dull material over the course of 30 min. CPMAS ^{13}C NMR: 135, 127 ppm. Metallic silver deposited in the film precluded infrared analysis.

Isomerization of PBV with ZnI_2. ZnI_2 has a limited solubility in THF, and hence a saturated solution was used with excess solid ZnI_2. This isomerization is slow and after 2 h the PBV films were red. After soaking in the ZnI_2 solution for 24 h, the films were black and shiny. These films were then rinsed multiple times with THF and were strong and flexible. Infrared: 3100 (s, sh), 2900 (m, br), 1410 (s, vbr), 1395 (w, sh), 1005 (s, vbr), 760 (s, vbr) cm^{-1}.

Isomerization of PBV with $(RhCl(COD))_2$. PBV films were soaked in a 1% solution of $(RhCl(COD))_2$ in THF for 5 days. The films slowly became red over this period and were brittle. These films were rinsed multiple times with THF. Infrared: 3090 (s, sh), 2900 (s, br), 1715 (s, vbr), 1650 (m, sh), 1430 (m, sh), 995 (s, br), 970 (s, br), 866 (s, br), 740 (s, br), 685 (s sh) cm^{-1}.

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Supplementary Material Available: Figures showing ^1H NMR of PBV produced with I and III and of PBV:PN block copolymer, thermogravimetric and thermomechanical analysis of PBV, CPMAS ^{13}C NMR of PBV after storage, and IR spectra of PPA (5 pages). Ordering information is given on any current masthead page.

Some Reactions and Properties of Molecular C_2. An Experimental and Theoretical Treatment

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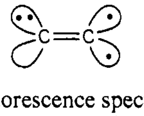
Contribution from the Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802, and the Department of Chemistry, Auburn University, Auburn University, Alabama 36849. *Received February 1, 1988. Revised Manuscript Received December 26, 1988*

Abstract: Diatomic carbon, C_2, reacts with propylene and (*E*)- and (*Z*)-2-butene in the condensed phase at 77 K. Products can be rationalized by a mechanism involving initial addition of C_2 to the alkene to generate a 1,4-diradical. This diradical may then either abstract hydrogens or add another alkene molecule to give a 1,6-diradical which disproportionates to an enyne. Thus, reaction of C_2 with propene gives 1-pentyne, 3-methyl-1-butyne, 4-methylhept-6-en-1-yne, 6-methylhept-1-en-4-yne, and oct-1-en-4-yne. Ab initio calculations at the HF/3-21G level predict that both $^1C_2$ and $^3C_2$ will add to ethylene without barrier. At the MP2/6-31G*//3-21G level, the triplet adduct is calculated to be more stable than $^3C_2$ and ethylene by 46.0 kcal/mol. The reactions of $^1C_2$ and $^3C_2$ with methane and hydrogen have also been investigated theoretically.

Diatomic carbon has been the subject of theoretical,[1-5] spectroscopic,[6-8] and kinetic studies,[9-17] but little is known of the mechanisms and products of its reactions. Ballik and Ramsay[6] have demonstrated that there are two low-lying electronic states of C_2, the singlet ($^1\Sigma_g$) and the triplet ($^3\Pi_u$), the triplet being only slightly above the ground state. Thus any thermal generation of C_2 will inevitably produce triplet–singlet mixtures. A theoretical calculation[1a] indicates the structure $\cdot C{\equiv}C\cdot$ for the ground state singlet and



for the triplet.[1b] With fluorescence spectroscopic methods, it has proved possible to follow the decay of both the lowest singlet and triplet states of C_2 in the presence of various substrates and to obtain kinetic information.[9-17]

Skell and co-workers have reported the products in the reaction of diatomic carbon at low temperature, in condensed phase, with alcohols,[18] carbonyl compounds,[19,20] alkenes,[21] alkanes, and ethers.[22,23] The known reactions of C_2 with C–H bonds include abstraction to generate acetylene, in which the hydrogens can come from the same carbon or from different carbons, and formation of cumulenes in what is formally a double C–H insertion. One of us has previously reported that C_2 reacts with C–C double bonds to generate vinylidene intermediates which subsequently add another molecule of alkene to produce alkylidenecyclopropanes.[21] In the present study, the reaction of C_2 with alkenes has been reinvestigated since the original structures of the addition products were based on primitive methods (by current standards) and were

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[†] Pennsylvania State University.

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(1) (a) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1972**, *94*, 8293. (b) Goddard, W. A., III Private communication.

(2) Lengsfield, B. H.; Phillips, D. H.; Schug, J. C. *J. Chem. Phys.* **1981**, *74*, 5176.

(3) Langhoff, S. R.; Sink, M. L.; Pitchard, R. H.; Kern, C. W.; Strickler, S. J.; Boyd, M. J. *J. Chem. Phys.* **1977**, *67*, 1051.

(4) Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Chem. Soc.* **1971**, *93*, 808.

(5) Jug, K.; Bursian, B. M. *Theor. Chim. Acta* **1979**, *52*, 341.

(6) Ballik, E. A.; Ramsay, D. A. *J. Chem. Phys.* **1959**, *31*, 1128.

(7) Ballik, E. A.; Ramsay, D. A. *Astrophys. J.* **1963**, *137*, 84.

(8) Herzberg, G. *Spectra of Diatomic Molecules*; D. Van Nostrand: Princeton, NJ; 1950.

(9) Reisler, H.; Mangir, M. S.; Wittig, C. *Chem. Phys.* **1980**, *47*, 49.

(10) Reisler, H.; Mangir, M. S.; Wittig, C. *J. Chem. Phys.* **1980**, *73*, 2280.

(11) Mangir, M. S.; Reisler, H.; Wittig, C. *J. Chem. Phys.* **1980**, *73*, 829.

(12) Pasternack, L.; Pitts, W. M.; McDonald, J. R. *Chem. Phys.* **1981**, *57*, 19.

(13) Pasternack, L.; Baronavski, A. P.; McDonald, J. R. *J. Chem. Phys.* **1980**, *73*, 3508.

(14) Pasternack, L.; McDonald, J. R. *Chem. Phys.* **1979**, *43*, 173.

(15) Filseth, S. V.; Hancock, G.; Fournier, J.; Meier, K. *Chem. Phys. Lett.* **1979**, *61*, 288.

(16) Donnelly, V. M.; Pasternack, L. *Chem. Phys.* **1979**, *39*, 427.

(17) Reisler, H.; Mangir, M.; Wittig, C. *J. Chem. Phys.* **1979**, *71*, 2109.

(18) Skell, P. S.; Harris, R. F. *J. Am. Chem. Soc.* **1966**, *88*, 5933.

(19) Skell, P. S.; Plonka, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 5620.

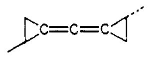
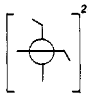
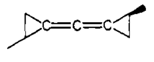
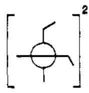
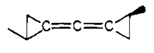
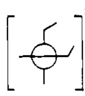
(20) Skell, P. S.; Plonka, J. H.; Harris, R. F. *Chem. Commun.* **1970**, 689.

(21) Skell, P. S.; Villaume, J. E.; Fagone, F. A. *J. Am. Chem. Soc.* **1972**, *94*, 7866.

(22) Skell, P. S.; Fagone, F. A.; Klabunde, K. J. *J. Am. Chem. Soc.* **1972**, *94*, 7862.

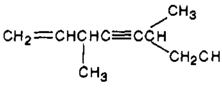
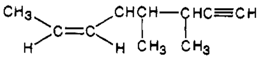
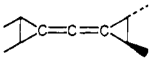
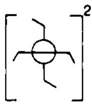
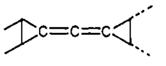
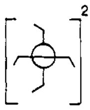
(23) Skell, P. S.; Havel, J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, *6*, 97.

Table I. Results of the Reaction of Carbon Vapor with Propylene

product (in increasing order of retention time)	yield,[a] mol %	prod comp nC_3H_6
$CH_2{=}CHCH{=}CH_2$[25]	8.0	C_1
$CH_3CH{=}C{=}CH_2$[25]	20.2	C_1
$CH_3CH_2CH_2C{\equiv}CH$ (I)	0.61	$C_2 + 2$ H
$(CH_3)_2CHC{\equiv}CH$ (II)	0.35	$C_2 + 2$ H
$CH_2{=}CHCH_2CH_3CHCH_2C{\equiv}CH$ (III)	0.24	C_2
$CH_2CHCH_2C{\equiv}CCH(CH_3)_2$ (IV)	0.60	C_2
$CH_2{=}CHCH_2C{\equiv}CCH_2CH_2CH_3$ (V)	0.99	C_2
  [24]	2.7	C_3
  [24]	2.7	C_3
  [24]	1.2	C_3

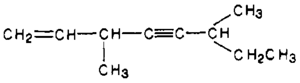
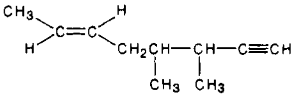
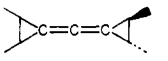
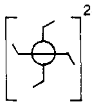
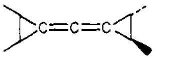
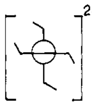
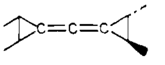
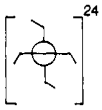
[a] All yields are based on total carbon vapor produced.

Table II. Results of the Reaction of Carbon Vapor with (*Z*)-2-Butene

product (in increasing order of retention time)	yield,[a] mol %	prod comp $2C_4H_8$
 VIA + VIB	1.33	C_2
 VIIA VIIB	0.47	C_2
  [24]	0.49 0.44	C_2 C_3
  [24]	4.63	C_3

[a] All yields are based on total carbon vaporized.

Tal le III. Results of the Reaction of Carbon Vapor Reaction with (*E*)-2-Butene

product (in increasing order of retention time)	yield,[a] mol %	prod comp $2C_4H_8$
 VIA + VIB	0.72	C_2
 VIIIA VIIIB	0.19 0.19	C_2 C_2
  [24]	5.1	C_3
  [24]	1.3	C_3
  [24]	0.25	C_3

[a] All yields are based on total carbon vaporized.

complex enough to raise some questions regarding the assignments.[21] We now report revised structures for the products of the addition of C_2 to two molecules of alkene. Included also are those products derived from C_1 and C_3.[24,25] In order to gain insight into the mechanism by which C_2 reacts with C–C double bonds and C–H bonds, we have also carried out an ab initio study of the reaction of diatomic carbon with a representative alkene, alkane, and with H_2. These calculations mark the first attempt to correlate theoretical and experimental investigations of the reaction pathways of C_2.

Results

Reaction of Carbon Vapor with Alkenes. Since the mechanism of acetylene formation in the reaction of C_2 with C–H bonds has been previously investigated in detail,[18-20] we have focused our attention on products in which C_2 has added to one or more molecules of alkene. The olefinic substrates used in these studies were propylene, the 2-butenes, and 1,3-butadiene. In each case, a large excess of alkene to carbon (200:1 mole ratio) was employed and careful searches were made on the product mixtures from a number of independently run reactions for compounds containing more carbons than the alkene substrate.

Reaction of Carbon Vapor with Propylene. This reaction yields, as major products, two four-carbon products (C_1 + propylene), two five-carbon products (C_2 + one propylene), three eight-carbon products (C_2 + two propylenes) and three nine-carbon products (C_3 + two propylenes). No seven-carbon products (C_1 + two propylenes) could be detected even after extensive sorting through the very minor products with GC/MS methods. Four-carbon and five-carbon products were first analyzed by GC and GC/MS. The three eight-carbon products were separated and collected by preparative gas chromatography. For each pure compound, structural assignment was made with high-resolution NMR as explained in the Appendix. Product structures and yields are shown in Table I. The products resulting from the reaction of C_2 with one or more propylenes proved to be 1-pentyne, I, 3-methyl-1-butyne, II, 4-methylhept-1-en-6-yne, III, 6-methylhept-1-en-4-yne, IV, and oct-1-en-4-yne, V. The three nine-carbon products could not be separated with preparative gas chromatography; these three compounds were collected together and found with high-resolution NMR to be three diastereoisomers of the previously identified 1,1′-dimethylethanobisallene.[24]

Reaction with 2-Butenes. The analysis of the products from the reaction of carbon vapor with the isomeric 2-butenes focused mainly on the high-boiling components resulting from two molecules of alkene and C_2 or C_3. Analysis for products resulting from the addition of C_1 to the butenes was not possible due to the difficulty of separating these compounds form the large excess of the 2-butenes employed. In the reaction of carbon vapor with (*Z*)-2-butene, the major products isolated are three 10-carbon products (C_2 + two butenes) and two 11-carbon products (C_3 + two butenes). The three 10-carbon products were separated and collected by preparative gas chromatography. Each pure compound was assigned a unique structure from its high-resolution NMR spectrum, as explained in the Appendix. These C_2 products proved to be 3,6-dimethyloct-1-en-4-yne, VI, and the two diastereomers of (*Z*)-3,4-dimethyloct-6-en-1-yne, VII. The two previously identified[24] 11-carbon products were analyzed as a mixture with high-resolution NMR (explained in the Experimental Section) to be diastereoisomers of 1,2,1′,2′-tetramethylethanobisallene. Results are shown in Table II.

In the reaction of carbon vapor with (*E*)-2-butene, the major products obtained are three 10-carbon products and three 11-

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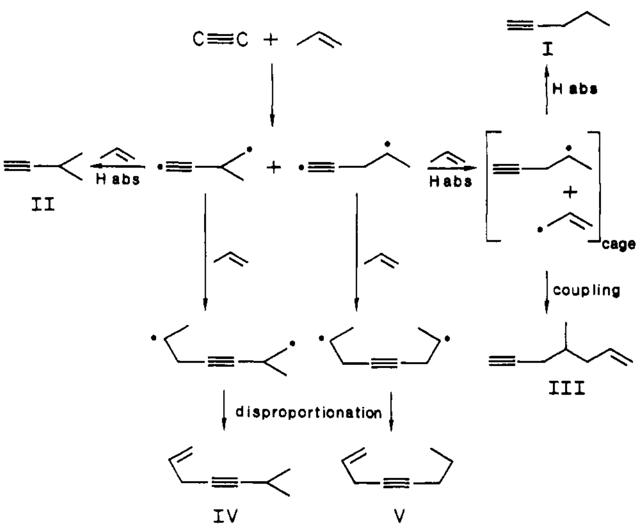
(24) Skell, P. S.; Wescott, L. D.; Golstein, J. P.; Engel, R. R. *J. Am. Chem. Soc.* **1965**, *87*, 2829.

(25) Skell, P. S.; Villaume, J. E.; Plonka, J. H.; Fagone, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 2699.

Scheme I. Reactions of C_2 with Propylene



carbon products.[24] They were analyzed as before, and the results are shown in Table III. The C_2 products were VI and the two diastereomers of (*E*)-3,4-dimethyloct-6-en-1-yne, VIII.

Reaction with 1,3-Butadiene. The reaction of carbon vapor with 1,3-butadiene yielded the previously identified three diastereoisomers of 1,1′-diethenylethanobisallene;[24] no 10-carbon products (C_2 + two butadienes) were detected.

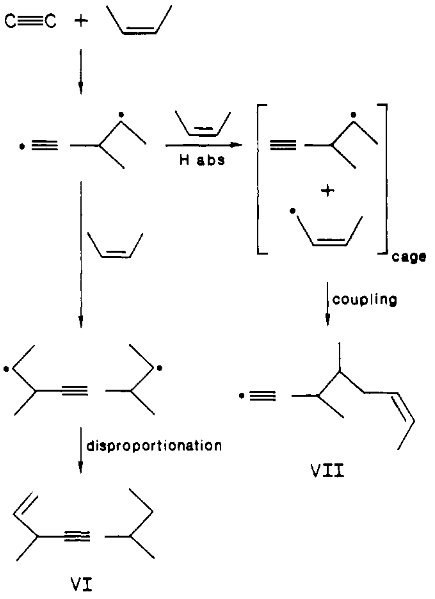
Discussion

In our earlier work, carbon was vaporized with low-voltage (12–15 V), high-current (50–200 A) arcing attained by touching, in vacuum, carbon pieces supplied with appropriate current source. The present study used high voltage (10 kV), low current (110 mA), electrostatically focused electron bombardment of a carbon disc held positive (+10000 V); the electron emitter was at ground potential; this configuration minimized electron bombardment of products and reactants on the wall. Both methods gave the same products with some differences in relative yields. Insofar as the products were analyzed, the previously identified products for C_1[25] and C_3[24] were obtained. It is noteworthy that a small amount of nonstereospecific addition of C_3 to the 2-butenes is observed with this E-gun vaporization, indicative of the presence of some excited-state triplet C_3. This result should be contrasted with the clearly stereospecific additions with thermally produced C_3 and the substantial nonstereospecificity with arc-produced C_3.[24] The addition products of C_2 to alkenes are the same as those reported previously[21] as indicated by their NMR spectra (see Appendix). However, the higher resolution NMR analysis of the present study demonstrates that these products are either alkynes or enynes, with no evidence for the structures containing three-membered rings which were reported earlier.[21]

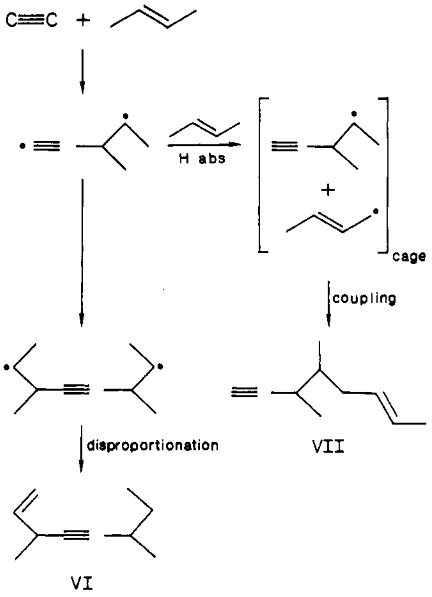
Two types of enynes are produced in the reactions of alkenes with C_2. One has a terminal acetylenic linkage and an alkenic linkage in which the double bond has the same location and stereochemistry as was present in the precursor. For example VII is formed from (*Z*)-2-butene, and VIII is formed from *E*-2-butene. These, respectively, contain a crotyl fragment, $CH_3CH{=}CHCH_2$, in which the double bond has the same configuration as the starting butene. The second product, VI, the same from each of the 2-butenes, contains a rearranged fragment structure, $CH_3CHCH{=}CH_2$. Analogous products are obtained in the propylene reactions, except that they are less revealing of the "rearranged" structure as a consequence of the symmetry in the allyl fragment, $CH_2{=}CHCH_2$.

These products may be rationalized by postulating an initial addition of C_2 to the alkene to generate a 1-alkyne-1,4-diyl biradical, $\cdot C{\equiv}CCC\cdot$, as illustrated in Scheme I for propylene. The 1,4-enynes IV and V result from addition of a second molecule of alkene to the ethynyl radical end of the 1,4-diradical to make a 1,6-diradical. Cyclization of this diradical would lead to a highly strained cyclohexyne. However, an intramolecular disproportionation by hydrogen atom transfer via a transition state resembling cyclooctyne suffers from no such steric proscription. This reaction results in enynes IV and V in the propylene system and "rearranged" enyne VI from either the (*Z*)- or (*E*)-2-butene (see Schemes II and III). It is noteworthy that in no instance does disproportionation involve the C–H bond adjacent to the triple bond (to make a conjugated enyne), ostensibly because this process would have a more strained transition state.

Scheme II. Reactions of C_2 with (*Z*)-2-Butene



Scheme III. Reactions of C_2 with (*E*)-2-Butene



The set of products with the "unrearranged" fragments are 1,6-enynes. It is proposed that the 1,4-diradical reacts with the alkene by abstracting an allylic hydrogen (instead of addition to the double bond), a reaction which should be more than 20 kcal/mol exothermic at the acetylenic radical site. This results in a caged radical pair which on coupling leads to products III, VII, and VIII, the latter two with retention of double bond stereochemistry, as expected from the known relatively slow interconversion of *cis*- and *trans*-crotyl radicals. Alternatively, escape from the cage would ultimately lead to the formation of I. The absence of 10-carbon products in the reaction of carbon vapor with butadiene can be explained by the fact that the diradical 10-carbon adduct of C_2 with two molecules of butadiene cannot

Table IV. Relative Energies (kcal/mol) of C_2 Electronic States at Different Levels of Theory

elec state	config	C–C, Å	HF/6-311G*	MP2/6-311G*	MP3/6-311G*	MP4SDQ/6-311G*	MP4SDTQ/6-311G*	exptl[a]
$^1\Sigma_g^{+}$[b]	$\sigma_u^2\pi_u^4\sigma_g^0$	1.257	0.0	0.0	0.0	0.0	0.0	0.0
$^1\Sigma_g^{+}$[b]	$\sigma_u^2\pi_u^2\sigma_g^2$	1.365	−58.5	30.5	−10.1	11.8	30.6	
$^3\Pi_u$	$\sigma_u^2\pi_u^3\sigma_g^1$	1.308	−59.1	4.7	−25.9	−4.8	9.8	2.0
$^3\Pi_g^-$	$\sigma_u^2\pi_u^2\sigma_g^2$	1.360	−69.5	26.2	−13.5	8.7	28.8	18.4
$^1\Pi_u$	$\sigma_u^2\pi_u^3\sigma_g^1$	1.315	−51.9	14.3	−19.0	1.9	17.4	24.0

[a] Hurley, A. C. *Electron Correlation in Small Molecules*; Academic Press: New York, 1976; p 20. [b] Since both configurations lead to the same $^1\Sigma_g^+$ electronic state, the perturbation expansion from each should converge to the lowest state of that symmetry. The $\sigma_u^2\pi_u^4\sigma_g^0$ occupation is the better configuration to use in the expansion as judged by the lower energy at the fourth order. However, the relative closeness in energy of the two configurations indicates that both will be important in describing the electronic state.

disproportionate but can easily polymerize.

An alternate route to III could involve addition of the biradical to propylene followed by disproportionation. However this route could not occur in the case of the 2-butenes as it would be expected to result in nonstereospecific formation of VII and VIII from both of the 2-butenes.

These schemes seem entirely satisfactory, suffering mainly from the failure to isolate from among the minor GC peaks two products which should be minor ones at best, 3-methyl-hept-6-en-1-yne from the propylene reactions and 3,4,5-trimethyl-hept-6-en-1-yne from the 2-butenes. Gas-phase kinetic studies indicate that the reactions of both singlet and triplet C_2 with C_2H_4 occur with second-order rate constants of 20×10^{10} and 9×10^{10} mol^{-1} s^{-1}, respectively, whereas C_2H_6 reacts with 10×10^{10} and 0.2×10^{10} mol^{-1} s^{-1}, respectively.[10,14,16] Because both states of C_2 react so rapidly with alkenes (according to the present study by addition to the double bond), the formation of these enynes do not provide a means of deciding whether singlet, triplet, or both of these are the precursor of the 1,4-diradicals.

A Theoretical Evaluation of the Reactions of C_2 with H_2, Methane, and Ethylene. In this section, we have attempted to survey theoretically a large number of possible reactions of C_2 with the representative substrates H_2, CH_4, and C_2H_4. In these calculations, which utilized the GAUSSIAN 86 program,[26] geometries were optimized with the 3-21G basis set at the single configurational level with the restricted Hartree–Fock method for closed-shell systems and the unrestricted method for open-shell systems.[27] Single-point calculations were made at various levels of theory up to the MP4SDTQ/6-311G* level for C_2 itself and up to the MP2/6-31G* level for various intermediates and transition states along the closed shell energy surface. The effect of the largest spin contaminant was projected out of the correlation energies for open-shell systems. Vibrational frequencies have been calculated at the HF/3-21G level in order to determine zero-point energies and to confirm the nature of the stationary points. Geometries of relevant intermediates, stationary points, and transition states are shown in Figure 1.

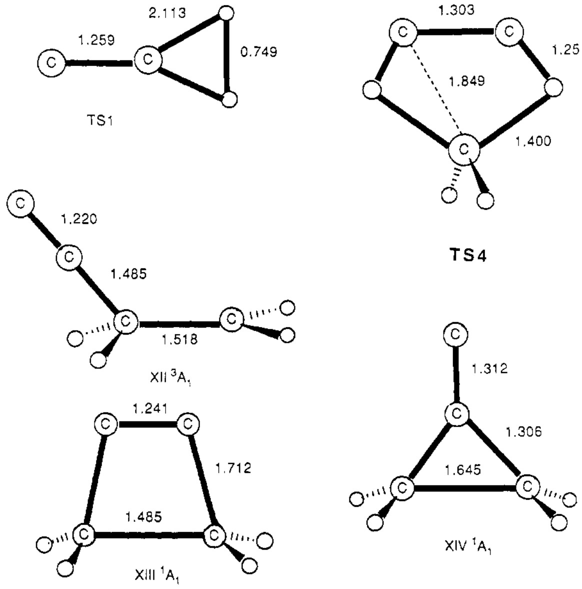
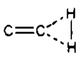
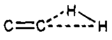


Figure 1. Geometries of relevant intermediates, transition states, and stationary points in the reaction of C_2 with hydrogen, methane, and ethylene.

Table V. Relative Energies (kcal/mol) of $C_2 + H_2$ at Different Levels of Theory[a]

molecule	elec sym	mol sym	NEV[b]	MP2/6-31G* (+ZPC)[c]	exptl ΔH_f[d]
$C_2 + H_2$	$^1\Sigma_g^+$, $^1\Sigma_g^+$	$D_{\infty h}$, $D_{\infty h}$	0	195.2 (185.6)	198.2
$C_2 + H_2$	$^3\Pi_u$, $^1\Sigma_g^+$	$D_{\infty h}$, $D_{\infty h}$	0	200.3 (190.5)	200.2[e]
 TS1	$^1A_1$	C_{2v}	1	201.7 (195.7)	
 TS2	$^3A'$	C_s	1	212.6 (202.0)	
CCH_2 (IX)	$^1A_1$	C_{2v}	0	104.3 (102.0)	97.7[f]
C_2H (X) + H	$^2\Sigma^+$, ^2S	$C_{\infty h}$, K	0	180.9 (171.4)	187.1[g]
HCCH	$^1\Sigma_g^+$	$D_{\infty h}$	0	54.3 (54.3)	54.3

[a] At the HF/3-21G level singlet C_2 adds to H_2 without barrier to form vinylidene, IX. [b] Number of negative eigenvalues of the force constant matrix at the HF/3-21G level. [c] Theoretical relative energies are compared relative to acetylene, which was given a value of 54.3 kcal/mol. [d] Unless otherwise noted, experimental heats of formation at 0 K are taken from Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Supplement 1 "JANAF Thermochemical Tables", 3rd ed. [e] The singlet–triplet splitting is added to the heat of formation of the ground state. [f] Davison, P.; Frey, H. M.; Walsh, R. *Chem. Phys. Lett.* **1985**, *102*, 227. [g] The heat of formation of X is 135 kcal/mol: ref 33.

The Electronic States of C_2. It has been pointed out that Hartree–Fock methods generally lead to a poor description of the C_2 diradical ground state.[1] However, it is not the purpose of this paper to attempt to carry out extremely high level calculations on C_2. Rather, we shall investigate a variety of potential reactions of C_2 at computational levels which are feasible in terms of computer time and at the same time lead to activation barriers which are in reasonable agreement with the experimental values. As will be demonstrated below, the activation energies we calculate deviate by no more than 7 kcal/mol from the experimental barriers that have been measured. A rigorous treatment of C_2 itself has recently been reported by Bauschlicher and Langhoff.[28] The deficiency of Hartree-Fock methods in treating C_2 is manifest in the irregular convergence of the singlet–triplet splitting with respect to levels of electron correlation. At the MP4SDTQ/6-311G* level we calculate a value of 9.8 kcal/mol for the singlet–triplet splitting ($^3\Pi_u - {}^1\Sigma_g$) while at the MP3/6-311G* level the value is −25.9 kcal/mol. The MP2 level of treatment seems to give the most balanced treatment of the singlet and triplet electronic states and the calculated splitting of 4.7 kcal/mol is in good agreement with the observed splitting. Table IV shows the relative energies of

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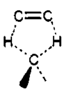
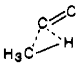
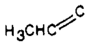
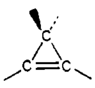
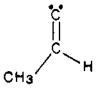
(26) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. GAUSSIAN 86; Carnegie-Mellon Quantum Chemistry Publishing Unit, Carnegie-Mellon University: Pittsburgh, PA.

(27) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York; 1986.

(28) Bauschlicher, C. W., Jr.; Langhoff, S. R. *J. Chem. Phys.* **1987**, *87*, 2919.

Table VI. Relative Energies (kcal/mol) of $C_2 + CH_4$ at Different Levels of Energy

molecule	elec sym	mol sym	NEV[a]	MP2/6-31G* (+ZPC)[b]	exptl ΔH_f[c]
$C_2 + CH_4$	$^1\Sigma_g^+, {}^1A_1$	$D_{\infty h}, T_d$	0	176.9 (171.4)	182.2
$C_2 + CH_4$	$^3\Pi_u, {}^1A_1$	$D_{\infty h}, T_d$	0	182.0 (176.3)	184.3[d]
 TS4	$^1A_1$	C_{2v}	2	175.9 (168.0)	
	$^3A_1$	C_{2v}	2	214.3 (201.9)	
 TS5	$^1A'$	C_s	1	212.8 (207.1)	
 TS6	$^3A'$	C_s	1	188.7 (180.4)	
$HC\equiv CCH_3$	$^1A_1$	C_{3v}	0	44.4 (44.4)	44.4[e]
	$^1A_1$	C_{2v}	0	67.1 (66.9)	66.2[e]
 XI	$^1A'$	C_s	0	98.6 (96.9)	90.1[f]
$CCH_2 + CH_2$	$^1A_1, {}^3B_1$	C_{2v}, C_{2v}	0	201.3 (191.0)	189.9[g,h]
$CCH_2 + CH_2$	$^1A_1, {}^1A_1$	C_{2v}, C_{2v}	0	223.1 (212.4)	198.9[g]
$HC\equiv CH + CH_2$	$^1\Sigma_g^+, {}^1A_1$	$D_{\infty h}, C_{2v}$	0	173.1 (164.7)	155.5
$CH_3 + C_2H$ (X)	$^2A_2'', {}^2\Sigma^+$	$D_{3h}, C_{\infty v}$	0	172.5 (163.1)	170.6[i]

[a] Number of negative eigenvalues of the force constant matrix at the HF/3-21G level. [b] Theoretical relative energies are compared relative to methylacetylene, which was given a value of 44.4 kcal/mol. [c] See footnote *d*, Table V. [d] See footnote *e*, Table V. [e] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: New York; 1970. [f] Estimated by subtracting the energy difference between ethylene and propane from the experimental ΔH_f of IX. [g] See footnote *f*, Table V. [h] The singlet–triplet splitting of methylene (9.0 kcal/mol) is added to the heat of formation of the ground-state methylene. [i] See footnote *g*, Table V.

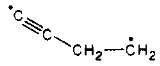
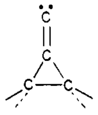
the various electronic configurations of C_2 calculated at several levels of theory.

The large number of reactions and the corresponding stationary points which we have considered mandate a computational method which provides a good compromise between speed and accuracy. As expected, calculated energies of C_2 + reactants are far too high as compared to experimental values when electron correlation is not included. However, incorporation of correlation at the MP2 level brings these energies to within 5–12 kcal of the experimental values. In fact, this treatment leads to a slight overestimation of the stability of C_2 when compared to the experimental and calculated energies of reference molecules such as acetylene, propyne, and vinyl acetylene (Tables V–VII). While transition states and stationary points leading from C_2 may also be poorly described by the Hartree–Fock method, we demonstrate below that the calculated activation barriers at the MP2/6-31G*//3-21G level are in reasonable agreement with experiment. An explicit CI treatment may give more accurate energies; however, we feel that the level of treatment employed here is appropriate to the extensive survey of C_2 chemistry that is presented.

We find that the use of the 3-21G basis set for geometry optimization is also a good compromise between speed and accuracy. While the 6-31G* basis set, which introduces d functions on non-hydrogens, is still practical, the improvement in geometries is expected to be small because it is still a single configurational treatment. On the other hand, geometry optimizations at the MP2/6-31G* level are difficult due to the large amount of required computer time. Therefore, we choose the 3-21G basis as a standard for determining geometries. As a check of the accuracy, both methods (3-21G and MP2/6-31G*) were used to locate the transition state for triplet C_2 reacting with H_2. The transition state located at the MP2/6-31G*//MP2/6-31G* level is only 2.4 kcal/mol lower in energy than at the MP2/6-31G*//3-21G level. It should be noted, however, that, in the present work, electron correlation in several instances reverses the order of stationary points. For this reason we have discussed geometries which are higher order stationary points on the 3-21G surface (i.e. greater than one negative eigenvalue of force-constant matrix) but are significantly stabilized by electron correlation. The implication is that these geometries may be true transition states on the correlated surface or may represent an upper limit to the true barriers.

Reaction of C_2 with Hydrogen. Tables V–VII list the relative energies of various intermediates and transition states in the reactions of C_2 with hydrogen, methane, and ethylene, respectively. Experimental and theoretical barrier heights are given in Table VIII for the reaction of $^1C_2$ and $^3C_2$ with H_2, CH_4, and C_2H_4. Absolute energies are given in Tables IX–XI, which are available

Table VII. Relative Energies (kcal/mol) of $C_2 + C_2H_4$ at the MP2/6-31G* Level of Theory[a]

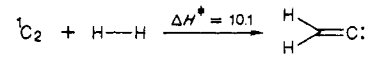
molecule	elec sym	mol sym	NEV[b]	MP2/6-31G* (+ZPC)[c]	exptl ΔH_f[d]
$C_2 + C_2H_4$	$^1\Sigma_g^+, {}^1A_g$	$D_{\infty h}, D_{2h}$	0	212.3 (207.5)	210.7
$C_2 + C_2H_4$	$^3\Pi_u, {}^1A_g$	$D_{\infty h}, D_{2h}$	0	217.4 (212.4)	212.7[e]
 XII	$^3A'$	C_s	0	169.5 (166.3)	165.5[f]
 XIV	$^1A_1$	C_{2v}	0	131.1 (130.5)	133.2[g]
	$^3B_2$	C_{2v}	0	170.8 (169.4)	
 XIII	$^1A_1$	C_{2v}	0	155.9 (153.8)	
	$^3B_2$	C_{2v}	1	165.6 (164.0)	
$H{-}C\equiv C{-}CH{=}CH_2$	$^1A'$	C_s	0	72.8 (72.8)	72.8[h]
$C_2H_3 + C_2H$	$^2A', {}^2\Sigma^+$	$C_s, C_{\infty v}$	0	212.8 (204.5)	205.4[i]
$H_2C{=}C{=}C{=}CH_2$	^1A_g	D_{2h}	0	84.3 (83.4)	79.3[j]

[a] At the HF/3-21G level singlet C_2 and triplet C_2 form an addition product with C_2H_4 without activation barrier. [b] Number of negative eigenvalues of the force constant matrix at the HF/3-21G level. [c] Theoretical relative energies are compared relative to vinylacetylene, which was given a value of 72.8 kcal/mol. [d] See footnote *d*, Table V. [e] See footnote *e*, Table V. [f] Heat of formation of XII is estimated from the bond-dissociation energy of an acetylenic and a primary C–H bond and the ΔH_f of 1-butyne. [g] Estimated by adding the energy difference between ethylene and methylenecyclopropane to the ΔH_f of IX. [h] Stull, E. F.; Westrum, Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969. [i] Reference 33. [j] Estimated by adding the energy difference between ethylene and allene to the ΔH_f of allene.

Table VIII. Comparison of Experimental and Calculated Activation Energies for Some Reactions of C_2

reaction	E_a (calcd)	E_a (exptl)	E_a (calcd − E_a (exptl)
${}^1C_2 + H_2$	10.1	2.9[b]	7.2
${}^3C_2 + H_2$	11.5 (9.1)[a]	6.0[b]	5.5 (3.1)
${}^1C_2 + CH_4$	0	0.6[b]	−0.6
${}^3C_2 + CH_4$	4.1	5.5[b]	−1.4
${}^1C_2 + C_2H_4$	0		
${}^3C_2 + C_2H_4$	0	0[c]	0

[a] Values in parentheses are the result of MP2/6-31G*//MP2/6-31G* calculations. All other values are calculated at the MP2/6-31G*//3-21G level. [b] Reference 29. [c] Reference 30.



IX

(1)

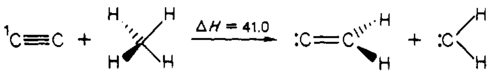
as supplementary material. When hydrogen is used as a substrate, it is possible for C_2 to insert into the H–H bond to form either vinylidene, IX (eq 1), or acetylene. Insertion to give IX is calculated to be proceed via TS1 with a barrier of 10.1 kcal/mol and an exothermicity of 83.6 kcal/mol. A low-energy transition state for direct formation of acetylene via a 2 + 2 cycloaddition could not be found. In contrast to singlet C_2, the most favorable reaction for ${}^3C_2$ is calculated to be the hydrogen abstraction in eq 2 to

$$ {}^3\text{C}_2 + \text{H-H} \xrightarrow{\Delta H^{\ddagger} = 11.5} \underset{\text{X}}{\text{H-C}\equiv\text{C}\cdot} + \text{H}\cdot \qquad (2) $$

generate ethynyl radicals, X, and hydrogen atoms with a barrier of 11.5 kcal/mol (TS2) and an exothermicity of 19.1 kcal/mol. The experimentally measured barrier to the reaction of ${}^1C_2$ with H_2 is 2.9 kcal/mol[29] while the triplet reacts with an activation energy of 6.0 kcal/mol.[30] Since IX will rapidly rearrange to acetylene[31] and X should abstract hydrogen to give acetylene, reaction of either singlet or triplet C_2 with H_2 is expected to generate acetylene. In principle one could determine the spin state of C_2 in this system by reacting it with a mixture of H_2 and D_2. The triplet would give acetylene statistically labeled with H and D while the singlet would generate only C_2H_2 and C_2D_2. Such an experiment would however be complicated if the rate of intersystem crossing were competitive with the reaction of C_2 with H_2. These calculations, which predict a more rapid reaction of ${}^1C_2$ than ${}^3C_2$ with hydrogen, are in qualitative agreement with experimental results which demonstrate that ${}^1C_2$ reacts at least 40 times faster with H_2 than does ${}^3C_2$.[10]

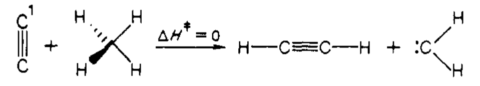
Reaction of C_2 with CH_4. Although the kinetics of the reaction of both singlet and triplet C_2 with methane have been measured,[10] the products have not been identified. As a model for the reaction of C_2 with saturated hydrocarbons, we have calculated transition states for a number of mechanistic pathways in the reaction of C_2 with methane. In this system, we have considered transfer of two hydrogens from methane to C_2 (eq 3 and 4), C–H insertion by C_2 (eq 5), and hydrogen abstraction (eq 6).

Hydrogen transfer from methane to C_2 could occur in two ways. Two hydrogens could be transferred to the same carbon (eq 3) or to the two different carbons on C_2 (eq 4). Although a transition state for the reaction in eq 3 could not be located, we calculate this process to be endothermic by 41.0 kcal/mol, indicating that the barrier must be at least this high.

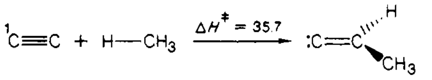


IX

(3)



(4)



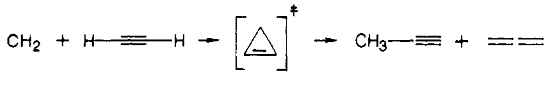
XI

(5)

$$ {}^3\text{C}\equiv\text{C} + \text{H—CH}_3 \xrightarrow{\Delta H^{\ddagger} = 4.1} \text{H—C}\equiv\text{C}\bullet + \bullet\text{CH}_3 \qquad (6) $$

In contrast, the transfer of two hydrogens from methane to two different carbons on C_2 to generate what is formally acetylene and methylene (eq 4) is calculated to be exothermic by 6.7 kcal/mol and is estimated to occur with little or no barrier. As indicated in Table VI, a true transition state (with only one negative eigenvalue) could not be located for the process in eq 4. Instead optimization at the 3-21G level gave a stationary point with two negative eigenvalues. Since the energy of this stationary point (TS4) is lower than that of $C_2 + CH_4$ at both the HF/3-21G and the MP2/6-31G* levels, we conclude that the process in eq 4 occurs with minimal barrier.

Although this reaction, which is shown in eq 4, would seem to lead to methylene and acetylene, some of the methylene would be expected to react with the acetylene to generate cyclopropene, which may react further to give allene and/or propyne as shown in eq 7.[32] An examination of the predominant negative mode in TS4 indicates that the motion along this reaction coordinate is toward cyclopropene. Thus the motion of C_2 and C_3 is toward C_1 in the transition state while the two hydrogens fold back to become terminal hydrogens on C_2 and C_3. The geometry of this stationary point indicates that it is closer to a complex between methylene and acetylene than it is to a complex between methane and C_2. Thus, the incipient C–H bond length (1.251 Å) in the acetylene is considerably shorter than the breaking C–H bond in the methane (1.400 Å). The abstraction of two hydrogens in eq 4 is forbidden (when C_{2v} symmetry is conserved) from the $\sigma_u^2\pi_u^4\sigma_g^0$ configuration of C_2 but allowed from the $\sigma_u^2\pi_u^2\sigma_g^2$ configuration. As Table VI indicates, when the energy of TS4 is calculated at the MP2/6-31G* level, it is lower in energy than ${}^1C_2$ + methane. Although the geometry of TS4 has not been optimized at this higher level, this result suggests that ${}^1C_2$ reacts with methane to produce either methylene and acetylene or cyclopropene with little or no barrier. It should be pointed out that the formation of cyclopropene in this system is calculated to be exothermic by 104.5 kcal/mol. Thus, there is ample energy for an initially formed cyclopropene to rearrange to propyne or allene. Such a rearrangement is apparently observed in the reaction of methylene with acetylene.[32a,b] It may be that a process such as this leads to the cumulenes which are formed when C_2 reacts with higher alkanes.[22] Although the products are not known, the reaction of ${}^1C_2$ with CH_4 proceeds with an experimentally determined barrier of 0.6 kcal/mol[29] in good agreement with our estimate of a minimal barrier.



(7)

The insertion of C_2 into a C–H bond of methane to give propenylidene (XI, eq 5) was found to occur with a barrier of 35.7 kcal/mol. Since this barrier is much higher than the near-zero barrier of eq 4, reaction via eq 5 is not expected to be important. As with the addition of H_2 to C_2, a low energy pathway for direct formation of the acetylenic product (propyne) could not be found. The hydrogen abstraction by ${}^3C_2$ in eq 6 is calculated to be exothermic by 13.2 kcal/mol and to proceed with an activation enthalpy of 4.1 kcal/mol as compared to an experimental value

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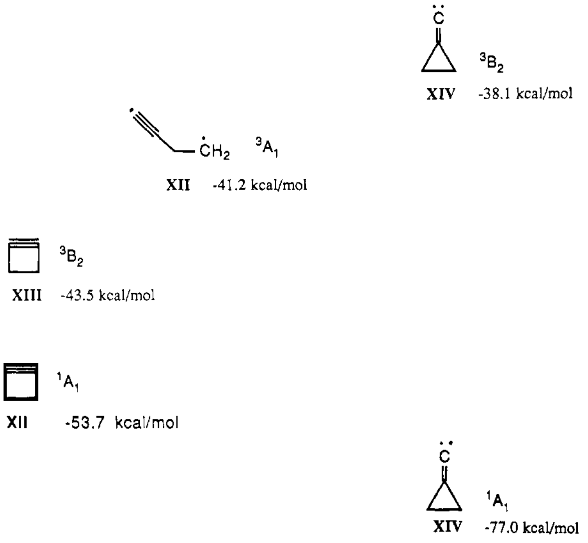
[29] Pitts, W. M.; Pasternack, L.; McDonald, J. R. *Chem. Phys.* **1982**, *68*, 417.

[30] Pitts, W. M.; Pasternack, L.; McDonald, J. R. *Chem. Phys.* **1981**, *57*, 19.

[31] The most reliable calculations give a classical barrier of 2–5 kcal/mol for $CCH_2 \rightarrow HCCH$. Dykstra, C. E.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 1378. Osamura, Y.; Schaefer, H. F.; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904. Raghavachari, K.; Frisch, M. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1981**, *79*, 408. Carrington, T., Jr.; Hubbard, L. M.; Schaefer, H. F.; Miller, W. H. *J. Chem. Phys.* **1984**, *80*, 4347.

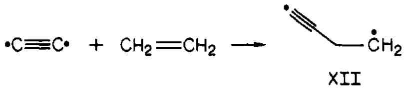
[32] (a) Frey, H. M. *Chem. Ind. (London)* **1960**, 1266. (b) Jacox, M. E.; Milligan, D. E. *J. Am. Chem. Soc.* **1963**, *85*, 278. (c) Karni, M.; Oref, I.; Barzilai-Gilboa, S.; Lifshitz, A. *J. Phys. Chem.* **1988**, *92*, 6924.

Scheme IV. Intermediates on the $C_2 + C_2H_4$ Energy Surface (Relative to $^1C_2$ and Ethylene)



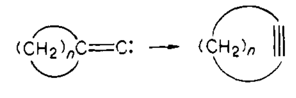
of 5.5 kcal/mol.[29] Since $^1C_2$ has considerable biradical character, the barrier for abstraction of a hydrogen from CH_4 should be similar for the singlet and triplet. This process was not explored for $^1C_2$. However, since eq 4 proceeds with little or no activation barrier for the singlet, this would be the preferred pathway. Thus, in the reaction of C_2 with methane, like that with hydrogen, the triplet may abstract hydrogen while the singlet may react by accepting two hydrogens from the methane.

Reaction of C_2 with Ethylene. In a system which is relevant to the experimental portion of this paper, we have used ethylene as a model for the reaction of C_2 with a C–C double bond. At the HF/3-21G level, both singlet and triplet C_2 are calculated to form addition products to ethylene without barrier. The reaction of $^3C_2$ with C_2H_4 has been observed to proceed with no barrier within experimental error.[30] In the case of $^3C_2$, this adduct corresponds to the 1,4-diradical XII. When the energy of XII is calculated at the MP2/6-31G* level, it is found to be more stable than $^3C_2$ and ethylene by 46.1 kcal/mol. It is interesting that, when the energy of XII is estimated from the bond-dissociation energy of an acetylenic[33] and a primary C–H bond[34] and the ΔH_f of 1-butyne, it is found to be 43.3 kcal/mol below $^3C_2$ and ethylene. Calculations on open-shell singlet XII are highly spin contaminated and probably do not represent an accurate picture of the energy of this species. Consequently, we shall assume that the energies of singlet and triplet XII, with their widely separated spins, are similar. Thus, $^1C_2$ is also predicted to add without barrier to ethylene.


XII

The addition of C_2 to ethylene is interesting in that it can also produce cyclobutyne, XIII, and cyclopropylidenecarbene, XIV. Scheme IV shows the relative energies of XII, XIII, and XIV calculated on both the singlet- and triplet-energy surfaces (singlet and triplet XII are assumed to have the same energy). It is not surprising that singlet XIII and XIV are calculated to be more stable than their triplet counterparts. Fitzgerald, Saxe, and Schaefer[35] have calculated that singlet XIII is an energy minimum with the triplet lying 13 kcal/mol above it. The singlet–triplet splitting in this rather sophisticated calculation may be compared to our value of 10.3 kcal/mol. It is interesting that triplet XII is only 2.3 kcal/mol above triplet cyclobutyne and it may be that the preferred pathway for decomposition of this species may be via diradical XII. It should be pointed out that the present calculations cannot eliminate the possibility of concerted cycloaddition of C_2 to ethylene to generate XIII. A possible first order decomposition pathway for XIII is simply an electrocyclic ring opening to butatriene (a product not observed) in which the symmetry plane bisecting the ring is conserved. This reaction differs from the electrocyclic ring opening of cyclobutene in that the product can be reached by a least motion pathway in which the methylene groups do not rotate. However, since both π orbitals and the relevant π bond of XIII are symmetric with respect to a plane bisecting the ring, and the HOMO of butatriene is antisymmetric, any ring opening in which this plane is conserved is symmetry forbidden. However, an alternative ring opening of XIII to butatriene in which the methylene groups rotate in a conrotatory manner is allowed.

Cycloalkylidenecarbenes are known to rearrange to the corresponding cycloalkynes in the cyclobutane and cyclopentane series (eq 8).[36] We have calculated cyclopentyne to be more stable than cyclobutylidenecarbene by 9 kcal/mol[37] and cyclohexyne to be more stable than cyclopentylidenecarbene by 19 kcal/mol.[38] However, this order of stability reverses itself in the present case with the cyclobutyne being less stable than the cyclopropylidenecarbene by 23.3 kcal/mol. On the triplet energy surface, the situation is again reversed and the carbene is less stable than the cyclobutyne by 5.4 kcal/mol.


(8)

Conclusion

The experiments reported herein demonstrate that C_2 adds to alkenes and that the resulting diradical is then trapped by the addition of another molecule of alkene in a second-order reaction. Since our calculations indicate that the addition of C_2 to a carbon–carbon double bond should be facile, they are in accord with the experimental results if it is assumed that the second-order reaction of the diradical with an additional molecule of alkene is competitive with cyclization to give either XIII or XIV. The fact that the present experiments were carried out by condensing C_2 with a large excess of alkene at 77 K would make this second-order reaction favorable.

Experimental Section

Diatomic carbon was produced simultaneously with C_1, C_3, and C_4 in the carbon vapor generated from a positive hearth electron-gun furnace similar to that described by Cloke and Green.[39] A stainless steel bell jar was used as the reaction vessel. Two tungsten filaments were heated by a current of about 38 A. The potential difference between the filaments and the positive hearth was slowly increased to induce electrons to bombard a small piece of carbon rod placed on the hearth. This electron bombardment resulted in the heating of carbon, eventually forming carbon vapor. Carbon vapor was then cocondensed with a large excess of reactants on the liquid nitrogen cooled walls of the reaction vessel at a very low pressure (2×10^{-5} Torr). Products were recovered by pumping into a secondary vacuum line.

Products were identified by the interpretation of the spectral data. Gas chromatographic analyses were performed on one of the following instruments; a Hewlett-Packard 5790A FID equipped with a 95% dimethylpolysiloxane–5% diphenylpolysiloxane (DB-5) quartz capillary column (30 m × 0.25 mm) and a HP3390A integrator, or a Gow-Mac 10-677 thermistor detector equipped with a 13-ft 20% SE-30 packed column and a Northrup Speed-O-Max G chart recorder. Yields were determined by gas chromatography. When possible, authentic samples were used as standards. However, in the reactions of C_2 with two alkenes,

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(33) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

(34) Doering, W. v. E. *Proc. Nat. Acad. Sci.* **1981**, *78*, 5297.

(35) Fitzgerald, G.; Saxe, P.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 690.

(36) Erickson, K. L.; Wolinsky, J. *J. Am. Chem. Soc.* **1965**, *87*, 1142.

(37) Tseng, J.; McKee, M. L.; Shevlin, P. B. Unpublished result.

(38) Tseng, J.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 5474.

(39) Cloke, F. G. N.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1938.

authentic samples were not available and products were quantitated by comparing peak areas with those of hydrocarbons of similar molecular weight: C_8 products with 1,7-octadiene, C_9 products with 1,8-nonadiene, and C_{10} products with 1,9-decadiene. Mass spectral analyses were carried out on an AEI-MS-902 spectrometer at low resolution. Due to poor resolution with 60-MHz NMR, ^1H NMR data were taken on a Bruker WM360 spectrometer.

Reaction with Propylene. In a typical reaction, 80.0 g of propylene was cocondensed with 130 mg of carbon on the liquid nitrogen cooled reaction vessel. At the conclusion of the experiment, the substrate–product mixture was warmed to room temperature and was then distilled into −104, −131, and −196 °C traps. The products in the −131 °C trap were analyzed by GC and GC/MS with a 95% dimethylpolysiloxane–5% diphenylpolysiloxane (DB-5) quartz capillary column (30 m × 0.25 mm). The major products were 1,2-butadiene,[25] 1,3-butadiene, 1-pentyne, and 3-methylbutyne. No seven-carbon product (C_1 + two propylenes) was found. The products in the −104 °C trap were first analyzed by GC and GC/MS with a 30-m DB-5 capillary column. There were three major peaks and one minor peak of molecular weight 108 (C_2 + two propylenes). The three major eight-carbon compounds were separated and collected separately by preparative gas chromatography using a 13-ft, 20% SE-30 packed column. Each separated compound was tested for purity by GC with a capillary column and was found to be about 99.9% pure. Each pure compound was then analyzed by high-resolution NMR and the structures were determined to be III, IV, and V. The Appendix gives details of the NMR analysis as well as spectral parameters. Since the three nine-carbon products (mol wt 120) could not be separated by preparative gas chromatography, these three compounds were collected together and were found to be three diastereoisomers of 1,1′-dimethylethanobisallene by high-resolution proton NMR. The NMR spectrum consists of a doublet (3 H) at $\delta = 1.3$, a broad triplet (2 H) at $\delta = 1.7$ and a multiplet (1 H) at $\delta = 1.9$. Results are shown in Table I.

Reaction with (*Z*)-2-Butene. In a typical reaction, 56.0 g of (*Z*)-2-butene was cocondensed with 125 mg of carbon on the liquid nitrogen cooled reactor surface. At the conclusion of the experiment, the substrate–product mixture was warmed to room temperature and was then trap-to-trap distilled through a −104 °C trap into a −196 °C trap. One liquid and one solid product was obtained in the −104 °C trap. The liquid was then easily distilled into another −196 °C trap. The solid product was sublimed into a second trap. Both solid and liquid products were analyzed separately by GC and GC/MS with a 30-m DB-5 capillary quartz column. The solid product was found to consist of two peaks of molecular weight 148 (C_3 + two butenes). High-resolution proton NMR consists of two multiplets, one at $\delta = 1.2$ (3 H) and the other at $\delta = 1.9$ (1 H), showing the formation of 1,2,1′,2′-tetramethylethanobisallene. In the liquid product, one minor six-carbon product (mol wt 82, C_2 + butene), two minor nine-carbon products (mol wt 124, C_1 + two butenes), and three major and four minor 10-carbon products (mol wt 136, C_2 + two butenes) were found. The three major 10-carbon products were separated and collected by preparative gas chromatography with a packed SE-30 column. Each separated compound was tested for purity by GC with a capillary column and was found to be 99.9% pure. Each pure compound was then analyzed by high-resolution NMR and determined to be VI and the two diastereomers of VII as explained in the Appendix. Results are shown in Table II. The low-boiling products in the −196 °C trap, containing mainly C_2–C_5 compounds, were not analyzed.

Reaction with (*E*)-2-Butene. In a typical reaction, 58.5 g of (*E*)-2-butene was cocondensed with 114 mg of carbon on the liquid nitrogen cooled reactor surface. The procedure was identical with that described above with (*Z*)-2-butene. One solid and one liquid product was obtained in the −104 °C trap, and they were separated as before. Both solid and liquid products were first analyzed by GC and GC/MS with a DB-5 quartz capillary column (30 m × 0.25 mm). The solid product was found to consist of three peaks of molecular weight 148 (C_3 + two butenes). High-resolution proton NMR of this solid product consists of two multiplets, one at $\delta = 1.28$ (3 H) and the other at $\delta = 1.5$ (1 H), showing the formation of diastereoisomers of 1,2,1′,2′-tetramethylethanobisallene. Three major and four minor 10-carbon products (mol wt 136, C_2 + two butenes) were obtained in the liquid product. The three major 10-carbon products were separated and analyzed as before and shown to be VI and the two diastereomers of VIII. Results are shown in Table III.

Reaction with 1,3-Butadiene. In a typical reaction, 50.0 g of 1,3-butadiene was cocondensed with 95 mg of carbon on the liquid nitrogen cold reactor surface. The procedure was identical with that described with (*Z*)-2-butene. The major product was found to be the previously identified 4-vinylcyclohexene, a dimer of 1,3-butadiene.[24] No 10-carbon product (mol wt 132, C_2 + two butadienes) was obtained. The previously identified,[24] three poorly resolved diastereoisomers of 1,1′-diethenylethanobisallene were obtained. They were analyzed by GC and GC/MS. The yield was 5.5%, based on carbon vaporized.

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Appendix

Structure Assignments (L.M.J.) for the Enynes Resulting from Condensation of C_2 with Two Molecules of Alkene. The proton NMR spectra of the various hydrocarbon products were readily analyzed with the aid of a few selective decoupling and/or COSY experiments. In all cases, the complex olefinic region was fully analyzed with the program LACOON3.[40] The spectral assignments lead to unequivocal determination of the structures. The NMR spectral parameters for compounds III–VII are listed in Tables XII–XVII, which are available as supplementary material.

The clearly separated isomeric products (C_8H_{12}) from C_2 and $2C_3H_6$ are III, IV, and V. To each of these an unequivocal structure assignment was made. There are enynes, III, with a terminal acetylene function and IV and V with internal triple bonds. The 1-en-4-yne structure is present in IV and V, pointing to a possible identical precursor for this pair of isomers.

The earlier structure assignments given to these propylene-derived products included cyclopropane structural units.[21] We reproduce the earlier 60-MHz ^1H NMR spectra, indicating that the same products are present but that the structure was incorrectly assigned. The incorrect assignments were wholly due to inadequate NMR resolution. The 360-MHz spectra resolved a crucial doublet feature into a triplet for the methyl group of compound V. The original doublet assignment was taken, mistakenly, as an indication of a methyl group attached to a cyclopropane ring. Our present analysis removes the evidence for that structure assignment.

Analogous isomeric enynes ($C_{10}H_{16}$) are obtained from C_2 + (*Z*)-2-butene and from (*E*)-2-butene. Again, unequivocal structure assignments were made. The 1,4-enynes VI from the cis and trans precursors are identical, consistent with the loss of the isomeric distinction due to the double bond as a result of shift of the double bond to the terminal position. Although the configurations at C_3 and C_6 indicate a pair of diastereomers should be present, there is no evidence either in the GC or the ^1H NMR spectrum for two stereoisomers of VI. We believe that these isomers are present but have indistinguishable properties (even with 360-MHz resolution), perhaps because the chiral centers are at opposite ends of the acetylenic linkage minimizing their interaction.

The 1,6-enynes, from the 2-butene reactions, show the expected isomerism for an internal double bond, and for two adjacent chiral centers. Two products are isolated from the (*Z*)-2-butene reaction (VIIA and VIIB), and two others from the (*E*)-2-butene (VIIIA and VIIIB). It is clear that (a) the cis or trans nature of the precursors survive in the products and that (b) adjacent chiral centers make possible GC separation and distinguishing ^1H NMR characteristics at 360 MHz. In the case of these four (±)-stereoisomeric 3,4-dimethyloct-6-en-1-ynes, a number of NMR parameters exhibited small but significant differences. Each stereoisomer, however, is best characterized by its values of $^3J_{3,4}$ and $^3J_{6,7}$. The latter, of course, assume the usual values for *E*- and *Z*-disubstituted alkenes. Although the values of $^3J_{3,4}$ for the 3,4-diastereomers differ by 1 Hz, an assignment of the relative configurations at C_3 and C_4 is not feasible.

Supplementary Material Available: Tables IX–XI give the absolute energies at the HF/3-21G, HF/6-31G*, and MP2/6-31G* levels from which the relative energies in Tables V–VIII were determined and Tables XII–XVII (10 pages). Ordering information is given on any current masthead page.

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(40) Bothner-By, A. A.; Castellano, S. M. In *Computer Programs for Chemistry*; Detar, D. F., Ed.; W. A. Benjamin: New York, 1968; Vol. 1, Chapter 3.