Reactions of Carbon Vapor. IV. Reactions of Metastable Carbon Atoms (^1S) with Olefins[1,2]

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Abstract: Carbon atoms have been produced in a low-intensity carbon arc under high vacuum, a method which yields a mixture of ground-state (^3P) and metastable excited-state species (^1D and ^1S). Using a 16-v (ac) arc, the metastables are the most abundant. The chemistry of the ^1S species in reactions with olefins is reported here; it reacts with one molecule of olefin by insertion into the double bond to form an allene.

We have previously reported the reactions of olefins with ground-state (^3P) carbon atoms produced in a low intensity carbon arc under high vacuum.[4-6] We now report on the reactions of these olefinic substrates with carbon atoms in the metastable excited ^1S state.

The ^1S state of atomic carbon is known to lie 2.7 ev above the ground state.[7] Yilmaz has predicted the radiative half-life of ^1S carbon atoms on purely theoretical bases[8] to be 2 sec for the process $^1S_0 \rightarrow {}^1D_2$. Calculations using the Boltzmann equation

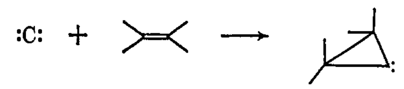
$$(n_{^1S}/n_{^3P}) \propto e^{-2.7\text{ev}/kT}$$

would indicate that at an arc temperature of 5000°K much less than 1% of the vaporized atomic carbon would be in the ^1S state. However, Ornstein, *et al.*,[9] and later Mason[10] found that the distribution among excited states of species Ba[9], Zn[9], CN[10] in a low-pressure arc is not described by the Boltzmann relation. Electronic excitations greatly in excess of that predicted from the Boltzmann equation were observed. The explanation given was that excitation was caused by electron bombardment in the absence of an equilibrating medium, *e.g.*, air. This mechanism of excitation has been demonstrated to apply in arc and hot-filament vaporizations of carbon species (unpublished results).

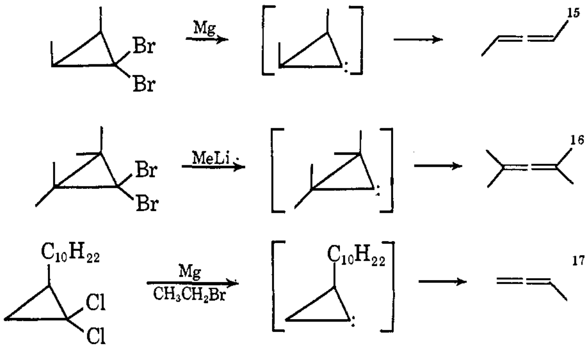
In our system where the pressure in the region of the arc is $\sim 10^{-4}$ torr (mean free path of ~ 50 cm), one might expect significant quantities of atomic carbon in the ^1S state to be produced.

The reactions of ^{11}C, produced by nuclear transformation processes, with ethylene have been extensively studied.[11-14] In this system allene has been found to be an important product (18%). However, owing to difficulties previously discussed,[6] it is not possible to define which electronic state of carbon is producing the allene.

By analogy with other carbene reagents, a carbon atom would be expected to add to the double bond of an olefinic substrate producing a cyclopropylidene intermediate.



A major reaction pathway for cyclopropylidenes prepared in solution is rearrangement to allenic products.[15-18]



However, since these species were generated in the presence of strong Lewis bases in the reaction media, they were probably complexed by these bases and were not "free carbenes." In the system used for our work the species would be expected to be "free" as there is only hydrocarbon present.

This paper describes the reactions of ^1S carbon atoms with olefins; the only products in significant amounts are the allenes resulting from insertion of the carbon atom into the double bond.

Method

The carbon arc and molecular flow system used in this study were as previously described.[19] In all of these

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[1] For paper III in this series, see: P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **88**, 4883 (1966).

[2] A preliminary communication has appeared: P. S. Skell and R. R. Engel, *ibid.*, **87**, 1135 (1965).

[3] National Science Foundation Cooperative Graduate Fellow, 1963–1966.

[4] P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).

[5] P. S. Skell and R. R. Engel, *ibid.*, **87**, 2493 (1965).

[6] R. R. Engel and P. S. Skell, *ibid.*, **88**, 3749 (1966).

[7] G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, N. Y., 1944, p 142.

[8] H. Yilmaz, *Phys. Rev.*, **100**, 1148 (1955).

[9] L. S. Ornstein, H. Brinkmann, and A. Beunes, *Z. Physik*, **77**, 72 (1932).

[10] R. C. Mason, *Physica*, **5**, 777 (1938).

[11] C. MacKay, P. Polack, H. E. Rosenberg, and R. Wolfgang, *J. Am. Chem. Soc.*, **84**, 308 (1962).

[12] J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 959 (1964).

[13] M. Marshall, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4741 (1964).

[14] J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964).

[15] W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

[16] L. Skattebøl, *Tetrahedron Letters*, 167 (1961).

[17] T. L. Logan, *ibid.*, 173 (1961).

[18] L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963).

[19] P. S. Skell, L. D. Wescott, Jr., J. P. Golstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965).

reactions a 16-v (ac) arc was employed which produced a mixture of ground- and excited-state carbon atoms as well as triatomic carbon. The arc current shows rapid fluctuations in intensity going as high as 100 amp but averaging about 40 amp. Time-delay reactions were run as previously described using a neopentane matrix.[2,6]

The allenic products were separated from the excess substrate by fractional distillation using a 36 × 0.5 in. vacuum-jacketed column packed with glass helices, followed by vacuum distillation and gas phase chromatography. They were identified by their infrared and mass spectra, measured on the materials collected from the gas chromatograph. A 22-ft column (0.25 in. diameter) of 30% hexamethylphosphorictriamide on Fisher Columnpak was used.

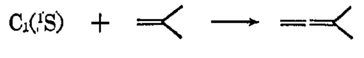
Results and Discussion

A. Electronic State of Carbon Atoms Leading to Allenes. Time-Delay Studies. In carbon vapor reactions of olefins using continuous arcing with continuous deposition of substrate, the allene, resulting from insertion of the carbon atom into the double bond, was formed to the extent of ~45% of the carbon atom addition product (*vide infra*), the remainder being distributed among a number of products.

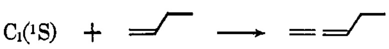
By depositing a layer of neopentane (~2 g) on the liquid nitrogen cooled walls of the reaction flask and then operating the carbon arc for a short period of time (10 sec) ~0.3 mg of vaporized carbon can be deposited. With this amount of carbon, diffusion into the matrix evidently occurs. If ~5 g of reactive olefin is added 15 sec later, causing temporary liquefaction of the system, all products found in the "continuous" reaction are present, *except for the allenic product which has essentially disappeared.* The carbon atom precursors for allenes have decayed to a lower electronic state in this time. By noting the amount of allene present after a 10-sec delay, ~2%, the half-life of this precursor has been estimated at ~2 sec.[2]

It is reasonable to assign to the allene-forming carbon atoms the designation of ^1S on the following bases: (a) the decay of this species of excited carbon increases the amounts of products resulting from both ground-state (^3P) and another excited-state (^1D) carbon species; (b) this species brings higher energy to the transition state (as is shown by the products, allenes *vs.* cyclopropane ring formation) than the ^3P and ^1D state species (*vide infra*).

B. Reaction of ^1S Carbon Atoms with Isobutylene. The reaction of $C_1(^1S)$ with isobutylene formed, as the only product which can not be attributed to ^3P and ^1D, 3-methyl-1,2-butadiene which was identified by comparison of its infrared and mass spectra with those of the known material. The 3-methyl-1,2-butadiene made up 40 mole % of the atomic carbon reaction products using a 16-v (ac) carbon arc.

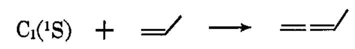


C. Reaction of ^1S Carbon Atoms with 1-Butene. The reactions with 1-butene yielded a single product, 1,2-pentadiene, which could be attributed to the $C_1(^1S)$ state. It was identified by comparison of its infrared and mass spectra with those of the known compound.

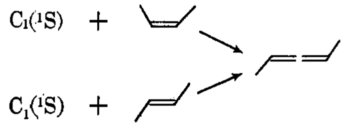


In the reaction using a 16-v (ac) carbon arc, the 1,2-pentadiene made up 45 mole % of the total carbon atom reaction product.

D. Reaction of ^1S Carbon Atoms with Propylene. The sole product attributable to the reaction of ^1S carbon atoms with propylene was the 1,2-butadiene which accounted for 45 mole % of the total product from carbon atom reactions using a 16-v (ac) arc. It was identified by comparison of its infrared and mass spectra with those of the known compound.



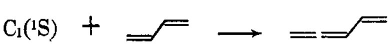
E. Reaction of ^1S Carbon Atoms with *cis*- and *trans*-2-Butene. From the reaction of either *cis*- or *trans*-2-butene with ^1S state carbon atoms, 2,3-pentadiene is the only product, from *cis*-2-butene 42 mole % and from *trans*-2-butene 43 mole % of the total carbon atom products.



The 2,3-pentadiene was identified by comparison of its infrared and mass spectra with those of the known material.

The earlier report[4] of this reaction indicated two products from ^1S carbon atoms, 2,3-pentadiene and an unidentified substance. The latter, on separation from the other components of this distillation fraction, proved to be 2,3-pentadiene; it had been trapped with the higher boiling reaction products, and its identity was not recognized immediately because different gas chromatography columns were used for further analysis of the low- and high-boiling fractions.

F. Reaction of ^1S Carbon Atoms with 1,3-Butadiene. The reaction of 1,3-butadiene with ^1S carbon atoms yielded a product not found in ^3P and ^1D reactions, a single substance easily separated from the excess substrate and assigned the structure of 1,2,4-pentatriene on the basis of its infrared and mass spectra. Its infrared spectrum corresponded to that reported for 1,2,4-pentatriene[20] and its low-voltage mass spectrum showed a parent peak at *m/e* 66 corresponding to C_5H_6. Using a 16-v (ac) arc 1,2,4-pentatriene comprises 47 mole % of the total carbon atom reaction products.



G. Competition Reactions of Olefins for ^1S Carbon Atoms. Competition reactions were run by equilibrating a known mixture of the olefins in the vacuum line and depositing this mixture on the cooled walls of the reaction flask while arcing. The reaction mixture was handled in the usual manner; product analysis was done by gas chromatography. The relative rates can then be calculated from the relative amounts of products. The results are shown in Table I. Although the differences are small, the order of reactivities

(20) L. Miginiac, *Compt. Rend.*, 247, 2156 (1958).

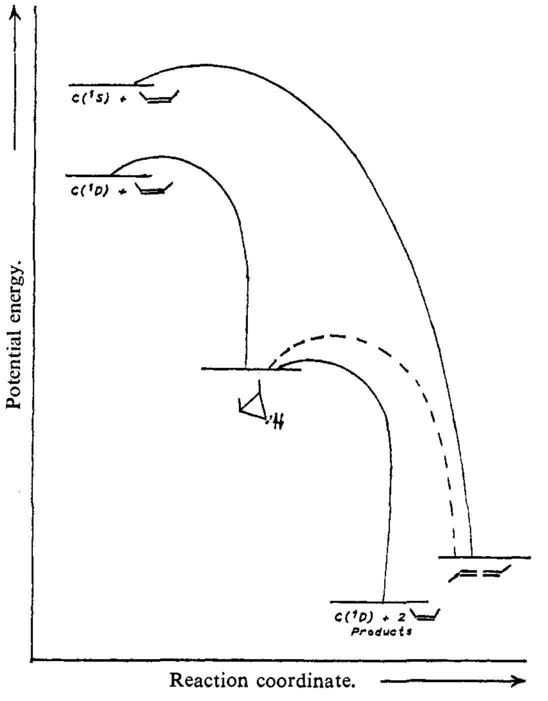
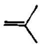
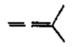
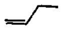


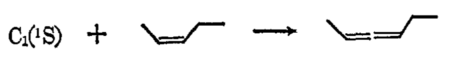
Figure 1. Energy profile for reaction of atomic carbon with olefins.

is in accord[21] with the proposal of a singlet attacking species of low selectivity.[22,23]

Table I

Olefin	Rel rate of reaction with $C_1(^1S)$	Product
	1.44	
	1.06	
	1.92	
	5.21	
	(1.00)	

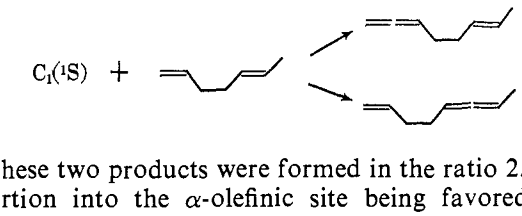
H. Reaction of ^1S Carbon Atoms with a Mixture of 1-Pentene and *cis*-2-Pentene. The reaction of ^1S carbon atoms with a mixture of 1-pentene and *cis*-2-pentene (ratio of 1.35:1.0) yielded two products, 1,2-hexadiene and 2,3-hexadiene, in the ratio 3.1:1.0. They were identified by comparison of their infrared and mass spectra with those of the known compounds.



These two products accounted for 25% of the *total* carbon vaporized using a 16-v (ac) arc (38% of the atomic carbon).

This result indicates that the ^1S carbon atom reacts 2.3 times as rapidly with the α-olefinic site as with the internal olefinic site.

I. Reaction of ^1S Carbon Atoms with 1,5-Heptadiene. From the reaction of ^1S atomic carbon with 1,5-heptadiene (one peak on gas chromatograph; presumably one isomer), two products were obtained, 1,2,6-octatriene and 1,5,6-octatriene, which were identified by their infrared and mass spectra.



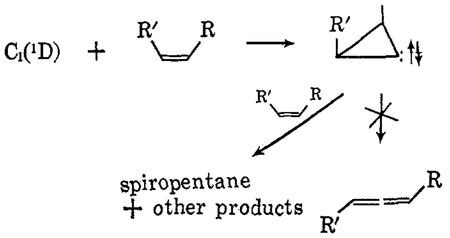
These two products were formed in the ratio 2.7:1.0, insertion into the α-olefinic site being favored over insertion at the internal olefinic site. This result compares favorably with that for a mixture of 1-pentene and *cis*-2-pentene (*vide supra*).

Using a 16-v (ac) arc, these two products accounted for 28% of the *total* carbon vaporized (42% of the atomic carbon).

J. Conclusions. In the time-delay experiments, carbon deposited on a neopentane matrix, using a delay of 15 sec, the only substances not present in the product mixtures being the allenes. After 15 sec most of the ^1D atoms are still present; they do not react with olefins to form allenes. Moreover, the decay of the precursor of the allenes enhances the yields of all of the ^1D products[24] by approximately the same factor, *i.e.*, their total yields are increased but they remain in about the same proportion, except for the spiropentanes (also derived from ^3P).

Thus, the ^1S carbon atoms are the only species leading to the formation of allenes. Also, it seems as if the allenes account for all or almost all of the ^1S carbon produced. Small amounts of the ^1D products may be formed from ^1S carbon atoms but certainly not large quantities, unless they are coincidentally produced in the same proportions as from the ^1D atoms. If such were the case, it would necessitate a common intermediate for the reactions of ^1S and ^1D carbon atoms which is not in accord with the evidence (*vide infra*).

It has been established that the reaction of ^1D carbon atoms with olefinic substrate leads to the formation of a singlet cyclopropylidene intermediate.[25] This intermediate then reacts with a second molecule of olefin leading to products. *None* of this intermediate rearranges to allene under our reaction conditions: liquid nitrogen cooling and a high concentration of olefin.



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[21] The high relative reactivity of 1-butene is anomolous. Although in the other cases (sections H and I) the α-olefinic site is attacked more readily than the internal site, the differences are not as great as here. We have no explanation for this unusual reactivity.

[22] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956).

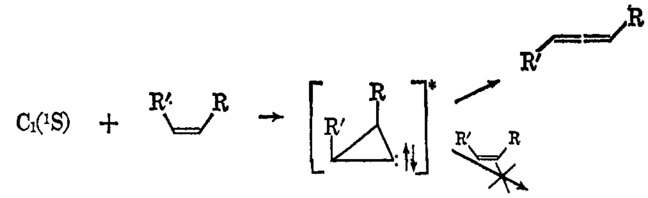
[23] W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

[24] Reports on the details of the reactions of the ^1D state will be presented elsewhere.

[25] Reference 2 and unpublished results.

The energy of activation for rearrangement must be greater than the energy of activation for addition to another molecule of olefin (Figure 1). At room temperature in solution rearrangement of singlet cyclopropylidenes to allenes takes place readily,[15–18] in competition with olefin addition.

The ^{1}S atom addition to an olefin should have a formal resemblance to the ^{1}D addition, the major difference being the 33-kcal/mole extra energy brought to the transition state by the higher energy atom. If this hot singlet cyclopropylidene were an intermediate of lifetime sufficient to permit trapping by olefins, the yields of allenes would vary with changing the substituents R and R′ since these substituents would be expected to influence the rate of ring opening to the allene. This is not the case, the yields of allenes being 40–47% with the variation in substituents reported here. Thus it follows the hot singlet cyclopropylidene is not a trappable intermediate. For ^{1}S + olefin the cyclopropylidene configuration may only represent a transition state.



Since the activation energy for ring opening of a normal singlet cyclopropylidene (from ^{1}D) is small, the species in the reactions of C$_1$(^{1}S) may bypass this configuration and go directly to the allene; the hot species may not be able to lose its surplus energy fast enough to lead to a thermally equilibrated cyclopropylidene intermediate.

The relative reactivities of olefins in competition for ^{1}S atoms is not highly informative since the spread of reactivities is small. Perhaps it is most significant that butadiene is less reactive than monoolefins, ruling out transition states with radical character.

An interesting and disturbing feature of these matrix systems must relate to their physical nature. The striking differences in reactivity of CH$_3$ groups for ^{1}S insertions in neopentane and isobutane was noted earlier in this study. Perhaps for related reasons the double bond of 1-butene is more reactive than those in propene, 1-pentene, and 1,5-heptadiene (terminal bond). No electronic rationalization of this effect is apparent.

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research and the Army Research Office (Durham).

A Simple Theory for Predicting the Effects of Substituent Changes on Transition-State Geometry[1,2]

Edward R. Thornton

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania. Received December 5, 1966

Abstract: A simple technique for analyzing the effects of substituent changes on transition-state geometry is outlined. The basic idea is to consider the effects of substituents as linear perturbations of the vibrational potentials for the normal coordinate motions both parallel to and perpendicular to the reaction coordinate motion. Effects parallel to the reaction coordinate then correspond closely to predictions based on "Hammond's postulate," while effects perpendicular to the reaction coordinate introduce a previously neglected effect which is expected to be smaller than the parallel effect in many, but not all, cases. Examples of application of the theory to S$_N$2, E2, S$_N$1, and other reaction mechanisms are presented. The theory is discussed in terms of the forces on nuclei predicted by the Hellmann–Feynman theorem. Using precise potential energy curves for diatomic molecules calculated by computer from spectroscopic data, it is concluded that the approximation that the perturbation is linear, if a relatively small substituent change is made, is probably a very good one. The result is: (1) any substituent change which makes an increase (decrease) in the normal coordinate X of a molecule or transition state more difficult will lead to a perturbed equilibrium geometry in which X is decreased (increased) if the force constant for X motion is positive, but in which X is increased (decreased) if the force constant for X motion is negative; (2) the effect of a substituent change on a normal coordinate motion can be predicted from the effect of the substituent on the reacting bond(s) nearest to the substituent and involved in that motion; (3) when two reacting bonds are equidistant from the substituent, the effect of the substituent should be nearly equal on both if both are of the same strength in the unperturbed transition state, but should be greater on the stronger than on the weaker (and greater on a σ than on a π bond); (4) an electron-supplying (withdrawing) substituent should make a bond more difficult to extend (compress) if attached to the basic, *i.e.*, more electronegative atom, end of the bond, but more difficult to compress (extend) if attached to the acidic, *i.e.*, less electronegative atom, end of the bond; (5) the substituent effect on geometry is the sum of individual effects on each normal coordinate.

Since substituent effects upon a stable molecule's structure, energy, and other properties are reasonably well understood in a qualitative way, it is fascinating to try to apply this qualitative understanding to predict the effects of the substituents on the structure, energy, and other properties of transition states, or

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[1] Supported in part by the Atomic Energy Commission (Contract No. AT(30-1)-3041) and by the National Science Foundation (Grants No. GP-2937 and GP-6047).

[2] *Cf.* (a) L. J. Steffa and E. R. Thornton, to be published; (b) G. J. Frisone and E. R. Thornton, to be published.