

## Hot-Atom Chemistry of Carbon

The hot atom chemistry of carbon is at once, one of the most complex areas of hot atom chemistry while being one of the most easily accessible for experimental study. This stems from the fact that the chemistry of the compounds of carbon is without question the most extensively studied of the compounds of any element in the periodic table. At the same time it is perhaps the most complex because of the multivalent nature of carbon and the fact that carbon can react with itself and with many other elements in near infinite variety. Thus the remarks which follow can apply in principle to other elements which are multivalent and whose chemical reactions have been studied in the gaseous, liquid and solid states.

One of the major difficulties in placing the chemistry of energetic carbon atoms in proper focus in the field of hot-atom chemistry in general is perhaps due to the fact that many efforts have been made to oversimplify these reactions and use as models the reactions of monovalent species such as tritium, fluorine, chlorine and bromine. While such comparisons have stimulated much useful work, sweeping generalities have been made in the past which do not stand up under closer scrutiny insofar as they answered the basic questions of the nature of the chemical interactions of the primary reactive encounter and how the primary encounters affected isolable-product distribution.

In studying carbon atom chemistry a distinction that is vital to any hypothesis is a clear delineation of the chemical system. Generalizations based on reactions in one system do not necessarily apply to all systems as

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it must be clear that electrophilic aromatic substitution reactions differ in kind and character from nucleophilic aliphatic substitution reactions. So reaction with unsaturated systems offers complexities and differences in quality and quantity from reactions in saturated systems.

The chemistry of energetic carbon atoms as considered here draws its hypotheses from reactions studied in saturated systems. In general the hypotheses generated are deduced from product analysis as is the case for essentially all of the work done in the field of hot-atom chemistry to the present time.

The experimental approach to these studies deserves some mention. Early work on hot-atom chemistry was done using carbon-14 atoms generated by the n,p reaction on nitrogen-14. While the early statistical theories of carbon atom reactions were based on these results, substantial progress was not achieved until gas phase reactions were studied and accelerator produced carbon-11 was accepted as the better radioactive species for basic studies. The most commonly used reactions are  $^{14}\text{N}(p,n)^{11}\text{C}$ ,  $^{12}\text{C}(p,pn)^{11}\text{C}$  and the  $^{12}\text{C}(\gamma,n)^{11}\text{C}$ . The use of the accelerator allowed control of concomitant radiation dose to the system under study and allowed studies of a single system in all phases. The control of radiation dose made it possible to separate radiation chemistry from hot-atom chemistry and the control of phase, especially the facile use of gas phase systems allowed insight into the intermolecular effects on intermediate species in addition to the physical effects on the reactive atom.

It is at this stage difficult to say whether or not energetic carbon atoms undergo truly unique reactions when compared with their thermal counterparts. It has been postulated that the formation of  $\text{H}^{11}\text{C}\equiv\text{N}$  in  $\text{N}_2\text{-H}_2$  mixtures and the formation of  $^{11}\text{CH}=\text{CH}$  and  $^{11}\text{CH}_2=\text{CH}_2$  in hydrocarbons

are true hot products. On careful consideration, however, what must be said is that until the chemistry of "Boltzmann-Distribution" carbon atoms in the ground state and perhaps the first three low lying electronic states is completely understood it is premature to state that HCN, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> are non-thermal carbon atom products. Reasons for this postulate will become apparent later in the text.

The chemistry of energetic carbon atoms must be considered in light of the electronic state of the atom in the first reactive encounter. Experimental differentiation of the electronic state-chemical reaction relationship are possible in gas phase studies. The electronic states of carbon are as follows: ground state <sup>3</sup>P; first excited state <sup>1</sup>D, 1.26 eV above ground state; <sup>1</sup>S, 2.68 eV above ground state, <sup>5</sup>S<sup>o</sup>, 4.18 eV above ground state. It is probable that the <sup>1</sup>S and <sup>5</sup>S<sup>o</sup> states are not involved in hot-atom reactions thus we can concentrate on the <sup>3</sup>P and <sup>1</sup>D states as being responsible for the reactions we presume take place. Another physical parameter of nucleogenic carbon that is worthy of note is its charge state on the first reactive encounter. While essentially all of the studies reported in the literature to date assume reaction by a neutral atom, it may be that some carbon ions are reacting in helium and neon moderated systems. This aspect of nucleogenic carbon chemistry is as yet wholly unexplored.

Studies of energetic carbon-atom reactions can benefit from the increasing amount of work which has been done on carbon atom chemistry over the several past six years. It has generally been reported under the heading of carbon atom reactions but in most cases is perhaps more properly described as rates of carbon atom disappearance in a variety of reactive substrates. Several striking features appear. The postulate raised in early work on the hot atom chemistry of carbon that the <sup>3</sup>P carbon atom is

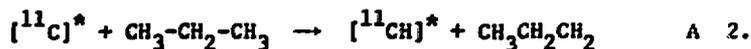
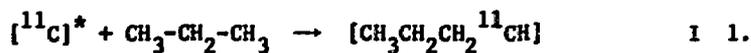
efficiently scavenged by oxygen was strikingly confirmed by a number of workers who measured the rate of disappearance (reaction) of  $^3\text{P}$  carbon in pure oxygen. It is the fastest known reaction of the  $^3\text{P}$  state studied to date. These various studies also showed that the disappearance rate of carbon atoms in hydrocarbons was  $10^4$  to  $10^6$  slower. The facts as to the rate of disappearance of the  $^1\text{D}$  state are somewhat less clear. The rate with oxygen may be comparable or an order of magnitude slower but the rate with hydrocarbons is very much faster than is the rate of reaction of the  $^3\text{P}$  state with hydrocarbons and may be as fast as the rate of  $^3\text{P}$  carbon with oxygen. From these observations we can say with certainty that in oxygen scavenged hot-atom systems,  $^3\text{P}$  thermal carbon atoms are not responsible for any of the products, other than  $^{11}\text{CO}$ , that are observed. Thus in developing a mechanistic basis for product formation brought about in systems containing nucleogenic carbons we need only consider three species: thermal  $^1\text{D}$  carbons, hot  $^1\text{D}$  carbons and hot  $^3\text{P}$  carbons.

In turning to the hot-atom chemistry of carbon it is well known that in most simple unsaturated oxygen scavenged systems three products usually account for over fifty percent of the atoms generated,  $^{11}\text{CO}$ ,  $^{11}\text{CH}=\text{CH}$ ,  $^{11}\text{CH}_2=\text{CH}_2$ . Numerous studies have shown that in  $\text{O}_2$  and in systems containing oxygenated compounds, carbon monoxide is the primary product produced by thermal and by hot reactions. The  $^{11}\text{CO}_2$  observed is due to radiolytic oxidation of  $^{11}\text{CO}$  or oxidation of secondary intermediates.

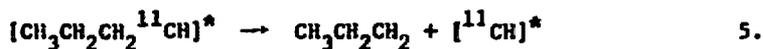
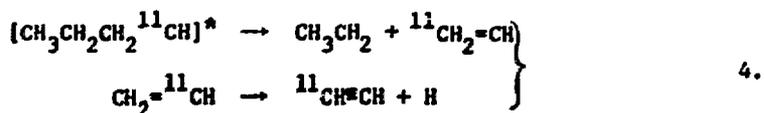
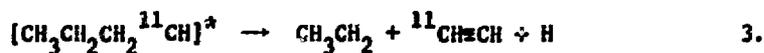
The hypothesis that underlies the mechanistic framework of hot carbon atom reactions is based on the postulate that the hot carbon atom ( $^3\text{P}$  and  $^1\text{D}$ ) can insert into a carbon hydrogen bond and that it ( $^3\text{P}$  and  $^1\text{D}$ ) can also abstract hydrogen. This hypothesis can be used to explain many of the products that are observed. Present evidence also supports postulates

involving stripping of carbon atoms and small groups from substrate molecules ultimately yielding products and replacement of carbon atoms and nitrogen atoms in "knock-on" collisions involving substrate molecules leading to labeled parent compounds. These mechanisms, however, at best probably play relatively minor roles in carbon atom chemistry.

Let us examine the basic reaction. An energetic carbon atom reacts with an alkane, e.g. propane, by either insertion (I) or abstraction (A) 1 and 2 (radical designations are omitted).



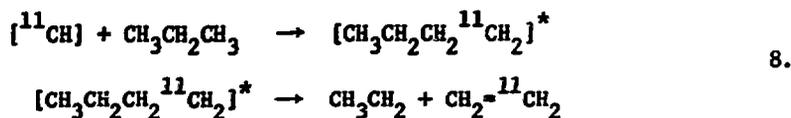
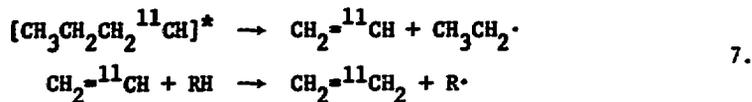
The intermediate in 1 can decompose to give acetylene by a concerted [if  $^1\text{D}$  insertion] or stepwise [ $^1\text{D}$  or  $^3\text{P}$ ] reaction 3 and 4, or it can decompose to give  $\text{CH}$ , 5 (insertion decomposition route) or it can react with  $\text{O}_2$  or substrate to give a secondary product 6



Experimental evidence using double label techniques strongly supports the formation of acetylene by an intramolecular mechanism. This means to say that the acetylene is formed from a single molecule which it encountered in reactive collision.

Two postulates have been put forth for the formation of ethylene.

One states that the excited insertion intermediate (reaction 1) undergoes unimolecular decomposition to give the vinyl radical which subsequently abstracts hydrogen to give ethylene, 7. The other states that methyne [ $^{11}\text{CH}$ ] inserts into a carbon-hydrogen bond to give an intermediate which undergoes unimolecular decomposition to give ethylene directly, 8.



The vinyl radical mechanism is probably not responsible for ethylene formation in the hot region. This conclusion is based on experimental evidence: 1. vinyl radicals react rapidly with oxygen and no appreciable diminution of ethylene yield is observed in oxygen scavenged systems; 2. observed deuterium isotope effects in ethylene formation are the opposite of what one would predict if vinyl radicals were the immediate precursors; 3. little or no vinyl chloride is observed in chlorinated hydrocarbons, the opposite of what one would predict; 4. drastically reduced yields of ethylene in halocarbons are not consistent with the mechanism given in equation 7; 5. evidence based on results from double label experiments is not consistent with the mechanism given in equation 7.

The same evidence outlined above is consistent with an intermolecular mechanism involving the formation of methyne in a hot reaction as the primary step leading to ethylene formation. It has also been possible to show that this intermolecular mechanism for ethylene involves only methyl groups as the immediate precursor of the product. The gas phase yield of ethylene

from compounds containing methylene groups only (e.g. cyclopropane, cyclobutane, cyclopentane, etc.) is negligible. The ethylene-<sup>11</sup>C that is observed must arise from some other mechanism.

Can anything be said about the hot reactions of the <sup>1</sup>D and <sup>3</sup>P carbon atoms? As a working hypothesis the following sequence is suggested in oxygen scavenged systems. The principal reaction of hot <sup>1</sup>D carbon atoms is to yield methyne which then inserts in substrate to ultimately yield ethylene. Isotope effect work would indicate that methyne formation occurs by insertion-decomposition in the hot region. The principal reaction of hot <sup>3</sup>P carbon atoms is to yield acetylene and a minor pathway yields methyne. At lower energies acetylene may also be formed via <sup>1</sup>D carbon atom insertion-decomposition, acetylene from <sup>3</sup>P reaction disappears, and a small component of <sup>3</sup>P abstraction reaction can lead to methyne which can then give ethylene. Evidence for this hypothesis is implicit in the previous discussion and is strengthened by moderator experiments in helium, neon, and xenon. The basic effect in all three is to increase the yield of CO as the moderator concentration increases (and the number of carbons reaching the thermal range increases) and to decrease the yield of acetylene and ethylene which is to be expected if these are primarily hot products. Furthermore an examination of the yield of acetylene relative to ethylene as the concentration of xenon increases shows a constantly increasing ratio. Xenon is an efficient non-reactive spin converter for carbon and is converting <sup>1</sup>D carbon to <sup>3</sup>P carbon thus enhancing products derived from the <sup>3</sup>P state and decreasing products resulting from the <sup>1</sup>D state. It is clear from these postulates that the problem of shadowing is very much with us in carbon hot-atom chemistry.

The theoretical calculations of Newton and Blint were not considered here since their impact on an understanding of carbon atom chemistry has been presented separately at this meeting. A summary of our present knowledge would suggest the following framework.

1. At the upper end of the energy range where the carbon atoms become chemically reactive
  - a.  $^3\text{P}$  carbon insertion reaction results in acetylene formation.  
 $^3\text{P}$  carbon abstraction reaction results in ethylene formation but this is a minor pathway for ethylene formation
  - b.  $^1\text{D}$  carbon insertion decomposition reaction results in ethylene formation.
2. At the lower end of the energy range
  - a.  $^3\text{P}$  carbons in the thermal and near thermal range are scavenged by  $\text{O}_2$ . Rate of reaction with organic substrates is so low as to be non-competitive.
  - b.  $^1\text{D}$  carbons still undergo insertion decomposition and ultimately yield ethylene. The insertion intermediate may also begin to fragment to yield acetylene.
3. Absolute yield depends on structure and phase. Substantial evidence exists that carbon atoms are powerful electrophiles, that bond energies, electron density and bond polarization factors affect yields, that the degrees of freedom of the intermediate (reflecting the ability of the intermediate to delocalize the vibrational energy resulting from the reactive encounter) affect the yield, and finally that the large reduction in yield on change in phase further supports the postulate of a vibrationally excited intermediate or intermediates. However, bond counting methods or structural dependence hypotheses tell us little about detailed mechanism.

It is essential to again stress that the framework outlined in 1 and 2 applies to gas phase reactions in alkanes and a few other classes of simple compounds which are scavenged by oxygen. For example, there is evidence in the literature that in some systems (e.g. cyclopropane and benzene) more than one mechanism is operative in the formation of acetylene. (As much as 40% of the acetylene can be formed by a second mechanism.) This underlines the comments made in the introduction that hot-atom chemistry in organic systems may indeed not be readily explained by one or two simple postulates about  $^1\text{D}$  and  $^3\text{P}$  carbon atoms.

#### Conclusion

What is perhaps most important at this stage is to comment on the direction that future work might take.

New experimental work on thermal carbon atoms is essential if we are to unravel and pinpoint those reactions which are uniquely due to kinetically excited carbon atoms. This is particularly true of the reactions of  $^1\text{D}$  (and possibly  $^1\text{S}$ ) carbon atoms. Their relative reactivity in a Boltzmann-Distribution situation has as yet not been determined. Thus, knowing the rate of disappearance of these atoms is only a beginning; the products resulting from their disappearance in a variety of substrates need to be determined. More accurate values for the rates of disappearance (and reaction) of the  $^3\text{P}$  carbon atom in non-oxygen containing systems are needed but admittedly the extraordinary rate of  $^3\text{P} + \text{O}_2$  makes such studies quite difficult experimentally.

Experimental work on carbon ions should be started. Efforts involving carbon ions in solids unfortunately suffers from complexities which make it difficult to delineate true ion-molecule reactions. Product analysis cannot easily provide a differentiation between ionic reactions and neutral-species-

reactions in these systems. Gas phase studies where one is certain of the charge state of the species undergoing chemically reactive encounter would probably be the most promising approach. Care to determine electronic state should be taken at the outset.

Continuing work on the alkanes to further strengthen the hypotheses (or replace them with new ones) put forth is essential. Much can still be done with gas phase work involving mixtures, moderators, spin convertors and other simple classes of compounds such as the haloalkanes. For example, the striking effect of halogen on the yield of ethylene is in need of further study. The minor products one sees as a result of carbon atom reactions are also in need of further study. For example, the formation of propane-<sup>11</sup>C from ethane, or toluene-<sup>11</sup>C from benzene, are explained in terms of the formation of methylene-<sup>11</sup>C [<sup>11</sup>CH<sub>2</sub>] which then inserts into a C-H bond to give the product. An alternate mechanism involving carbon atom insertion to give [CH<sub>3</sub>-CH<sub>2</sub>-CH]\* (and [Ø<sup>11</sup>CH]\*) which intermediate then abstracts the necessary hydrogen from the surroundings has not been unequivocally ruled out by any published experimental evidence. The gas phase has been stressed here. Liquid phase studies are particularly easy to carry out and many areas are in need of study. Some early work on solid phase reactions has been reported but here experimental difficulties involving the isolation of radiochemically pure products make these studies somewhat less accessible to the use of carbon-11 and perhaps are best carried out using carbon-14.

Extensive comment has been made on some theoretical aspects of studying the hot-atom chemistry of carbon. This is perhaps one of the most exciting new fields. Only recently has theoretical work been applied to carbon. Theoretical work on tritium atoms has been extensive not only by hot-atom chemists but by numerous individuals who have no direct interest in

the field. That this has not been the case with carbon is perhaps easily understood. The complexities are compounded enormously by the systems one needs to deal with. Theoretical work on carbon atoms plus simple alkanes is a necessary complement to the hypotheses about carbon atoms generated from presently available experimental work. Configuration interaction calculations would materially enhance the ability to separate  $^3P$  from  $^1D$  reactions and provide a new basis for further experimental work. Dynamic calculations have as yet not been carried out. The implications of such calculations in being able to understand results in alkanes, alkyl halides, alcohols and olefins is clear. Hopefully an effort similar to that in the tritium field will evolve.

Experimental verification or elimination of current postulates is still very much a part of the hot-atom chemistry of carbon. Much work still needs to be done before we understand the chemical reactions of  $^3P$ ,  $^1D$  and  $^1S$  carbon atoms both thermal and kinetically excited. Hot-atom chemistry provides a unique tool for these studies since it can focus on the microscopic properties of systems and can help us understand what happens on the first reactive encounter of a carbon atom and a substrate molecule. This basic understanding is essential to a broad area ranging from reactions at the molecular level to predicting the properties of macroscopic systems.

#### Acknowledgements

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