyclopropane	65.5	*14*
iso-Butane	32.6	*30*
n-Butane	24.1	*33*
2,2-Dimethylbutane	32.3	*27*
Cyclopentadiene	23.0	*22*
Cyclohexane	14.0	*27*
Benzene	5.6	*27*

tography provides a convenient means not only for separation but also for identification and assay even in this range; typical data are shown in Fig. 2.

So powerful is this method that it has recently become possible to separate quickly deuterium-labeled molecules, such as $H_2C{=}C^{11}HD$, from their fully protonated counterparts. This permits tracing not only the C^{11}, but using deuterium as a second tracer to reveal the origin of the hydrogen atoms in product molecules. Study of the interaction of C^{11} with partially deuterated systems (such as CH_3CD_3) can thus provide a severe test of many proposed reaction mechanisms (*10, 11*).

Ability to separate and swiftly recover a given product also permits the determination by chemical degradation of the position of a C^{11} atom in a product molecule. Such degradations must be accomplished in only 100 minutes, and so special procedures are required. As an example, the allene resulting from the reaction of C atoms with ethylene has been degraded by the procedure outlined in Fig. 3 (*12, 13*).

Advantages of the Nuclear Technique

At present the nuclear technique is the method of choice for the study of free-carbon atom chemistry under controlled conditions because of its several unique advantages. First of these is that it is self-tracing. We can determine not only what kinds of molecules the C^{11} forms but also the position in those molecules in which it becomes located. Second, the C atom is introduced as a very-high energy species, and the effect of excess kinetic energy on the modes of reaction of the C atom may therefore be studied.

Third, the technique is extremely sensitive. The very low concentration of C atoms makes certain that they will react with a chosen molecule rather than with each other; thus the intervention of polymeric species such as C_2^{11} and C_3^{11} is ruled out. Moreover, even reactive products resulting from C-atom attack on the chosen molecules cannot react with each other, and this further simplifies interpretation of experiments.

Fourth, the atom can usually be generated *in situ*. This eliminates complications which would arise if a separate source molecule were required; such generation also affords easy study of a range of experimental conditions, including solid and liquid phases.

There is much to be said for working with a material that has a 20.5-minute half-life. One important experimental result of this work has been to show that, if a graduate student really tries, he can accomplish almost anything in four to five half-lives of C^{11}, about 100 minutes.

Conversion of Carbon-11 Ions to Energetic Atoms

Nuclear reactions cannot produce C^{11} atoms directly. In the more common type of nuclear reaction, represented by the $C^{12}(\gamma, n)C^{11}$ process, a particle is emitted from a C^{12} nucleus. The recoil from this emission provides the C^{11} with a kinetic energy of the order of 1 million ev. Two important questions then arise. (i) At these energies the C^{11} is certainly a positive ion. What is the probability that it will reach the energy range (<100 ev) where it can react and combine as an atom rather than as an ion? (ii) When the C^{11} first enters this "chemical" energy range it has a kinetic energy about 1000 times that of a thermal reactant, that is, it is a "hot" atom. What influence does this kinetic energy have on the types of chemical reactions which the C atom can undergo?

The general subject of the equilibrium charge state of particles being slowed from 100,000 to a few thousand electron volts has been investigated extensively. Results of this work are summarized adequately in a simple mathematical relation, the "resonance rule." This rule has been applied to recoil C^{11} (*8, 13*) and predicts that below 100 ev the carbon will be neutral and in a "low-lying" electronic state. The ground-state species $C(^3P)$, with two unpaired electrons ("triplet"), should be most common, but $C(^1D)$ and $C(^1S)$, with no unpaired electrons ("singlet"), may also be present. Since, in chemical reactions involving light atoms only, spin is usually conserved (that is, triplets react to give triplet products and singlets give singlet products), the triplet and singlet atoms should have somewhat different properties. This must be kept in mind in postulating reaction mechanisms.

The influence of large amounts of kinetic energy on C atom reactions, the "hot atom" chemistry of carbon, will be taken up later. We shall partly anticipate this discussion by saying that, in general, C atoms at thermal energies react to form the same primary intermediates as do hot C atoms. Since hot and thermal reactions are so similar, the following remarks are based largely on "unmoderated" systems in which both "hot" and "thermal" reactions can occur.

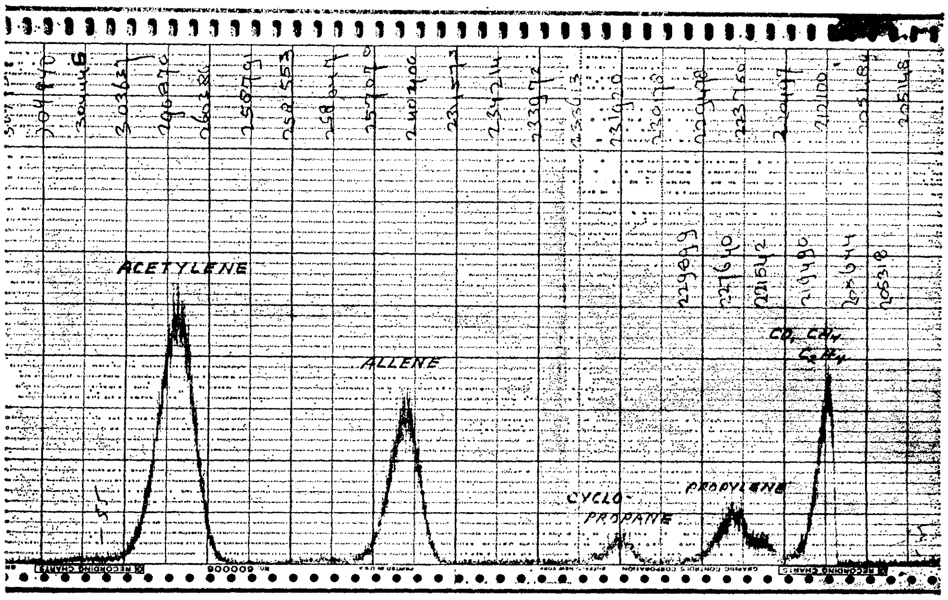


Fig. 2. Radio-gas chromatograph of products resulting from reaction of C^{11} atoms with ethylene.

Reactions of C Atoms with Hydrocarbons

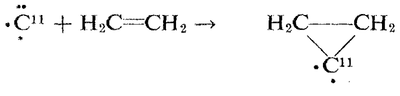
In stable carbon-containing molecules the C atom shares in eight electrons. Since the free carbon atom is a four-electron species it is, in a sense, extremely electron deficient; as a result it will tend to enter rapidly into forms of chemical combination in which it shares more than four electrons. With hydrocarbons three such types of reaction have been observed.

(i) Insertion into the C—H bond, as

$$\cdot\ddot{\underset{\cdot}{C}}{}^{11} + CH_3—CH_2—H \rightarrow$$

$$CH_3—CH_2—\dot{\underset{\cdot}{C}}{}^{11}—H \quad (7)$$

(ii) Attack at the π-bond of unsaturates, as



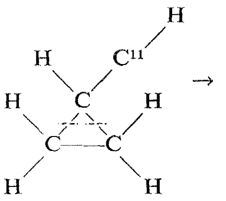
(8)

(iii) A reaction whose net result is abstraction of an H atom, as

$$\cdot\ddot{\underset{\cdot}{C}}{}^{11} + CH_3—CH_3 \rightarrow$$

$$CH_3—CH_2\cdot + \cdot\underset{\cdot}{C}{}^{11}H \quad (9)$$

The C—H bond insertion reaction. Identification of the major products formed in C atom reactions with saturated hydrocarbons (Eq. 7) provided the basis for the original proposal that the C atom could insert efficiently into the C—H bond (*5*, *14*). For example, with ethane such a reaction leads to an excited carbene, $CH_3—CH_2—\dot{C}^{11}H$ (Fig. 4). From the resonance rule one can predict that the major reacting species is a triplet atom [$C(^3P)$]. In accord with the spin-conservation principle then, triplet carbenes with two unpaired electrons should be formed. Decomposition of such an excited triplet carbene provides a means of reaching a more stable configuration while conserving spin. For a singlet carbene, formed by insertion of a singlet [$C(^1D)$] atom, decomposition should also be an important process because of the high excitation energy derived from the bonding of the carbon atom plus any kinetic energy it has brought to the reaction. The most commonly observed mode of decomposition is to acetylene (Fig. 4 and Table 1). Indeed, the original postulate of C-atom insertion into the C—H bond received its strongest support from the observation of a particularly high yield of acetylene from cyclopropane (*14*). The adduct formed by insertion into the C—H bond of cyclopropane has open to it a particularly favorable mode of decomposition, that to acetylene and ethylene.



$$HC\equiv C^{11}H + H_2C=CH_2 \quad (10)$$

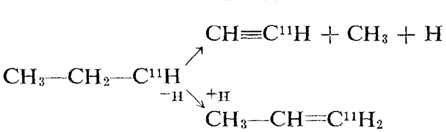
(The 10^8 molecules of ethylene formed in this process are unlabeled, and therefore cannot be detected.)

By means of the double-labeling technique described it has recently been possible to provide more direct evidence for the proposed mechanism of acetylene production. Studies of deuterium-labeled acetylene, formed both in a mixture of C_2D_6 and C_2H_6 and in CD_3CH_3, have shown that the acetylene is formed largely as C_2D_2 and C_2H_2 as required by the proposed insertion mechanism (*11*) (Fig. 4). Similar results are found with a mixture of C_2D_4 and C_2H_4 and with CD_2CH_2.

The carbene formed by the insertion of a C atom into the C—H bond of ethane, $CH_3—CH_2—C^{11}H$ (Fig. 4), has the same stoichiometric composition as propylene, and so it is not surprising that propylene is one of the products formed from ethane (Table 2). The relatively low yield of this product is due to the fact that the initially formed $CH_3—CH_2—C^{11}H$ is highly excited and therefore prone to decomposition. Evidence that even propylene formation entails decomposition rather than a direct unimolecular rearrangement comes from double-tracer experiments. In a mixture of C_2D_6 and C_2H_6, propylene is produced as $C^{11}C_2H_5D$ and $C^{11}C_2D_5H$, as well as in the forms $C^{11}C_2D_6$ and $C^{11}C_2H_6$; this indicates that the carbene, $CH_3—CH_2—C^{11}H$, rearranges to propylene by a mechanism whose net result is the elimination of a hydrogen atom at the No. 2 carbon and an addition of a different H atom at the No. 1 carbon (*10*).

That propylene is largely formed from ethane by insertion into the C—H rather than into the C—C bond has been verified by degradation. In the gas phase more than 95 percent of the propylene is labeled at the No. 1 carbon, giving $CH_3—CH=C^{11}H_2$, the species resulting from C—H insertion (*15*).

Further important evidence bearing on the validity of the C—H insertion mechanism comes from studies of reactions of the C atom with liquid ethane (*16*). Decomposition of the excited carbene, $CH_3—CH_2—C^{11}H$, to acetylene competes with stabilization as propylene.



$$CH_3—CH_2—C^{11}H \begin{array}{l} \nearrow CH\equiv C^{11}H + CH_3 + H \\ \xrightarrow[]{-H\ \searrow\ +H} CH_3—CH=C^{11}H_2 \end{array} \quad (11)$$

Therefore in liquid ethane, where molecular collisions can remove the energy required for decomposition of the $CH_3—CH_2—C^{11}H$ adduct to acetylene more quickly, a higher yield of propylene is found (Table 2) (*16*). Such removal of energy from a C atom adduct *after* its formation, for which the term "de-excitation" is used, must be distinguished carefully from the removal of energy from a C atom *before* reaction, for which the term "moderation" is used.

A further possible decomposition mode of the carbene formed by C-atom inser-

Table 2. Products of carbon atom reactions with hydrocarbons. The yields are given as percentages of total activities.

Product	System			
	C_2H_6*		C_2H_4†	
	Gas, 1 atm, 25°C	Liquid, −166°C	Gas, 1 atm, 25°C	Liquid, −130°C
Carbon monoxide	0.8 ± 0.1	0.5	} 1.2 ± 0.2	0.5 ± 0.1
Methane	2.1 ± 0.1	3.7 ± 0.1		
Ethane	1.1 ± 0.1	0.9 ± 0.1	<0.2	<0.1
Ethylene	23.7 ± 0.2	15.7 ± 0.1	1.1 ± 0.3	1.7 ± 0.5
Acetylene	31.2 ± 1.8	17.4 ± 0.5	38.5 ± 3.0	17.5 ± 2.0
Propane	12.6 ± 0.6	11.5 ± 0.3	<0.1	<0.7
Propylene	4.7 ± 0.6	13.3 ± 0.1	2.9 ± 0.5	4.0 ± 0.5
Cyclopropane			3.2 ± 0.5	2.2 ± 0.5
Allene		2.0 ± 0.1	16.5 ± 2.0	11.5 ± 1.5
Methylacetylene			4.5 ± 0.5	4.0 ± 1.0
Butene-1			<0.5	2.0 ± 0.8
1,3-Butadiene			<0.5	2.4 ± 0.8
1,2-Butadiene			<0.5	1.4 ± 0.3
Ethylacetylene			0.8 ± 0.4	1.6 ± 0.4
Vinylacetylene			10.0 ± 1.0	2.5 ± 0.4
Pentene-1			1.0 ± 0.3	10.0 ± 2.0
1,2-Pentadiene			3.3 ± 1.2	4.4 ± 0.5
1,4-Pentadiene			<0.5	3.3 ± 0.4
Pentyne-1			6.6 ± 1.0	6.5 ± 1.5
Vinylcyclopropane			<0.5	1.4 ± 0.2
Spiropentane			<0.5	<0.5

* Data from (*16*). † Data from (*17, 24*).

tion into ethane is to the vinyl radical, $CH_2C^{11}H$. If this then abstracts an H atom, labeled ethylene results. Table 2 shows that $CH_2C^{11}H_2$ is a major product in the reaction with ethane, and double labeling experiments show that this is a possible mechanism for its formation (*10*).

Similarly most of the experimental evidence on the reactions of C atoms with saturated hydrocarbons can be interpreted consistently only in terms of the C—H-bond insertion mechanism.

Insertion into the C=C π-bond: Other differences between unsaturated and saturated compounds. The reactions of C atoms with unsaturated hydrocarbons differ from those with saturated hydrocarbons in several important respects. First of all, unsaturated hydrocarbons seem to be somewhat more reactive. Second, yields of products corresponding to the composition of the original C atom plus the original molecule are markedly higher in unsaturates than in saturates. For example, in the gas phase the yield of propylene (C_3H_6) from ethane (C_2H_6) is 4.7 percent, whereas the summed yields of allene, CH_2CCH_2, and methyl acetylene, CH_3CCH, from ethylene is 21 percent (Table 2). As an explanation of these differences, C-atom attack at the double bond was postulated (*5*, *17*) (Fig. 5). Such an attack (Eq. 8) by a singlet C atom would lead to a singlet cyclopropylidene which can collapse rapidly to allene (*18*). (Allene will also be formed by C-insertion into C-H.) Similar bridged intermediates are postulated in the reactions of the electronically analogous species $:CH_2$ (*1*), $CH_3—CH_2—O—CO—N:$ (*19*), $:\ddot{N}H$ (*20*), and in oxygen atom chemistry (*21*).

Insertion at the double bond should lead to ring enlargement with cyclic compounds; this has been tested through the reaction with cyclopentadiene, C_5H_6. A 15-percent yield of benzene, C_6H_6, is observed (*22*). The contrast between this result and the failure to find C_5 cyclic hydrocarbons in the reaction with cyclobutane which has no double bonds is striking (*5*). Thus not only is the C=C-insertion mechanism supported, but also the conclusion that C—C insertion is relatively unimportant is reinforced.

The postulated mechanisms for allene production have been put to two critical tests. (i) They require that allene arise chiefly from reaction of a single carbon atom with a single ethylene molecule. Thus, allene produced from an equal mixture of C_2D_4 and C_2H_4 should be, for the most part, in the forms C_3D_4 and C_3H_4; and indeed these species do account for 90 percent of the allene yield (*10*). (ii) If the C=C insertion predominates there should be a corresponding yield of allene labeled at the No. 2 carbon. Labeling at the No. 1 carbon is expected as a result of C—H-bond insertion. The scheme for fast allene degradation (Fig. 3) showed that 64 percent of the allene formed from ethylene gas was labeled at carbon No. 2, $H_2CC^{11}CH_2$. The contrast with the almost exclusive end labeling found in propylene formed from ethane is striking, and it is consistent with the thesis that the double bond is a more reactive site for C-atom attack than is the C—H bond (*22a*).

Whereas allene is a characteristic product of C-atom reaction with ethylene, Table 2 shows that there are also large yields of various unsaturated C_5 compounds, most of which seem to arise from the same initial $C^{11}—C_2H_4$ adducts that also yield acetylene (Fig. 6). If these adducts do not have the internal excitation energy or the necessary time to decompose to acetylene, they undergo other reactions involving addition of another ethylene molecule to give a C_5 product.

Fragmentation to acetylene is a high-energy process, and should be favored in "hot" reactions. Moderation by neon should therefore reduce the acetylene

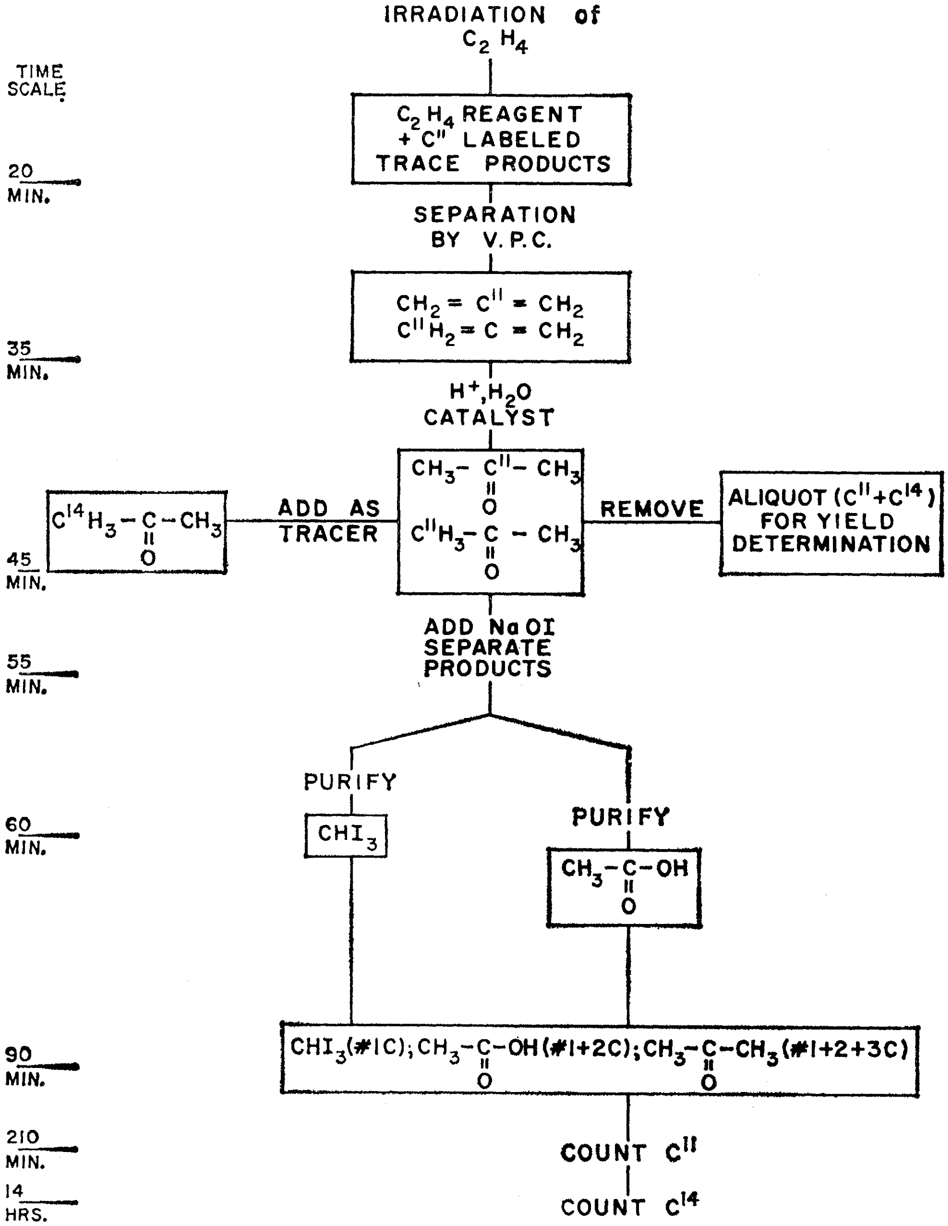


Fig. 3. Degradation of C^{11}-allene ($CH_2=C=CH_2$) to determine intramolecular distribution of C^{11} atoms. After conversion of C^{11}-allene to C^{11}-acetone a measured quantity of C^{14} labeled acetone is added so that chemical yields in subsequent steps may be easily determined. A measured portion of this C^{14}–C^{11} mixture is removed and counted before proceeding. The number 1 carbon of allene shows up in iodoform; the number 1 and 2 carbons in acetic acid, and the unconverted acetone contains the number 1, 2, and 3 carbon atoms.

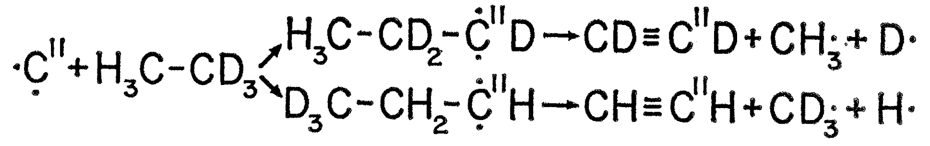


Fig. 4. Mechanism of acetylene formation in reaction of free C^{11} atoms with typical hydrocarbon (CH_3CD_3).

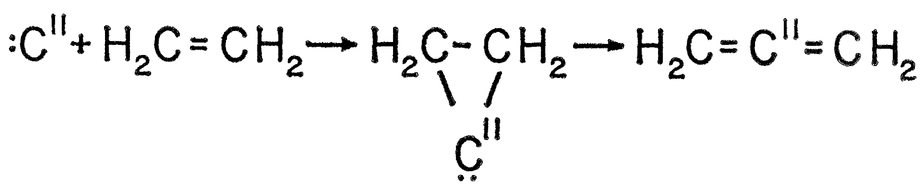


Fig. 5. Mechanism of allene formation by attack of C^{11} on the π-bond of ethylene.

yield as has been observed (Fig. 7). With hot atoms in condensed phase where energy is more efficiently removed from the primary C_3H_4 adduct, acetylene yields should be lower than in the gas phase. Thus both moderation and reaction in the condensed phase independently reduce the acetylene yield. It might then be expected that with moderated atoms in condensed phase the acetylene yield should be further reduced in importance, the amount of such reduction depending on the efficiency with which energy is removed from the $C{-}C_2H_4$ adduct. This expectation has recently been confirmed in experiments with solid xenon-ethylene mixtures (*23*).

These results are also consistent with the prediction that both singlet and triplet carbon atoms can take part in such reactions. We may properly ask why, if the initial $C^{11}{-}C_2H_4$ adduct does not have the energy to decompose to acetylene, it does not rearrange to a stable singlet molecule such as allene. One answer is that the required transition of a triplet C_3H_4 to a singlet C_3H_4 is of a type usually considered to be "forbidden." However, such adducts may undergo other reactions such as a typical free-radical addition to ethylene, which can eventually lead to various C_5 products. The fact that the allene yield shows a pattern of behavior different from that for the C_5 compounds both on moderation (Fig. 7) and on phase change (Table 2) indicates that it may arise from a different precursor. As we have seen, it is formed by a simple, rapid reaction with a single ethylene molecule. Such a reaction to give singlet allene is "permitted" only if the carbon atom is in the singlet state. Figures 6 and 8 summarize the current hypotheses concerning the reaction of singlet and triplet carbon atoms with ethylene.

All but two of the products formed from ethylene can be accounted for simply by the two basic mechanisms already discussed (*13*, *24*). The exceptions are propylene and cyclopropane. We now turn to examination of the source of these and related products found in reactions with saturated hydrocarbons.

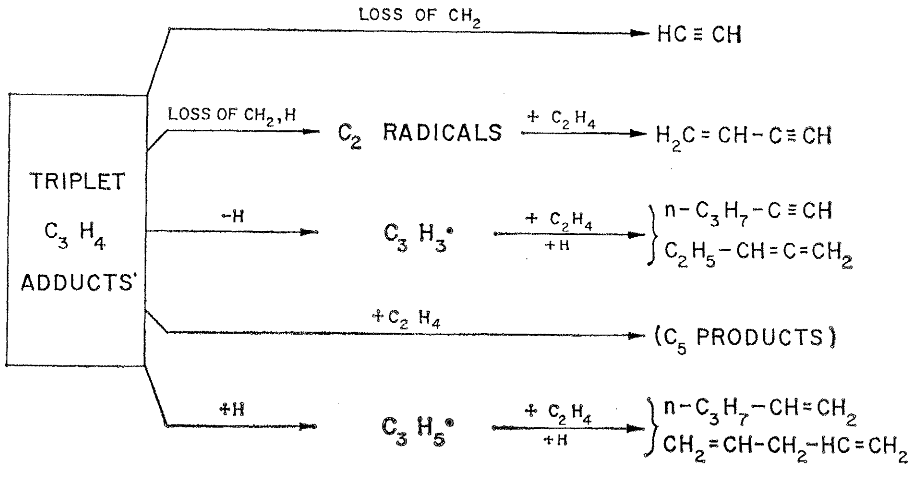


Fig. 6. Further reaction of triplet adducts formed by insertion of $C(^3P)$ into C–H or C=C bonds of ethylene. Fragmentation reactions (top two pathways) are favored with hot atoms and in the gas phase. Addition reactions (bottom two pathways) are favored with thermalized atoms and in the condensed phase. Parentheses indicate minor pathways for associated products.

Hydrogen-atom abstraction by the C atom. One of the earliest suggestions concerning mechanisms involved in C atom chemistry was based on the assumption that the C atom successively abstracted hydrogen (Eq. 9), with the resultant formation of the CH, CH_2, and CH_3 radicals, and the CH_4 molecule (*3*). Yields of CH_4 from hydrocarbons are usually quite low (*7*, *8*); CH_3 has been identified by its reaction with molecular iodine to form CH_3I, and this product accounts for only a small percentage of the reacting species (*25*). Of the other two species, there is considerable evidence regarding the role of CH_2, but little is known of CH.

Evidence that CH_2 plays an important role in these systems comes from early studies with C^{14}. Not only were the products characteristic of CH_2 insertion into the C—H bonds of liquid alkanes such as C_6H_{14} from C_5H_{12} identified, but also they were found to be in the characteristic statistical ratio (*3*). Later work with C^{11} in liquid propane supported this finding (*16*).

Work in the gas phase also supports CH_2 as a product of carbon atom reaction in hydrocarbons (*5*, *16*). With ethylene, for instance, cyclopropane and propylene are produced. As mentioned, these products cannot be formed by direct insertion of a C atom; indeed the ratio of their yields is the same as that found in studies of the reactions of CH_2 with ethylene (*17*, *24*). Similarly the propane formed from reaction with ethane (Table 2) probably arises from insertion of a CH_2 intermediate into an ethane molecule.

Although some studies of the reactions of CH have been made (*26*), its properties are still largely unknown and its yield is therefore difficult to assess. In principle it could react to form many of the observed products, but the evidence indicates that most of these are formed by direct C atom insertion reactions (*5*, *7*, *17*, *24*, *27*). However, CH (methyne) has been suggested specifically as an alternate source of the ethylene found as a product in alkane systems (*28*).

$$:\dot{C}^{11}H + R{-}CH_3 \rightarrow R{-}CH_2{-}\dot{C}^{11}H_2 \rightarrow R\cdot + CH_2{=}C^{11}H_2 \quad (12)$$

Thus carbon atoms can abstract hydrogen atoms, but the actual mechanism by which they do so is not known. An H atom could be transferred directly during a collision of the carbon atom with a hydrocarbon molecule. Alternatively, the initial mechanism could be insertion of the C atom into a C—H or C=C bond, followed by decomposition of the adduct to give CH or CH_2.

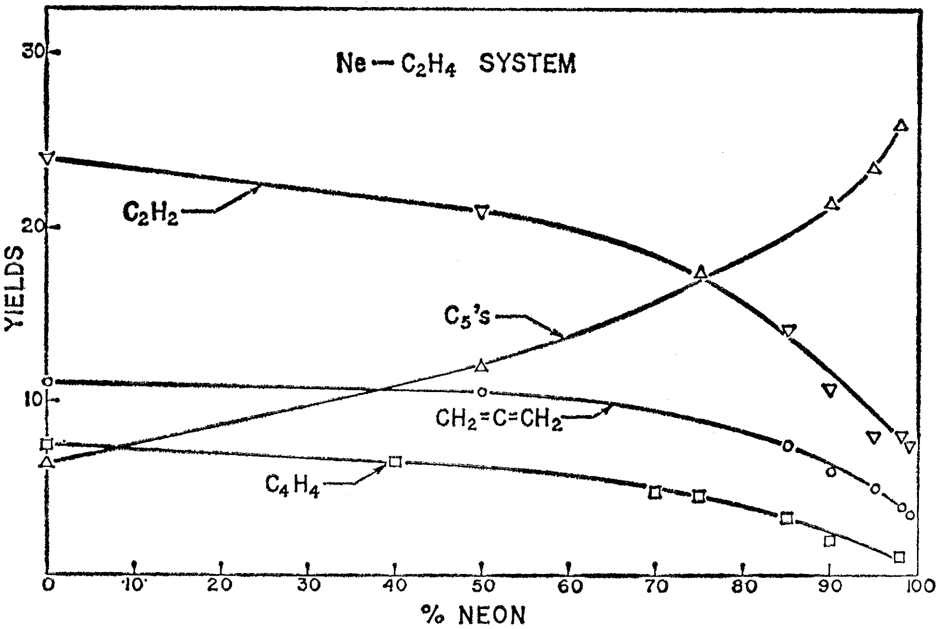


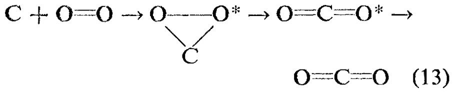
Fig. 7. Effect of neon acting as moderator on products formed by reaction of C^{11} with ethylene (yields based on total amount of C^{11} available).

Inorganic Oxides and Nitrogen

The "end-on" attack mechanism. As we have seen, reaction with the π-bonds of organic compounds appears to proceed by a "sideways" attack of the carbon atom as the first step, followed by its insertion into the double bond. With simple π-bonded inorganic molecules the possibility of a new mode of attack must be considered. In contrast with unsaturated organic molecules the inorganic molecules have electron pairs which are not already used in binding and which are often localized on terminal atoms. A simple representation of this situation is provided by the Lewis structure for CO_2, $:\ddot{O}{=}C{=}\ddot{O}:$. Such molecules can provide electrons in two places, at the π-bond or at the terminal atom. One mode of attack is similar to the aforementioned "sideways" attack on the π-bond of ethylene (Eq. 8), and the other can be described as "end-on" attack.

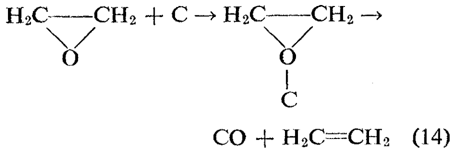
As a first approximation, if only donation of a terminal electron pair to the C atom by the O atom of an oxide is considered, "end-on" attack seems the less likely because it entails an unfavorable transfer of electron density from an element of higher electronegativity, oxygen, to one of lower electronegativity, carbon. This viewpoint is oversimplified, as more detailed examination of the particular atomic and molecular orbitals involved reveals. As an example, consider the reaction of a $C(^3P)$ atom with the O_2 molecule to form a C—O—O adduct. Figure 9 shows conventional diagrams of the p atomic orbitals of carbon, and of the antibonding molecular orbitals of oxygen. The unoccupied $2p_x$ orbital of carbon is in a very favorable position to interact with the $\sigma(2s)^*$ orbital of oxygen, which holds a pair of electrons. In such an interaction there is a partial transfer of electrons in the unfavorable direction from oxygen to carbon. However, this can be compensated for by a transfer of electron density in the reverse direction, from carbon to oxygen, through interaction of the singly occupied $2p_y$ and $2p_z$ orbitals of the carbon atom with the singly occupied π_y^* and π_z^* orbitals of oxygen. Such a "synergic effect" has been invoked to explain the stability of the carbonyl compounds of the transition metals (*29*). In the example considered, it leads to formation of a chemical bond analogous to the C—O bond in carbon monoxide, one of the strongest of chemical bonds. In view of these considerations, it would not be surprising if "end-on" attack were the primary mode of reaction of the C atoms with simple inorganic molecules.

The very simplicity of the inorganic molecules studied makes it difficult to determine experimentally the relative importance of "sideways" and "end-on" attack. However, two results indicate dominance of the "end-on" attack. (i) The mechanism of "end-on" attack requires that CO be the only product of the reaction of C with O_2 under all experimental conditions. In contrast, by analogy to the ethylene reaction, "sideways" attack at the π-bond could lead to CO_2 if the high excitation energy of the C—O_2 adduct were removed quickly, as indeed it might be in the liquid phase.



$$\mathrm{C + O{=}O \rightarrow \underset{\diagdown\ C\ \diagup}{O{-}{-}O^*} \rightarrow O{=}C{=}O^* \rightarrow O{=}C{=}O} \quad (13)$$

Thus the finding that CO is essentially the sole product of the reaction of C atoms with liquid O_2 is significant. (ii) "End-on" attack on the O atom in ethylene oxide should lead to a high yield of CO.



$$\mathrm{\underset{\diagdown\ O\ \diagup}{H_2C{-}{-}CH_2} + C \rightarrow \underset{\underset{|}{\overset{\diagdown\ O\ \diagup}{}}\atop C}{H_2C{-}{-}CH_2} \rightarrow CO + H_2C{=}CH_2} \quad (14)$$

In fact CO does account for 55 percent of the volatile yield (*30*). There is also a

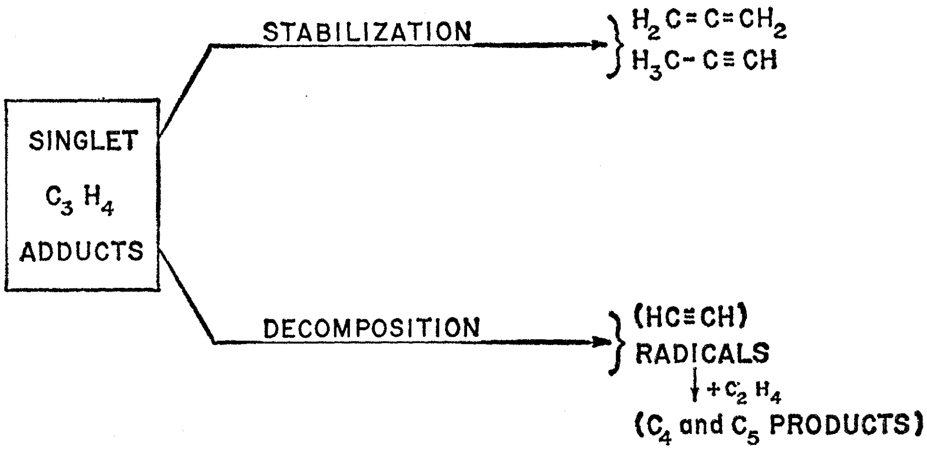


Fig. 8. Further reaction of singlet adducts formed by insertion of $C(^1D)$ into C–H or C=C bonds of ethylene.

40-percent yield of acetylene from the C—H bond insertion (Table 1).

The results of other experiments also are consistent with "end-on" attack (*9*). Thus all inorganic oxides studied have terminal O atoms, and CO is always a major product. Furthermore, with N_2, NO, and N_2O, all of which have terminal N atoms, the CN radical is formed in good yield as follows:

$$C^{11} + N_2 \rightarrow C^{11}N + N \quad (15)$$

The efficient production of such secondary species illustrates another possibility inherent in the nuclear technique of atom production. It makes possible an investigation of their properties—often poorly understood—under conditions where both primary and secondary radical-radical reactions are minimized.

Significance of these results for the natural radiocarbon cycle. The not unexpected finding that C^{11} atoms react with O_2 to form $C^{11}O$ and with N_2 to form $C^{11}N$ draws attention to a previously unconsidered but significant question. Natural C^{14} formed by nuclear reaction in the upper atmosphere should react with O_2 and N_2 to form the same two products. These products must then be converted into $C^{14}O_2$, the form in which C^{14} is thought to enter the biosphere and the radiocarbon dating cycle. We shall now consider the pathways by which this happens and the time scale for these reactions.

The oxidation of $C^{14}N$ to $C^{14}O$ or $C^{14}O_2$ seems to be rapid (*31*). This is consistent with the finding that at atmospheric pressure interaction of C^{11} with air yields 88 percent of $C^{11}O$ and 12 percent of $C^{11}O_2$ (*31*). Therefore $C^{14}O$ would seem to be the first persistent chemical form in which a major fraction of the C^{14} resulting from nuclear reaction in the upper atmosphere is combined. Since there is no known pathway for the rapid chemical conversion of $C^{14}O$ to $C^{14}O_2$ or to some other form in which it might enter the biosphere, the mean residence time of $C^{14}O$ in the atmosphere may be long. Measurements of the specific activity of natural carbon monoxide (the ratio $C^{14}O : C^{12}O$) might reveal this. Although such measurements have been made they are not definitive (*32*). Therefore this part of the natural radiocarbon cycle is still quite unclear.

Effect of Kinetic Energy on Carbon Atom Reactions

Carbon atoms formed by nuclear transformation are "hot," that is they have kinetic energy far in excess of that of atoms at thermal equilibrium with their environment. Indeed, at present the principal technique for studying the reactions of "hot" atoms involves producing them by a nuclear reaction. As initially formed, these atoms are usually too energetic to enter into chemical combination. After a large number of collisions, energies comparable to those of chemical bonds (2 to 10 ev) will be reached. Combination may then occur. If it does not, further collisions will reduce the energy of the atoms until they are in the thermal-energy range. Any reaction at this stage is termed "thermal" rather than "hot." In a system consisting only of nucleogenic C atoms and a reagent, both hot and thermal reactions occur. The best way of distinguishing these reactions is to dilute the system with a noble-gas moderator. For example, dilution with neon reduces the number of high energy collisions with the reagent and therefore the fraction of atoms reacting while hot. When the moderator is present in large excess, almost all the carbon atoms are reduced to and react in the thermal-energy range.

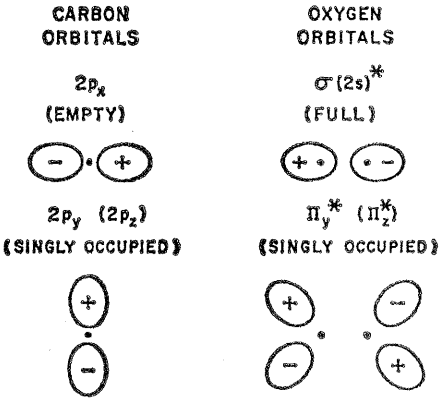


Fig. 9. Orbitals taking part in reaction of C atoms with O_2.

As a simple example, consider the reaction

$$C(^3P) + N_2 \rightarrow CN(^2\Sigma) + N(^4S)$$

This reaction is endothermic, by 50 kilocalories, and therefore can occur only with hot atoms. Thus it is not surprising that, as the N_2 reagent is diluted with neon, the yield of cyanide tends to disappear. Since the thermalized carbon atoms cannot react with N_2 to form cyanide they are found as CO, presumably due to reactions involving oxygen impurities.

However, the reaction of carbon atoms with nitrogen is atypical. The more common situation is illustrated in Fig. 7, which shows the effect of neon moderation on the yields of the products of the reaction of carbon atoms with ethylene. The yield of vinylacetylene, $CH_2{=}CH{-}C{\equiv}CH$, tends to vanish at high moderation, as expected for a product resulting exclusively from hot reaction. In contrast, although the yield of acetylene also decreases sharply, it is still significant at the highest moderations studied. Thus it appears to be a preferred product of a hot reaction, but can also result from reaction of a thermal carbon atom in the gas phase. The reasons for this and for the complementary rise in C_5 products with moderation have already been considered in connection with the discussion of mechanisms.

A situation similar to that described for ethylene also exists for ethane in that most products can be formed in both thermal and hot reactions. Thus in the gas phase the reaction properties of hot and thermal carbon atoms are qualitatively similar, though there can be considerable quantitative differences. This situation results from two related factors: (i) many reactions of thermal carbon atoms are highly exothermic; (ii) the intrinsic reactivity of the thermal carbon atom appears to be so high that its threshold or activation energy for many processes is close to zero.

Atomic carbon thus differs sharply from the only other species whose hot and thermal reactions have been investigated extensively, atomic hydrogen in the form of tritium produced by the $He^3(n, p)T$ nuclear reaction. The characteristic reactions of hot hydrogen with hydrocarbons are: H-atom substitution, $CH_4 + T \rightarrow CH_3T + H$; substitution of other atoms and groups, $CH_3X + T \rightarrow CH_3T + X$; H atom abstraction, $CH_4 + T \rightarrow CH_3 + HT$ (*8*). Of these only the abstraction reaction also occurs with thermal atoms. The reasons for these differences between C and H atoms are clear. Hydrogen, lacking only one electron to complete its valence shell, has less intrinsic chemical potential and reactivity than carbon, which lacks four. Hence addition of kinetic energy to the hydrogen atom results in entirely new modes of reaction.

The effects of moderation on the probability of reaction of hot hydrogen have been treated successfully by a simple kinetic theory of hot reactions (*8*). However, application of this formalism to hot C atom reactions is difficult. In the case of hot H atoms, the only important effect of the moderator is the removal of translational energy from the atom, but with atomic carbon other effects must be considered. Atomic carbon, unlike atomic hydrogen, is an insertion reagent, and so usually reacts in two steps. The first is the formation of a highly excited adduct, and the second involves possible decomposition of this adduct. Thus the efficiency with which the moderator can remove excitation energy from this adduct influences the modes of its decomposition, and therefore the products that result. A third possible effect of the moderator is the alteration of the ratio of singlet to triplet atoms available for reaction. Since the relative importance of these three effects is unknown, quantitative treatment of the C-atom moderator experiments is difficult. Nevertheless such experiments are useful in revealing the important generalization that the primary intermediates formed in the reactions of thermal and hot carbon atoms are similar, and in providing tests for the individual mechanisms postulated.

Conclusion

The studies of the chemistry of free carbon atoms described here represent only a start toward understanding the properties of this intriguing species. Although many important aspects of its chemistry, such as the influence of its electronic-spin state, are still poorly understood, some generalizations may be made.

Atomic carbon lacks four of the electrons making up the normal valence shell and may be regarded as the most electron-deficient of the simple neutral species yet studied. Its intrinsic chemical potential is therefore so high that it is best produced by nuclear reaction. As a result of this high intrinsic chemical potential, not even addition of further energy in the form of translational motion seems to change its properties in any marked way.

The products formed by carbon-atom reactions with hydrocarbons, though numerous, can be explained for the most part in terms of three simple fundamental mechanisms; insertion into C—H bonds, insertion into C=C bonds, and abstraction of hydrogen atoms. These properties of the free carbon atom can be understood as an extrapolation of the properties of species deficient in two electrons, such as $:CH_2$ (methylene), $:\ddot{N}—R$ (nitrenes), $:\underset{\cdot}{\ddot{O}}\cdot$ (atomic oxygen), and others. The carbon atom differs from these species in being more reactive, and in showing less discrimination for attack at bonds as different as C—H and C=C. It has in common with them the property of not readily reacting at C—C bonds.

Inorganic π-bonded molecules present two potential reaction sites at which electrons can be easily shared with the C atom: the π-bond and the terminal bond. Here, attack at the terminal atoms seems to predominate, with the resulting transition state in some ways resembling the compounds formed by the transition metals with CO and other π-bonded molecules.

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1a. *Note added in proof.* Apparently there will be a more vigorous exploitation of other techniques in the future. Since preparation of this manuscript we have received preprints of pertinent papers by P. S. Skell and R. R. Engel of the Pennsylvania State University, and by J. L. Sprung, S. Winstein, and W. F. Libby of the University of California, Los Angeles. Both papers describe experiments in which carbon vapor is allowed to react with solid organic substrates held at liquid nitrogen temperature. Skell and Engel worked with aliphatic olefins, while Sprung, Winstein, and Libby worked with benzene. Since carbon atoms are among the reactive species present in carbon vapor, certain products are postulated to arise from carbon atom reactions at the surfaces of these substrates. Those reported by Skell and Engel are consistent with the mechanisms discussed in this review. It is not so clear that this also holds for the work of Sprung *et al.* The reactions of carbon atoms with benzene have not been as extensively investigated as have those with aliphatic hydrocarbons. However, the evidence does indicate that there are similarities.

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22a. *Note added in proof.* Further evidence on double-bond addition comes from recent work of Skell and Engel (*J. Amer. Chem. Soc.*, in press) on the reaction of carbon vapors deposited on surfaces. They suggest that their results are consistent with the hypothesis that carbon atoms in the three lowest states of excitation (^3P, ^1D, ^1S) are among the reactive species present. It was found that these species could undergo π-bond addition with two molecules of olefin to form spiropentanes. In contrast with the gas-phase experiments on free carbon atoms, breakup of the initial adducts to form species such as acetylene does not seem to occur. This is reasonable, since, as discussed in the text, adducts formed by thermalized species in the condensed phase are less likely to fragment.

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