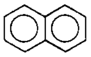
Table XV. Computation Times T for One SCF Calculation[a]

Molecule	T, s			
	MINDO/3	MNDO	STO-3G[b]	4-31G[b]
CH_4	0.44	0.53	4.60	22.07
C_2H_6	1.65	1.98	26.09	155.91
C_3H_8	3.11	4.21	93.79	
	6.59	7.16	255.56	1759.8
	39.14	48.97	1279.0	

[a] Central processor time on a CDC 6600. The STO-3G and 4-31G programs were provided by Dr. A. Komornicki. [b] On the CDC system, the user is additionally charged for the disk storage of integrals which amounts to about 40% of the total TM charges.

will find numerous applications in the study of reaction mechanisms and other chemical behavior.

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Effect of Electronic State of Carbon Atoms on Their Reactions with Cyclopentadiene in Inert Gas Moderated Systems

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Abstract: Products of the reactions of hot and moderated free carbon atoms with cyclopentadiene have been studied in pure and oxygen scavenged systems. Experiments with different rare gas moderators have provided evidence that both triplet and singlet carbon atoms react with cyclopentadiene and oxygen with comparable efficiencies and many similar products result. In distinction from previous work on oxygen scavenged alkane systems, acetylene is thought to be formed to some extent by thermal or near thermal $C(^3P)$ atoms. The formation of the ring expansion product, benzene, also appears to result in part from $C(^3P)$ reactions. On the other hand, the straight chain C_6H_6 isomers are attributed almost exclusively to singlet atoms.

In the past decade as the result of the application of a variety of techniques,[2] the broad outlines of the chemistry of the free carbon atom have been traced. Insertion into the C–H bond, addition to the π bond, and abstraction of oxygen and halogen atoms have all been identified.[13] While some progress has been made in understanding the effects of excess kinetic energy on carbon atom reactivity, the problem is complex because of the need to sort out the effects of electronic excitation from those due to translational energy. This in turn is complicated by the fact that our knowledge of the differences in the chemistry of the ground $C(^3P)$ and low-lying $C(^1D)$ and $C(^1S)$ states is rudimentary. Some progress in unraveling these problems have been made recently as the result of a series of experiments involving production of C atoms by flash photolysis of C_3O_2 in the presence of simple substrates.[3] The decay of these atoms was followed spectroscopically and rate constants were deduced. This work has shown that the $C(^1D)$ atom reacts efficiently with both methane and ethylene. Acetylene is a major product of the methane reaction in agreement with earlier results of experiments with nucleogenic carbon atoms.[13] The $C(^3P)$ atom appears to react slowly with methane, and there is evidence from microwave discharge experiments with C_3O_2 that its reaction with ethylene is also slow.[6] Such information is of considerable value in the interpretation of more complex systems.

Also of significance is the finding of Peterson[14] that the choice of rare gas used as moderator in the nucleogenic experiments has a marked effect on triplet/singlet atom ratio, which varies from about 0.45 with neon to 2.3 or more with krypton and xenon. Taylor, Ache, and Wolf[15] have also carried out moderation experiments in oxygen scavenged alkane systems. Their results have lead to the proposals that hot $C(^1D)$ forms methyne, hot $C(^3P)$ and thermal $C(^1D)$ lead to acetylene, and thermal $C(^3P)$ reacts 10^4 to 10^6 times faster with oxygen than alkanes. Thus nucleogenic systems can provide information on the chemical properties of triplet and singlet atoms as well as on the effects of excess kinetic energy.

We have studied the reactions of nucleogenic carbon atoms with cyclopentadiene in systems containing inert gas moderators to help clarify our understanding of the effect of electronic state on carbon atom reactions. A preliminary report of carbon atom reactions in unmoderated systems has appeared.[16] This work has shown that quenching of the excited adducts formed by the primary C–H insertion and π bond addition is more likely with cyclopentadiene than with smaller molecules. The result is a larger sampling of structures more closely related to those of the precursor adducts than are the fragmentation products formed in unimolecular decay processes. Among the stabilized structures are products such as benzene formed by ring enlargement reactions. Since cyclopentadiene itself is in a cis configuration, retention or loss of this geometry in the expected ring opening reactions might also give some indication of the nature of spin state of the precursor adduct. Finally, cyclopentadiene is known to react efficiently with triplet molecules,[17] and therefore might prove to be more reactive toward the $C(^3P)$ atom than the organic molecules studied up until now. One possible product of such a reaction is benzene. Given the fact that triplet aromatic molecules often have appreciable lifetimes,[18] and given the potentiality of cyclopentadiene as a triplet scavenger, there are possibilities for detecting some triplet intermediates.

This paper is primarily concerned with the effect of the electronic state of the carbon atom on its reactions with cyclopentadiene. Detailed considerations of mechanisms involved in carbon atom reactions with cyclopentadiene and other cyclic molecules are presented elsewhere.[19,20]

Experimental Section

Procedure. Radioactive carbon atoms (20.5 min half-life) were produced by the $^{12}C(\gamma,n)\ ^{11}C$ reaction using the bremstrahlung from the Yale Electron Accelerator (EA) or by neutron stripping reaction of a 120 MeV ^{12}C ion beam produced by the Yale Heavy Ion Linear Accelerator (HILAC). The details of carbon atom production by these two methods have been described previously.[21] The reaction vessels were filled on a high vacuum line fitted with greaseless stopcocks. Glass irradiation vessels were used for the EA and brass vessels for the HILAC. The samples were irradiated for periods ranging from 10 to 20 min. Radiation dosage was measured using benzene formation from acetylene and was found to be less than 10^{-2} eV/molecule.[22] Samples which contained inert gas moderators other than He were irradiated on the HILAC to reduce the formation of activities other than ^{11}C. Most of the other irradiations were done on the EA to produce higher activity. Irradiations of similar samples on both accelerators gave similar results within experimental error.[23] The total activity was monitored by oxygen samples on the HILAC and ethane samples on the EA using standard normalization procedures described previously.[19,21]

After irradiation the products were analyzed by standard radiogas chromatographic methods. Since only radiogas chromatography is sensitive enough to detect the products of these experiments, standard methods of instrumental identification could not be used. The carbon oxides and C_2 hydrocarbons were separated on a 30 ft deactivated alumina column, the C_3 and C_4 hydrocarbons on a 60 ft SF-96 silicone oil (15%) column, and cyclopentadiene and the C_6 hydrocarbons on a 4 ft β,β'-oxydipropionitrile (20%) column. First identification of the products was based on the agreement in relative retention volume between the radioactive peak and an inactive carrier peak of a known compound. The identity and purity of each compound were then confirmed by adding an authentic sample suspected to be identical with the radioactive product, trapping the two together from one column, and injecting the mixture on other columns of different separating characteristics. If the activity and the authentic compound were not separated by such procedures, they were presumed to be identical. The verification schemes for products having less than six carbon atoms have been reported.[24] The C_6 products were trapped from the polar β,β' column and reinjected onto an 11 ft silicone column which separates compounds according to their boiling points. In addition, the C_4 products, fulvene, and *cis*- and *trans*-1,3-hexadien-5-yne were reduced to their saturated analogues by passing them through a 6 in. heated column packed with palladium on asbestos using hydrogen as a carried gas. The saturated compounds were then identified on a silicone column. Finally, irreversible trapping on a 3 in. silver nitrate column supported identification of compounds with terminal triple bonds.

Materials. Cyclopentadiene was prepared by cracking the commercially available dimer and was stored at dry ice temperature. Gas chromatographic analysis showed that it contained less than 0.5% volatile impurities. The cyclopentadiene was meticulously degassed on a vacuum line using the freeze–thaw technique before the samples were prepared. Other gases used as reagents were obtained from Matheson and Co. and were used without further purification. The minimum stated purities were 99.995% for the rare gases and 99.6% for oxygen.

The compounds used to identify products and/or to calibrate the gas chromatographic columns were all obtained from commercial sources except for the following:[19] diacetylene, prepared by alcoholic dehydrogenation of 1,4-dichloro-2-butyne; fulvene, produced by the reaction of cyclopentadiene with formaldehyde in a potassium ethoxide solution;[25] and 1,3-hexadien-5-yne, where both cis and trans isomers were prepared simultaneously by isomerization of 1,5-hexadiyne in a potassium *tert*-butoxide solution.[26] These products were purified by gas chromatography, and their identities were confirmed by comparison of their IR spectra with those in the literature[25–28] and/or through the hydrogenation of the unsaturated species to form saturated compounds with previously determined retention volumes on the chromatographic columns.

Experimental Variables. The effects of addition of oxygen scavenger and different inert gas moderators were used in this work. Addition of O_2 has several effects. First of all it can scavenge or compete for some of the atomic species present. It is known to react very rapidly with the $C(^3P)$ atom[3] and so in competition with a substrate which reacts slowly with this state, such as methane, can act as a scavenger for the $C(^3P)$ atom. The $C(^1D)$ atom reacts so rapidly with methane that at best O_2 can only compete, but cannot scavenge, even if the higher of the two reported rate constants is correct.[3] This will probably be true for saturated hydrocarbons in general. According to the only available rate measurements for the $C(^1S)$ atom, its reactions with both O_2 and CH_4 occur at about the same rate and are about three orders of magnitude slower than those of the $C(^1D)$ atom with CH_4 or of the $C(^3P)$ atom with O_2.[29] It seems unlikely that O_2 will be an effective scavenger of the $C(^1S)$ atom, and it may not be able to compete effectively with some molecules for this state. The second effect of O_2 is as a general radical scavenger both of ^{11}C labeled radicals produced in the atomic reactions and of radicals produced by the radiation field which necessarily accompanies the ^{11}C generation process.

Effects due to the addition of a noble gas can also be complex. As the proportion of inert gas is increased, the average kinetic energy of the reactant atom is reduced, and, in principle, the resulting changes in product spectrum can help to sort out thermal and hot processes. However, two other effects must be considered as the moderator substitutes for the reactive substrate. The ratio of triplet to singlet atoms and the ability to de-energize an intermediate can also change from those characteristic of the substrate alone to those determined primarily by the moderator. The triplet/singlet ratio should be different for different noble gases, as we shall discuss further below. In general for adducts formed with a constant energy content by a carbon atom reaction with substrate, increased moderator concentration would be expected to enhance the probability of the adducts' decomposition, since noble gases are less effective at removing energy in collision than are substrate molecules.

Results

Table I compares the yields of the principal volatile products from the reactions of carbon atoms with cyclopentadiene using neon and argon moderating gases at 95 and 99% moderator concentrations in the absence of oxygen.[30] In the moderated system there is a decrease in fragmentation products and an increase in C_6 yields relative to the pure sample, consistent with the expected formation of adducts of lower energy in the moderator experiments. Within the C_4 group the yield of di-

Table I. Absolute Yields of Principal Products in Reaction of ^{11}C with Cyclopentadiene in Neon and Argon Moderated Systems

Product	Reaction mixture[a] Pure c-C_5H_6	95% Ne	99% Ne	95% Ar	99% Ar
Carbon monoxide	0.7 ± 0.4	2.0 ± 0.7	3.0 ± 1.0	1.4 ± 0.5	1.6 ± 0.3
Acetylene	10.0 ± 0.1	2.7 ± 0.1	2.8 ± 1.0	3.2 ± 0.1	3.1 ± 0.6
Vinylacetylene	3.8 ± 0.4	2.0 ± 0.1	2.5 ± 0.1	2.8 ± 0.2	3.6 ± 0.1
Diacetylene	8.5 ± 1.0	3.1 ± 0.5	2.4 ± 0.3	4.7 ± 0.5	2.2 ± 0.1
Fulvene	2.8 ± 0.7	0.4 ± 0.2	n.d.[b]	0.4 ± 0.2	n.d.[b]
Benzene	9.3 ± 0.8	11.0 ± 1.0	8.3 ± 1.2	10.8 ± 0.7	7.6 ± 0.2
cis-1,3-Hexadien-5-yne	2.3 ± 0.3	4.3 ± 0.9	4.5 ± 0.7	4.1 ± 0.8	7.7 ± 0.4
trans-1,3-Hexadien-5-yne	1.0 ± 0.5	3.3 ± 0.6	3.6 ± 1.1	4.1 ± 0.5	5.0 ± 0.6

[a] All the samples with moderator were run at a total pressure of 80 cm. The pure cyclopentadiene sample pressure was 30 cm. [b] Not determined.

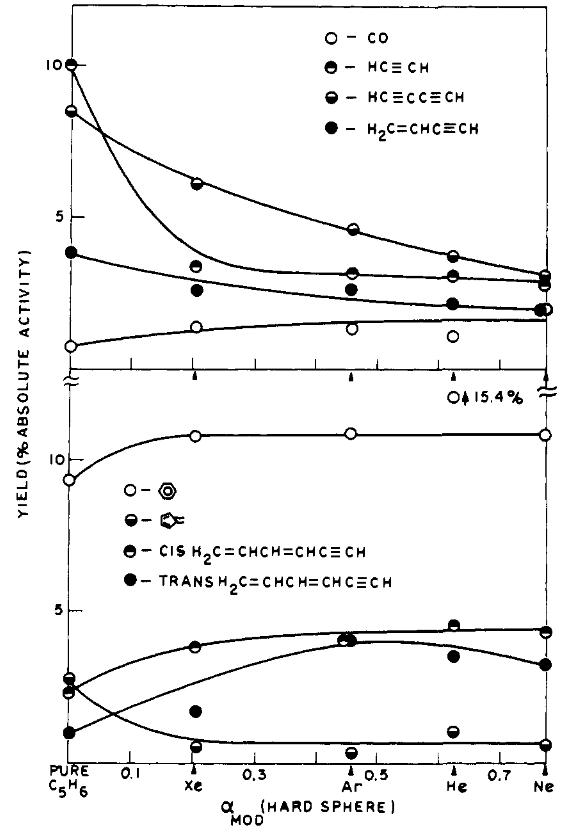

Figure 1. ^{11}C-labeled products from the reaction of atomic ^{11}C with gaseous cyclopentadiene (5%) in the presence of various noble gas moderators (95%). Yields are expressed in percent absolute activity. α_{mod} is the average energy loss of the ^{11}C per collision with the moderator based on hard-sphere interactions. $\alpha_{C_5H_6}$ is arbitrarily assumed to be zero.

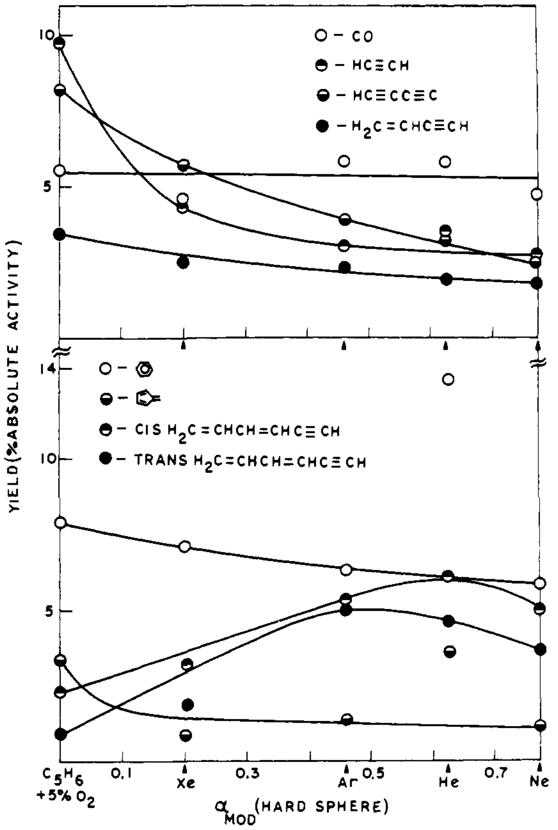

Figure 2. ^{11}C-labeled products from the reaction of atomic ^{11}C with gaseous cyclopentadiene (4.75%) in the presence of oxygen (0.25%) and various noble gas moderators (95%). Yields are expressed in percent absolute activity. α_{mod} is the average energy loss of the ^{11}C per collision with the moderator based on hard-sphere interactions. $\alpha_{C_5H_6,O_2}$ is arbitrarily assumed to be zero.

acetylene drops relative to that of vinylacetylene. This is reasonable since diacetylene formation requires loss of hydrogen in addition to the rupture of two C-C bonds, a process more likely with intermediates formed from hot atoms than with those formed at lower energy.

Since increasing the percent moderator from 95 to 99% changes the ratio of moderator to cyclopentadiene fivefold, the failure to observe a significant change in a product yield in this range indicates that for that product the full effects of the reduction of C atom kinetic energy, of changes in the energy transfer properties of the medium, and of any other effects of substitution of noble gas for substrate are already fully realized at 95% moderation. Comparison of the 95 and 99% moderator samples shows at most only a small decrease in the sum yield of C_4 and C_2H_2 fragmentation products and a small increase in the yields of C_6H_6 compounds as moderation is increased.

The decrease in benzene yield from 95 to 99% moderation cannot be a translational energy effect, since the yield increased up to 95% moderation, and probably reflects the poorer de-energizing ability of the 99% noble gas sample as discussed above.

The effects of the use of different rare gas moderators on cyclopentadiene products in the absence and presence of oxygen are shown in Figures 1 and 2, respectively. Yields are absolute and are estimated to be ±20% for the hexadienyne isomers and ±10% for the other products on the basis of at least two determinations for each compound. The abscissa, α_{mod}, is the average logarithmic energy loss per collision between ^{11}C and the rare gas on the basis of the hard sphere approximation.[13e] Although it does have some moderating ability, cyclopentadiene is placed arbitrarily at $\alpha_{mod} = 0$ since it represents the system in which hot reactions are most important.

While every other yield trend shown in Figures 1 and 2 is monotonic, benzene and fulvene show maxima in the helium moderator experiments. We have considered two possible explanations: (1) significant numbers of ions enter the chemical energy range in helium as seems to be true for tritium recoils in helium moderator;[31] (2) the distribution of neutral atomic states reacting is different in helium than in the other noble gases. The resonance rule of atomic physics can serve as a basis for discussion of the first possibility. In accord with this the absolute values of the energy changes for the neutralization and reionization reactions have been used to locate the relative energies at which the cross section for each process is a maximum.[19] For both helium and neon the cross section maxima for reionization are in the same energy range as those for neutralization, while for argon they are somewhat lower. The resonance rule per se thus is equivocal on the question of C^+ reactions in helium and neon. However, two considerations do raise questions as to whether ions play a significant role. (1) The argon and neon data are similar indicating that ions are of little if any importance in neon. Therefore neutralization must be considerably more efficient than reionization in both of these gases despite the fact that these processes occur in the same energy range in neon. In view of the general observation that ionization is most efficient when the masses of the colliding partners are nearly equal,[32] formation of C^+ ions should be even less likely in helium than in neon. (2) Cyclopentadiene has a low ionization potential (8.6 eV) and so even at low energies neutralization of ions should compete very efficiently with their chemical reaction.[33] These arguments undermine the case for ions playing a role in helium and so the alternate possibility that helium provides a different distribution of atomic states becomes relatively more attractive. Since helium should be the least efficient of the noble gases in promoting transitions from excited atomic states, significant concentrations of higher excited states such as $C(^1S)$ are more likely in it than in neon, argon, and xenon, and these might be a source of benzene and fulvene.

Discussion

The principal volatile products formed from carbon atom reactions with cyclopentadiene can be divided into two categories according to their structure and the effect on their yields of changes in reaction conditions. These two groups are (1) fragmentation products in which at least two C-C bonds of the ring system are broken, i.e., acetylene and the C_4 straight chain hydrocarbons; and (2) stabilization products which have the stoichiometry of the reactant plus a carbon atom. Included in this group are benzene, fulvene, and the hexadienyne isomers. Our primary interest here is with those aspects of formation of these groups of products which give information concerning the effect of the electronic state on the carbon atom reaction. Detailed mechanistic considerations of the formation of these products and those of lower yield are discussed elsewhere.[16,19,20,34,35]

Relative Reactivities of Triplet and Singlet Atoms toward Cyclopentadiene and Oxygen. While there is general agreement that the reactions of the $C(^1D)$ atom with organic substrates are rapid, the situation with respect to the $C(^3P)$ atom is somewhat confused. The spectroscopic studies show that its reaction with methane is slow,[3] and there is evidence in nucleogenic studies that this might be true for ethane and propane as well.[13a,15] Early work with graphite vapor generated by drawing an electric arc provided some stereochemical evidence that the $C(^3P)$ atom reacted with olefins, but later work of Skell et al.[32] using thermally produced vapor in which atoms should be in the ground (^3P) state found no isolable products from propylene. Experiments with atoms produced by microwave discharge in C_3O_2 indicated that the reaction of the $C(^3P)$ state with ethylene is slow.[6] Thus it appears that the $C(^3P)$ atom is a more discriminating reagent toward organic substrates than is the $C(^1D)$ atom, and there is a question as to whether there are any organic molecules with which the triplet reacts efficiently. With the $C(^1D)$ atom the situation is reversed. The evidence is strong that it reacts efficiently with methane and presumably with other saturated hydrocarbons as well,[13a,15] but there is some question about the rate of its reaction with oxygen relative to that with methane.[3]

Peterson has used the established rapid reaction of the $C(^3P)$ atom with oxygen to show that the fraction of triplet atoms present in a moderated system is markedly influenced by the choice of a noble gas moderator.[14,37] At 0.99 mol fraction of xenon he has observed an 84% yield of CO in an O_2-CH_4 mixture of ratio 1/20. By contrast a similar reactant mixture at a 0.99 neon mol fraction gave a 31% yield of CO. From these results it seems clear that in going from neon to xenon moderator the ratio of triplet to singlet atoms is altered markedly, and at high xenon moderations the atoms reacting are predominantly in the ground $C(^3P)$ state. This interpretation is supported by the rate constant measurements of Husain and Kirsch,[38] which indicate that xenon deactivates the $C(^1D)$ atom to the $C(^3P)$ ground state on almost every collision, and thus that at high moderations deactivation must compete effectively with reaction with any substrate. In neon and argon, on the other hand, the rate constants indicate that deactivation does not compete effectively at the moderator concentrations which we report here.

These conclusions can be used in interpreting our results. Since the CO yield in oxygen-cyclopentadiene mixtures is unaffected by the change in rare gas from neon to xenon with its attendant change in the singlet/triplet ratio, both the singlet and triplet atoms must show about the same *relative* reactivities toward oxygen and cyclopentadiene. Given the strong evidence that the $C(^3P)$ reaction with O_2 is rapid,[3b,13a] we conclude that the $C(^3P)$ reaction with cyclopentadiene is also efficient. Further, on the plausible assumption that the reaction of the $C(^1D)$ atom with cyclopentadiene is rapid, we infer that its reaction with oxygen is also efficient. Support for the rapidity of the $C(^1D)$ reaction with cyclopentadiene comes from competitive experiments in 95% neon moderator in which, as discussed above, singlet atoms predominate. At substrate/oxygen ratios of 19/1 we find a CO yield of 13% from ethylene and 5% from cyclopentadiene, indicating that cyclopentadiene is about 2-3 times as reactive as ethylene, about what one would expect from the ratio of the gas kinetic cross sections. Since cyclopentadiene, ethylene, and oxygen thus react with comparable efficiencies, and since ethylene appears to react on virtually every collision, these results indicate that of the rate constants reported for the $C(^1D)$ reaction with oxygen the value of $\sim 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} [3b] is probably closer to the mark than the limiting value, $< 5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} also reported.[3a]

Acetylene Formation by Thermal $C(^3P)$ Atoms. As discussed above, flash photolytic experiments have shown that insertion into the C-H bond of CH_4 occurs rapidly with the $C(^1D)$ atom,[3,13] and this state must be involved in production of acetylene here as well. These same flash photolytic experiments show that the $C(^3P)$ state reacts slowly with methane but rapidly with oxygen. Studies with nucleogenic carbon atoms in oxygen-alkane systems have indicated that while hot $C(^3P)$ reactions yield acetylene, thermalized $C(^3P)$ does not because of its low reactivity toward alkanes.[15]

In our work both in the presence and absence of oxygen the xenon moderator experiments show the same yield of acetylene as do those with the other rare gases. Since the triplet concentration is enhanced in xenon, these results imply that the $C(^3P)$ atom can react with cyclopentadiene to yield acetylene as one product. If spin is conserved, acetylene production by a thermal or near thermal triplet atom from a single molecule is endoergic.[39,40]

$$C(^3P) + C_5H_6 \rightarrow C_2H_2 + CH_2{=}CHC{\equiv}CH(T) \qquad (1)$$
$$\Delta H \simeq 10 \text{ kcal}$$

However, fission of the initial adduct into two radicals will conserve spin and is energetically allowed

$$C(^3P) + C_5H_6 \rightarrow C_2H + C_4H_5 \qquad (2)$$
$$\Delta H = -19 \text{ kcal}$$

Insofar as reaction 2 contributes to acetylene formation, the acetylene formed from a mixture of hydrogenated and deuterated substrates would be isotopically mixed. An analogous reaction may be in part responsible for the high yield of mixed acetylenes from hydrogenated and deuterated cyclopropanes[41] since such a fission is highly exothermic, particularly for thermal $C(^1D)$ atoms and for hot atoms in general.

The changes in yield of diacetylene under various experimental conditions show many similarities to those of acetylene. Its formation is also endoergic if arising directly from a spin conserved $C(^3P)$ reaction.[40,42]

$$C(^3P) + C_5H_6 \rightarrow HC{\equiv}CCCH + C_2H_4(T) \quad (\Delta H \simeq 40 \text{ kcal})$$
$$\text{or} + C_2H_2(T) + H_2 \quad (\Delta H \simeq 20 \text{ kcal})$$

It can proceed, however, via decomposition to radicals followed by H atom transfer. The increase in diacetylene yield on going from neon to xenon moderator indicates that it can in fact be formed from $C(^3P)$ atoms as well as from singlets.

Formation of the C_6H_6 Products. The C_6H_6 products can be divided into those having a ring structure, benzene and fulvene, and the open chain hexadienyne isomers. In the cyclic group in unscavenged systems, fulvene decreases sharply on moderation, while benzene is little affected. On addition of oxygen benzene yields are decreased somewhat and fulvene yields are not. On the other hand the sum yield of *cis*- and *trans*-1,3-hexadien-5-yne increases with moderation, is little affected by oxygen, and is lowest when xenon is used as a moderator.

The mechanism of the cyclic product formation has been discussed previously as arising through a prefulvene bicyclo[3.1.0]hex-2-ene diradical resulting from either C-H insertion or C=C addition.[16,20,35] Similarly, 1,3-hexadien-5-yne can be formed by several routes which have the common feature of introducing the central double bond between two atoms whose initial stereochemistry is defined by the cyclopentadiene molecule rather than by the reaction intermediate.[19,20] The cis geometry of the parent molecule is, therefore, favored in the products.

Formation of both groups of products involves concerted *intra*molecular rearrangements. Such mechanisms should be particularly favorable for an adduct formed by a singlet carbon atom since its paired spins permit facile formation of bonds in the last step of the reaction. The low hexadienyne yields with xenon moderation imply that $C(^3P)$ atoms do not in fact form these products as efficiently as do singlets. This conclusion is also consistent with the preservation of cis stereochemistry noted above and with the lack of an oxygen effect in the pure and moderated systems. The benzene yield data indicate formation by two routes, one of which is oxygen sensitive. Thus benzene may come in part from reaction of a $C(^3P)$ atom to give a triplet intermediate which oxygen intercepts in some way, or from a route involving a scavengable radical. Since the fulvene yield is unaffected by oxygen it presumably arises only through reaction of a singlet atom.

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(1) (a) Texas A&M University; (b) Haverford College.
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High-Temperature Ion–Molecule Chemistry. A Kinetic Study of Gas-Phase Reactions of Magnesium Atoms with D_3^+, Methanium, Ammonium, and *tert*-$C_4H_9^+$ Ions

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Abstract: An apparatus is described for experimental investigations of ion–molecule reactions of metal vapors. The technique is applied to a study of charge and proton transfer reactions of D_3^+, CH_5^+, CH_4D^+, CD_4H^+, CD_5^+, $NH_nD_{4-n}^+$, and *tert*-$C_4H_9^+$ with Mg atoms. D_3^+ reacts with Mg(g) exclusively by a charge-transfer process. Methanium ions react with Mg(g) by charge- and proton-transfer mechanisms. Ammonium ion and *tert*-$C_4H_9^+$ react with Mg(g) by proton transfer. A lower bound of 8.37 eV is set on the proton affinity of the Mg atom. The bimolecular rate constant for the reaction of D_3^+ with Mg(g) and the composite rate constant for the reaction of CH_4D^+ with Mg(g) have been obtained from ion intensity data and ion residence times estimated from rate constants for known reactions ($k = 1.6 \pm 0.4 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} and $1.4 \pm 0.4 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, respectively). Some mechanistic implications are drawn from kinetic measurements on the reaction of CH_4D^+ with Mg(g).

Current experimental research in gas-phase ion–molecule chemistry is generally limited to studies of substances with adequate volatility for operation at ordinary temperatures. For studies of ion–molecule reaction of metal atoms, high-temperature conditions are necessary and the technology for this type of investigation has not been fully developed. In this paper we report results of a "high-temperature" investigation of ion–molecule reactions of Mg(g) with a series of charge and proton transfer reagents including D_3^+, CH_5^+, CH_4D^+, CD_4H^+, CD_5^+, $NH_nD_{4-n}^+$ ($n < 4$), and *tert*-$C_4H_9^+$. The relative simplicity of the chemistry in these systems offers opportunity for examination and study of the fundamental aspects of processes occurring in ion–molecule reactions.

Experimental Section

The mass spectrometer used in these studies was constructed from a quadrupole mass filter from an EAI Quad 150A residual gas analyzer. The ion detector was a 14-stage electron multiplier. The ion source, capable of operating at a temperature as high as 900 °C, is illustrated in Figure 1. The ion–molecule reaction chamber was constructed entirely of stainless steel (type 304). The central section consisted of a piece of thin walled stainless steel tubing, 0.75-in. × 0.75-in. o.d. The top and bottom sections of the source were welded with vacuum tight seams to the main body of the source. A gas inlet tube was constructed from a piece of stainless steel tubing, 1.875-in. × 0.25-in. o.d. The electron entrance aperture and the ion exit aperture were 0.025-in. in diameter. The electron entrance aperture was located 1 cm below the ion exit aperture. The base of the source inlet stem was connected through a copper gasket to a stainless steel mounting plate. The source was electrically insulated from ground by a ceramic feed-thru. For most experiments the source was maintained at a potential of +22.5 V, and the drawout potential was held at −90 V. The filament used for the electron beam source was constructed from a piece of 0.001-in. × 0.025-in. rhenium ribbon. The electron accelerating voltage was set at −140 V with respect to the source. A repeller electrode was not employed in these experiments.

The source was heated radiatively from a spiral-shaped heating filament formed by stranding three 0.030-in. annealed tantalum wires. This filament was heated electrically by a set of transformers capable of delivering 190 A at 15 V. It was found that an output of 4 V and 35 A was sufficient to heat the source to 350 °C with constant temperature regulation. With the heating filament off, the ambient temperature reached 80 °C by radiation from the electron beam filament. A water-cooled grounded plate was located between the source and the mass filter assembly. This served as a heat shield to prevent heating of the quadrupole rods and as a collector of magnesium which had effused from the source. The temperature of the reactor was measured with a chromel-alumel thermocouple spot-welded to the base of the source. The thermocouple readings were calibrated against the melting points of indium and tin. The uncertainty in temperature was found to be ±3 °C.

Since the measurement of source pressure is an important quantity in these experiments, a series of flow calibration experiments were performed to correlate the source pressure with the pressure at the gas inlet line. A known quantity of gas was leaked into the source through a Nupro B-4MG metering valve for a known period of time. The pressure at the inlet was monitored with a McLeod gauge. Assuming the gas flow from the source is effusive, the gas pressure inside the source was calculated from the flow rate, the source temperature, and the standard effusion equation. For H_2 and D_2, a linear relationship was found between the inlet and source pressure to about 200 μm. For source pressures above 200 μm, some departure from linearity in the calibration curves was noted. However, most of the quantitative data reported in this paper were obtained from measurements at source pressures between 50 and 200 μm.

Magnesium was placed in the source as thin strips of metal in a configuration that did not block the ion exit and the electron entrance beams. In the absence of a reagent gas, Mg^+ was observed as the major ion in the spectrum. An ion signal of Mg_2^+, approximately 1% of the Mg^+ intensity, was also observed. As we note in Figure 2, the intensity of Mg^+ paralleled the temperature dependence of magnesium vapor (from JANAF tables[1]). The pressure of magnesium within the source was independently calibrated by measuring the rate of effusion of magnesium at 416 °C over a period of several hours. It was found that the vapor pressure of Mg at this temperature was about 10% higher than that calculated from the data in JANAF tables.[1] For a second method of calibration, a low pressure of Ne gas was introduced into the source and the relative intensities of Mg^+ and Ne^+ were recorded