

Low-Lying Electronic States of Unsaturated Carbenes. Comparison with Methylene

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Abstract: The lowest singlet and triplet electronic states of methylene, H_2C ; vinylidene, H_2CC ; and vinylidenecarbene, H_2CCC ; are studied theoretically at the spin-unrestricted Hartree-Fock (HF) and spin-unrestricted many-body perturbation theory (MBPT) levels of approximation. Calculations at both levels predict a triplet ground state for methylene and singlet ground states for vinylidene and vinylidenecarbene. MBPT singlet-triplet energy splittings are found to be -13.1 kcal/mol for methylene, 51.1 kcal/mol for vinylidene, and 48.7 kcal/mol for vinylidenecarbene. A comparison of the effects of correlation on electronic structure is made between the parent carbene, methylene, and each of these unsaturated carbenes. From electronic structure trends observed in H_2C ; H_2CC ; and H_2CCC ; singlet ground states are predicted for the extended unsaturated carbenes H_2CCCC ; and H_2CCCCC ; the next members of the series. The importance of d-type carbon polarization functions in basis sets used for the calculation of electronic structure properties in unsaturated carbenes is demonstrated by comparison with results in which d functions are not included in the basis.

Introduction

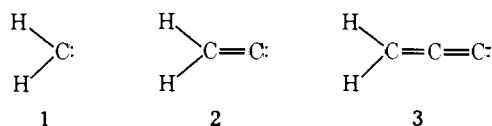
In recent years, increasing attention has been focused on reactions in which unsaturated carbenes appear as intermediates.^{2,3} However, little is known about the "isolated-molecule" properties of these highly reactive species, since direct spectroscopic observation has not yet proven to be generally feasible. Because the two lowest carbene electronic states that one is interested in probing are of different spin symmetry, the use of conventional optical spectroscopy is not practical. To the best of our knowledge, the laser photodetachment of H_2C^- by Zittel et al. to yield $^1\text{A}_1$ H_2C and $^3\text{B}_1$ H_2C is the only quantitative gas-phase experimental investigation of the singlet-triplet splitting in a carbene.⁴ Several earlier studies have been reported, however, in which the methylene singlet-triplet splitting was estimated from the photolysis of ketene, CH_2CO .⁵⁻⁷ Analogous experiments have not yet been performed for any unsaturated carbene.

Although much valuable information about the electronic states of other carbenes has been inferred from the nature of the chemical reactions they undergo^{2,3} (e.g., one-step stereospecific addition to olefins for the singlets, two-step nonstereospecific reactions for the triplets), the validity of such inferences often depends upon assumptions concerning the rate at which the nascent carbene is relaxed to its ground state. Moreover, the results of such condensed-phase experiments contain the effects of the solvent on the carbene's electronic states. In light of the above experimental difficulties, we believe that it is of great importance to acquire a more fundamental understanding of those aspects of the carbene's geometrical and electronic structure governing the relative stability of the lowest singlet and triplet states in the "gas-phase" species. Because of the considerable difficulty that arises in experimental studies of these highly reactive intermediates, state of the art quantum chemical calculations provide the only practical and reliable access to most of the spectroscopic, bonding, and geometrical information bearing upon the chemical behavior of these carbenes. The potential contributions of quantum theoretical calculations to carbene chemistry have already become rather clear. Since Mulliken's pioneering theoretical work in 1932,⁸ numerous authors have investigated the important methylene problem by means of semiempirical⁹ and, more recently, ab initio⁹⁻²⁹ theoretical methods. In particular, Staemmler,^{15,18} Harrison,^{10,20} Bender et al.,^{17,23,24} Schaefer et al.,^{17,23-26} Bauschlicher et al.,^{17,23,24,26,29} and Harding and Goddard²⁷ have carried out careful ab initio

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studies on methylene within the last 5 years that have had substantial impact on the area. These studies have served to clarify the interpretation of experimental data (e.g., the geometry of the triplet ground state) and to place in proper perspective the body of earlier ab initio and semiempirical work in which the highly correlated $^1\text{A}_1$ state was not well described owing to deficiencies in the choice of basis set and/or configuration space. However, only a few semiempirical^{30,31} and ab initio³²⁻³⁴ calculations have been performed on vinylidene, $\text{H}_2\text{C}=\text{C}$; the simplest unsaturated carbene, and to our knowledge, only one HF-level ab initio theoretical study has been done on vinylidenecarbene, $\text{H}_2\text{C}=\text{C}=\text{C}$;³⁵ the prototypical system for the class of $\text{RR}'\text{C}=\text{C}=\text{C}$: intermediates whose reactions constitute an active and growing area of experimental focus in carbene chemistry.^{2,3}

In this paper, we explore the electronic structure of vinylidene (**2**) and vinylidenecarbene (**3**) at several levels of theoretical approximation making comparisons, where appropriate, with methylene (**1**). Our study concentrates on two properties



of particular interest in carbene chemistry: the spin multiplicity of the electronic ground state and the energy splitting between this state and the first excited state. These properties are clearly very relevant to an understanding of the chemical behavior of unsaturated carbenes. For example, reaction channel choice must accommodate the spin multiplicity of the carbene intermediate without violating quantum mechanical state symmetry constraints. Similarly, the susceptibility of such reactions to thermal or photochemical alteration is determined in part by the energy gap between the ground and first excited states of the intermediate carbene species.

Computational Details

A. Geometry. Calculations on **1** were carried out at the geometries of the $^1\text{A}_1$ and $^3\text{B}_1$ potential surface minima as determined by Bauschlicher and Shavitt ($^1\text{A}_1$, $\theta_{\text{HCH}} = 102.4^\circ$, $R_{\text{CH}} = 1.116$ Å; $^3\text{B}_1$, $\theta_{\text{HCH}} = 132.4^\circ$, $R_{\text{CH}} = 1.082$ Å).²⁹ Spin-unrestricted HF and correlated calculations on **2** were performed at the geometry of the $^3\text{B}_2$ potential surface minimum reported by Davis, Goddard, and Harding (C_{2v} symmetry, $R_{\text{CH}} = 1.076$ Å, $\theta_{\text{HCH}} = 116.6^\circ$, $R_{\text{CC}} = 1.36$ Å).³³ It is reasoned that the HCH angle in **2** should be similar to the

ethylene HCH angle. HF-level calculations on this system were also carried out with $R_{CC} = 1.35 \text{ \AA}$, the geometry these authors identify as the 1A_1 potential surface minimum. Our HF-level calculations indicate that changes due to the 0.01 \AA C–C bond distance change are small. Hence, we have restricted our correlated calculations to the Davis, Goddard, and Harding triplet minimum energy geometry. For carbene **3**, all calculations were carried out with the same C–H distances and HCH angle used for **2**. We make the reasonable assumption that these parameters would be influenced only slightly by the attachment of another carbon atom at the opposite end of carbene **2**. The C–C bond distances were shortened to 1.32 \AA in **3** to correspond more closely with the C–C distance of 1.31 \AA reported by Herzberg for the structurally similar species allene, $H_2C=C=CH_2$.³⁶

It should be stressed that the singlet–triplet energy splittings we report for carbenes **2** and **3** are vertical rather than adiabatic splittings. Choice of geometries at which to perform ab initio calculations on larger many-electron systems such as **2** or **3** necessarily involves a compromise between computational expense and detailed knowledge of the potential energy surfaces of the states of interest. While our geometries were selected with careful regard for relevant experimental and theoretical information, the picture of the singlet and triplet potential energy surfaces we present is extremely limited. The arguments advanced by Moule and Walsh with regard to formaldehyde lend support to our assumption of planar C_{2v} symmetry in the 1A_1 and $^3B_{1,2}$ states of **2** and **3**.³⁷ A more detailed study of these states, which will consider variations of C–C bond coordinates and the HCH angular coordinate, is now in progress and will be reported in a subsequent paper.

B. Basis Sets. Three types of basis sets were used in the ab initio calculations. The Dunning (4s2p/2s) \equiv (C/H) contraction³⁸ of Huzinaga's (9s4p/4s) primitive Gaussian basis³⁹ served as the reference basis set in this work. Other basis sets were derived from this by addition of polarization functions, known to be important in theoretical descriptions of **1**,^{10,12,13,15,25,28,29} to the carbene or terminal carbon atoms in **2** and **3**. The need for better description of the terminal carbon atom is suggested by the localization of the nonbonding valence electrons in this region of the unsaturated carbene. In carbene **2**, a basis set containing d functions on both carbon atoms, a duplication of the Davis, Goddard, and Harding basis set,³³ was also used. Comparison between HF-level results on **2** employing one and two d function basis sets suggests that restriction of the d function to the terminal carbon is a reasonable compromise between basis set size and basis flexibility (e.g., 1A_1 – 3B_2 HF-level splitting in **2** is 11.1 kcal/mol with the (4s2p,4s2p/2s) basis, 17.6 kcal/mol with the (4s2p,4s2p,4s2p,4s2p/2s) basis, and 15.7 kcal/mol with the (4s2p,4s2p,4s2p,4s2p,4s2p/2s) basis. 1A_1 HF-level energies for the three basis sets are -76.7401 , -76.7592 , and -76.7634 hartrees, respectively). It is seen that adding a d function on the carbene carbon stabilizes the 1A_1 HF state by 6.5 kcal/mol relative to the 3B_2 HF state. By including a methylene carbon d function as well, the 3B_2 HF state is stabilized by another 1.9 kcal/mol , which reduces the 1A_1 stabilization for this basis to 4.6 kcal/mol . Although a carbene carbon d function alone slightly overstabilizes the 1A_1 HF state, its presence in the basis yields a much better overall picture of the singlet–triplet splitting. For our correlated studies of **1**, **2**, and **3**, we employ the (4s2p,4s2p/2s), (4s2p,4s2p,4s2p/2s), and (4s2p,4s2p,4s2p,4s2p/2s) basis sets, respectively. A d function exponent of 0.6769 was used in all of our calculations.³³

C. Ab Initio Methods. Symmetry-adapted atomic integrals for use in the HF and correlated calculations were generated by the MOLECULE integral program.⁴⁰ This is a component of the PROPAGATOR program system for the calculation of molecular electronic structure, which uses many-body tech-

Table I. Methylene ($H_2C:$) Calculations^{d,e}

method	1A_1	3B_1	$\Delta(^1A_1-^3B_1)$
HF	-38.8766^a	$-38.9221^{a,c}$	-0.0455^a (-28.6) ^b
MBPT-4	-38.9967	-39.0201	-0.0234 (-14.7)
MBPT-[3-2]	-39.0020	-39.0221	-0.0201 (-12.6)
MBPT-8	-39.0012	-39.0220	-0.0208 (-13.1)
MBPT-[3-3]	-39.0023	-39.0221	-0.0198 (-12.4)

^a hartrees (1 hartree = 627.5 kcal/mol). ^b kcal/mol. ^c ($2S + 1$) = 3.01 UHF . ^d (4s2p,4s2p/2s) basis set, mixed hydrogen exponential scale factors; $s_1 \sim (1.2, 1.0, 1.0)$, $s_2 \sim (1.0)$. ^e Geometries: 1A_1 , $\theta_{HCH} = 102.4^\circ$, $R_{CH} = 1.116 \text{ \AA}$; 3B_1 , $\theta_{HCH} = 132.4^\circ$, $R_{CH} = 1.082 \text{ \AA}$.

Table II. Vinylidene ($H_2CC:$) Calculations^{d,e}

method	1A_1	3B_2	$\Delta(^1A_1-^3B_2)$
HF	-76.7634^a	$-76.7384^{a,c}$	0.0250^a (15.7) ^b
MBPT-4	-77.0146	-76.9354	0.0792 (49.7)
MBPT-[1-1]	-77.0193	-76.9375	0.0818 (51.3)
MBPT-8	-77.0207	-76.9393	0.0814 (51.1)
MBPT-[3-3]	-77.0215	-76.9401	0.0814 (51.1)
DECI-RSPT-4	-77.0016	-76.9295	0.0721 (45.2)

^a hartrees (1 hartree = 627.5 kcal/mol). ^b kcal/mol. ^c ($2S + 1$) = 3.27 UHF . ^d (4s2p,4s2p,4s2p/2s) basis set, hydrogen exponential scale factor = 1.0 . ^e Geometry: 1A_1 , 3B_1 ; $\theta_{HCH} = 116.6^\circ$, $R_{CH} = 1.076 \text{ \AA}$, $R_{CC} = 1.36 \text{ \AA}$.

Table III. Vinylidenecarbene ($H_2CCC:$) Calculations^{d,e}

method	1A_1	3B_1	$\Delta(^1A_1-^3B_1)$
HF	-114.5800^a	$-114.5761^{a,c}$	0.0039^a (2.4) ^b
MBPT-4	-114.8799	-114.8046	0.0753 (47.3)
MBPT-[1-1]	-114.8929	-114.8081	0.0848 (53.2)
MBPT-8	-114.8885	-114.8109	0.0776 (48.7)
MBPT-[3-3]	-114.8897	-114.8138	0.0759 (47.6)
DECI-RSPT-4	-114.8554	-114.7975	0.0579 (36.3)

^a hartrees (1 hartree = 627.5 kcal/mol). ^b kcal/mol. ^c ($2S + 1$) = 3.40 UHF . ^d (4s2p,4s2p,4s2p,4s2p/2s) basis set, hydrogen exponential scale factor = 1.2 . ^e Geometry: 1A_1 , 3B_1 ; $\theta_{HCH} = 116.6^\circ$, $R_{CH} = 1.076 \text{ \AA}$, $R_{CC} = 1.32 \text{ \AA}$.

niques^{41–44} developed and implemented by two of us (G.P. and R.J.B.). Singlet HF calculations were restricted to be eigenfunctions of spin and spatial symmetry. HF calculations on the triplet states were performed using the spin-unrestricted formalism (UHF) in which spatial parts of orbitals of different spin are allowed to be different. However, each spin orbital was required to be of pure spatial symmetry. For example, orbitals of symmetry a_1 were not allowed to mix with orbitals of other symmetries such as b_2 . Since it is well known that UHF-level calculations are not exact eigenfunctions of spin, expectation values of the spin multiplicity ($2S + 1$) were calculated for the triplet states at the UHF level and are reported in Tables I–III.

Correlated calculations were obtained by adding to the HF total energies the many body perturbation theory (MBPT) correlation corrections that arise from double excitation type diagrams (DEMBPT) through eighth order.^{41,44} This double excitation method is particularly appropriate for treating correlation in low-lying 1A_1 carbene states where $\sigma^2 \rightarrow \pi^2$ double-excitation configurations are known to be important. For the triplet states, a spin-unrestricted MBPT formalism was used.⁴⁵ Since higher order corrections to the average spin multiplicity are introduced by the correlation, this method provides a better approximation to the triplet multiplicity than the UHF. The DEMBPT model is similar in conceptual simplicity to the established double-excitation configuration interaction method (DECI), but avoids the systematic "size-

Table IV. HF and Correlated 1A_1 - ${}^3B_{1,2}$ Energy Splittings, Correlation Energies, and Correlation Energy Differences (kcal/mol)^h

carbene	ΔE_{HF}	$\epsilon_c({}^1A_1)$	$\epsilon_c({}^3B_{1,2})$	$\Delta\epsilon$	$\Delta E_{\text{HF}} + \Delta\epsilon_c = \Delta E_c$
1 H ₂ C:	(-28.6), -25.0, ^a -24.8 ^c	(78.2), 95.3, ^a 13.9 ^{b,c}	(62.7), 80.9, ^a 0.0 ^{b,c}	(15.5), 14.4, ^a 13.9 ^{b,c}	(-13.1), -10.6, ^{a,d} -11.1, ^b -10.9 ^c
2 H ₂ CC:	(15.7), 31.0, ^e 27.2 ^f	(161.5), 70.7, ^e 103.2 ^f	(126.1), 55.8, ^e 98.0 ^f	(35.4), 14.9, ^e 5.2 ^f	(51.1), 45.9, ^e 32.4 ^f
3 H ₂ CCC:	(2.4), -1.5 ^g	(193.6)	(147.3)	(46.3)	(48.7)

^a Reference 29, (6s4p2d/3s2p) basis set, UHF triplet, multiconfiguration correlation. ^b Reference 29, (6s4p2d/3s2p) basis set, UHF triplet, two-configuration singlet. ^c Reference 25, (9s6p3d/4s2p) basis set, UHF triplet, two-configuration singlet. ^d Reference 27, 5s3p2d/2s1p) basis set, multiconfiguration correlation. ^e Reference 33, (4s2p1d,4s2p1d/2s) basis set, RHF triplet, multiconfiguration correlation. ^f Reference 34, (4s2p,4s2p/2s) basis set, RHF triplet, limited correlation. ^g Reference 35, (6-31G*) polarized basis set, UHF triplet. ^h Our HF and MBPT-8 results appear in parentheses. Basis sets used in our work are **1**, (4s2p1d/2s); **2**, (4s2p1d,4s2p1d/2s); **3**, (4s2p,4s2p,4s2p1d/2s). Our HF-level splittings are taken with respect to a UHF triplet.

consistency error"^{41,45-48} inherent in the DECI method. Excitations from the carbon 1s core electrons were not included in any of the correlated calculations.

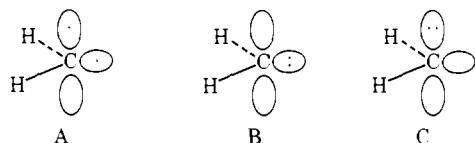
Theoretical results for carbenes **1**, **2**, and **3** are summarized in Tables I, II, and III, respectively. Table IV provides a comparative listing of singlet-triplet splittings and correlation energies for carbenes **1**, **2**, and **3**. Results from other recent theoretical studies on these systems are also included in this table. In addition to the linear sums of MBPT corrections through fourth and eighth order, MBPT corrections were resummed using [1-1], [3-2], and [3-3] Padé approximants⁴⁹⁻⁵² to provide other estimates of the infinite-order results. Also reported in Tables II and III are the fourth-order Rayleigh-Schrödinger perturbation theory (RSPT) approximations to the DECI calculation. The difference between the approximate DECI results and the MBPT results is a rough measure of the size-consistency error of the DECI method.^{41,43,48} As these tables show, the magnitude of the size-consistency error increases substantially with the number of electrons from about 6 kcal/mol for **2** (14 electrons) to 12 kcal/mol for **3** (20 electrons).

The calculations were performed in double precision on a Univac 1108 at the University of Utah and in single precision on a CDC 6400 at Battelle Columbus Laboratories. The time required for calculations on the 3B_2 state of **2** (H₂CC:) breaks down as follows: integral generation, 15 min; 30 SCF iterations, 3 min; unrestricted two-electron integral transformation, 11 min; unrestricted MBPT calculations through eighth order, 11 min.

Electronic Structure Details

A. Methylene. Our discussion of the low-lying states of unsaturated carbenes **2** and **3** is conveniently prefaced by a simple orbital description of the two lowest states of carbene **1**. Following the IUPAC suggestion for molecules with C_{2v} symmetry,³⁷ the z axis is chosen as the molecular symmetry axis and the hydrogens are assumed to lie in the yz plane. With this convention, σ orbitals along the z axis have a_1 symmetry, π orbitals perpendicular to the molecular plane have b_1 symmetry, π orbitals parallel to the molecular plane and perpendicular to the z axis have b_2 symmetry, and C-H bonding orbitals have either a_1 or b_2 symmetry. We retain this convention for carbenes **2** and **3**.

The simple molecular orbital (MO) picture of the 3B_1 ground state of carbene **1** is shown in A. It consists of a filled carbon 1s atomic orbital with a_1 symmetry, two C-H bonding orbitals of a_1 and b_2 symmetry, and a nonbonding valence orbital occupancy designated by $\sigma\pi$, or a_1b_1 :



$$|{}^3B_1\rangle_{\text{H}_2\text{C}} \approx [1a_1^2 2a_1^2 1b_2^2] 3a_1 1b_1 \equiv [\text{core}] a_1 b_1 \quad (1)$$

The first excited state of **1**, the 1A_1 state, can be described as a mixture of the two configurations B and C, with B the dominant configuration and C the secondary but important $3a_1^2 \rightarrow 1b_1^2$ double-excitation configuration of B:

$$|{}^1A_1\rangle_{\text{H}_2\text{C}} \approx C_B[\text{core}] a_1^2 + C_C[\text{core}] b_1^2 \quad (2)$$

Thus in eq 2, we have $|C_B\rangle|C_C\rangle$ with the condition $|C_B|^2 + |C_C|^2 \approx 1$ (e.g., $C_B = 0.9617$ and $C_C = 0.1943$ in the CI study of O'Neil, Schaefer, and Bender¹¹). Several authors have pointed out that the two-configuration description of the 1A_1 state is necessary to ensure treatment of the a_1 and b_1 valence orbitals on an equivalent footing at a "HF" level of approximation.^{10,12,13,25,26,28} In the 3B_1 ground state, the single configuration A suffices, since the valence orbital occupancy includes both of these orbitals.

It should be noted that with the two-configuration valence description of the 1A_1 state and the single-configuration function for the 3B_1 state, Meadows and Schaefer²⁵ and Bauschlicher and Shavitt²⁹ obtained adiabatic 1A_1 - 3B_1 energy splittings for **1** of -10.9 and -11.1 kcal/mol, respectively. However, these values are in almost exact agreement with the best multiconfiguration results of Bauschlicher and Shavitt,²⁹ and independently, Harding and Goddard,²⁷ at -10.6 kcal/mol. From this, we conclude that the 1A_1 and 3B_1 core-electron correlation energies are nearly identical, which allows the simple orbital descriptions (eq 1 and 2) to model accurately the distinctive valence characteristics of these states.

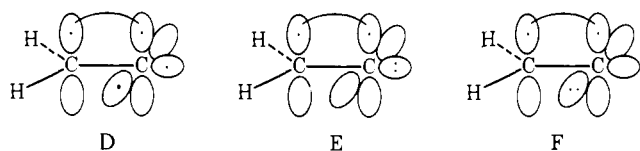
Single-configuration HF calculations on both states of **1** (i.e., $C_B = 1$, $C_C = 0$ in eq 2) by Meadows and Schaefer²⁵ and Bauschlicher and Shavitt²⁹ gave splittings of -24.8 and -25.0 kcal/mol, respectively. Thus, a correlation contribution of $|24.8 - 10.9|^{25} = |25.0 - 11.0|^{29} = 13.9$ kcal/mol can be ascribed to the double-excitation configuration C of the 1A_1 state. While multiconfiguration correlation significantly lowers the energy of each state (e.g., with respect to single-configuration HF values, Bauschlicher and Shavitt report that CI lowers the 1A_1 energy by 95.3 kcal/mol and the 3B_1 energy by 80.9 kcal/mol), almost all of the $|95.3 - 80.9| = |25.0 - 10.6| = 14.4$ kcal/mol HF-CI differential decrease can be attributed to the presence of configuration C in the multiconfiguration 1A_1 state, since this value is within 0.5 kcal/mol of the 13.9 kcal/mol one- vs. two-configuration differential decrease calculated with the same basis set and geometry.²⁹ Thus, including the double-excitation configuration C in the 1A_1 state description, either at the two- or multiconfiguration level, lowers the 1A_1 excited state energy about 14 kcal/mol relative to the corresponding 3B_1 ground-state energy, hence diminishing the 1A_1 - 3B_1 splitting by this amount as well. These results are summarized in Table IV.

To test the applicability of the MBPT method as a model for carbene electronic structure within our choice of basis set, we performed calculations on the 1A_1 and 3B_1 states of **1** at the

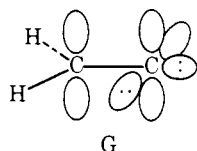
minimum energy geometries reported by Bauschlicher and Shavitt.²⁹ These results are presented in Table I. It is interesting to note that when both states are correlated through eighth order in the MBPT, the singlet–triplet splitting is diminished with respect to our single-configuration HF splitting by $|28.6 - 13.1| = 15.5$ kcal/mol.

The final eighth-order MBPT splitting of -13.1 kcal/mol comes within 2.5 kcal/mol of the best extended basis set CI estimates of -10.6 kcal/mol.^{27,29} This can be considered excellent agreement given the modest (4s2p1d/2s) polarized basis function space over which the MBPT is defined in our calculations, since Bauschlicher and Shavitt got a full CI splitting of -12.2 kcal/mol when they employed a comparable, but slightly better, (4s2p1d/2slp) basis set.²⁹ Significantly, the extended polarized basis sets used in these other studies of **1** (e.g., (9s6p3d/4s2p),²⁵ (6s4p2d/3s2p)²⁹) also yielded HF-level 1A_1 – 3B_1 splittings whose magnitudes are about 4 kcal/mol smaller than our HF-level splitting of -28.6 kcal/mol (see Table IV). Thus, our results demonstrate that the MBPT method is capable of rendering adequate descriptions of both states of interest within our choice of basis.

The effectiveness of the two-configuration 1A_1 and the one-configuration 3B_1 valence descriptions in **1** suggests that considerations of valence electronic structure in **2** and **3** will provide good insights into the nature of the low-lying states of these unsaturated carbenes as well. Even though the valence electronic structures of **2** and **3** are more complicated than the simple valence configurations A–C of **1**, the descriptions of the lowest triplet states of these unsaturated carbenes will be dominated by configurations analogous to A, while configurations analogous to B and C will contribute significantly to the lowest singlet states. The MBPT theory provides a convenient means for building a state description around such dominant configurations while automatically taking account of other significant configurations that manifest themselves in unsaturated carbene states. In what follows, we will make frequent reference to configurations that arise from various occupancies of the valence orbitals of **2** and **3**. The relative importance of these configurations will be adduced from simple structure and bonding arguments.



B. Vinylidene. The dominant valence configurations of **2** corresponding to configurations A–C of **1** are D–F. To these configurations, we must also add another valence configuration, G.



Configuration G does not preserve the C–C π bond, but it is still favorable on the basis of orbital energetics (i.e., it can be viewed as a double excitation from the b_1 π orbital, the highest occupied molecular orbital (HOMO) of the dominant singlet configuration C, to the lowest unoccupied molecular orbital (LUMO) of C, the b_2 π orbital. Configurations D and F, on the other hand, involve excitations from the a_1 σ HOMO-1 orbital of E). From configurations D–G for **2**, which correspond to all possible valence configurations of the appropriate spin and spatial symmetry, we can write the state descriptions

$$|^3B_2\rangle_{H_2CC} \simeq [\text{core}] a_1 b_1^2 b_2 \quad (3)$$

$$|^1A_1\rangle_{H_2CC} \simeq C_E[\text{core}] a_1^2 b_1^2 + C_F[\text{core}] b_1^2 b_2^2 + C_G[\text{core}] a_1^2 b_2^2 \quad (4)$$

where $|C_E|^2 + |C_F|^2 + |C_G|^2 \simeq 1$ in eq 4.

The core in carbene **2** consists of two filled carbon 1s atomic orbitals with a_1 symmetry, a C–C σ bond with a_1 symmetry, and two C–H bonding orbitals with a_1 and b_2 symmetry. The valence region is comprised of a π bonding orbital with b_1 symmetry and, depending on the state or configuration, a π nonbonding orbital with b_2 symmetry lying in the plane of the hydrogens, and a hybridized nonbonding σ orbital with a_1 symmetry.

To understand the bonding and state ordering in **2**, it is helpful to make comparisons between it and carbene **1**. Directing our attention to the valence region, we note that carbene **2** differs from carbene **1** in three important ways. First, the π valence nonbonding orbital in **1** has b_1 symmetry, but in **2** it has b_2 symmetry and lies in the molecular plane. The possibility for a hyperconjugative interaction between the b_2 C–H bond and the b_2 nonbonding orbital must be considered in both the 1A_1 and 3B_2 states of **2**. Second, the bonding b_1 π orbital in the valence region of **2** has no analogue in carbene **1**. As we have seen, double excitations from this orbital can give rise to another valence configuration contribution to the 1A_1 state, G. Third, the orbitals localized on the carbene atoms of **1** and **2** are hybridized in different ways. For example, triplet state Mulliken population analysis shows that the four L shell (i.e., $2s^2 2p^2$) carbene carbon electrons of **2** are hybridized as ³³

$$p(sp)^2 \sim p_{b_1(CC \pi)} p_{b_2(nb \pi)} (sp)_{a_1(CC \sigma)} (sp)_{a_1(nb \sigma)} \quad (5)$$

contrasting with the

$$p(sp)^3 \sim p_{b_1(nb \pi)} (sp^2)_{a_1(CH)} (sp^2)_{b_2(CH)} (sp^2)_{a_1(nb \sigma)} \quad (6)$$

hybridization found in triplet **1**.^{26,29} Similarly, singlet **2** exhibits

$$p(s^{\ll 1} p^{\sim 1}) (s^{\sim 2} p^{\ll 1})^2 \sim p_{b_1(CC \pi)} (s^{\ll 1} p^{\sim 1})_{a_1(CC \sigma)} \times [(s^{\sim 2} p^{\ll 1})_{a_1(nb \sigma)}]^2 \quad (7)$$

carbene carbon hybridization,³³ whereas the hybridization in singlet **1** is^{26,29}

$$(s^{\ll 1} p^{\sim 2})^2 (s^{\sim 2} p^{\ll 1})^2 \sim (s^{\ll 1} p^{\sim 2})_{a_1(CH)} \times (s^{\ll 1} p^{\sim 2})_{b_2(CH)} [(s^{\sim 2} p^{\ll 1})_{a_1(nb \sigma)}]^2 \quad (8)$$

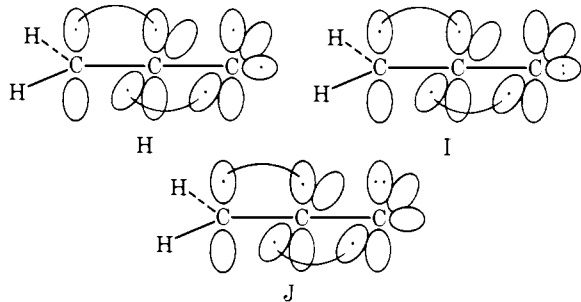
The singlet valence configurations B in **1** and E, G in **2** all arise from placement of the nonbonding electron pair in an a_1 σ valence orbital. From eq 5–8, it is seen that the a_1 σ nonbonding valence orbital in **2** has greater s character and hence lower orbital energy than the analogous orbital in **1** (e.g., -0.46 hartree in singlet **2** vs. -0.39 hartree in singlet **1**). The greater s character of this valence orbital helps to make singlet orbital occupancy in **2** more favorable energetically.

In view of these differences between carbenes **1** and **2**, particularly carbene carbon orbital hybridization and the additional singlet configuration G, our prediction of a 1A_1 ground state for **2** is not surprising. The ab initio calculations of Davis, Goddard, and Harding³³ and Dykstra and Schaefer,³⁴ as well as recent experimental data,³ also suggest singlet spin multiplicity for the ground state of **2**. Early HF and semiempirical studies on this carbene predicted a singlet ground state as well.^{30–32} The correlation contributions of the $a_1^2 \rightarrow b_2^2$ and $b_1^2 \rightarrow b_2^2$ double excitation configurations F and G in **2** lower the energy of the 1A_1 ground state, thereby increasing the magnitude of the calculated 1A_1 – 3B_2 energy splitting relative to the splitting determined with single-configuration state descriptions (i.e., only configuration E for the 1A_1 state, configuration D for the 3B_2 state). Thus, we find that the 3B_2 state

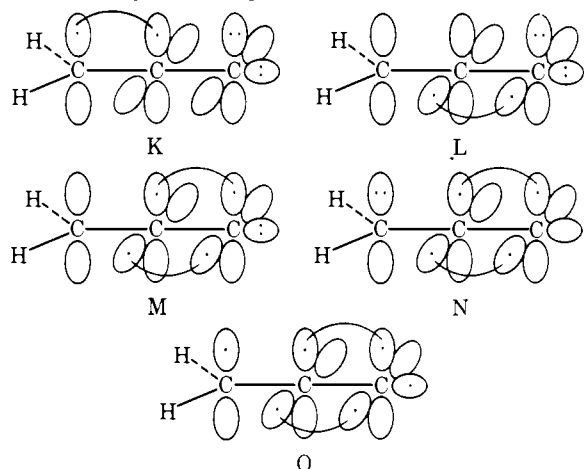
of **2** lies 51.1 kcal/mol above the 1A_1 state in an eighth-order MBPT calculation where account is taken of the 1A_1 configurations F and G as well as all other double excitation configurations, but our HF-level single-configuration calculations place this excited triplet state only 15.7 kcal/mol above the 1A_1 state (see Table II). Since the 1A_1 state lies above the 3B_1 state in carbene **1**, the effect of the analogous $a_1^2 \rightarrow b_1^2$ double excitation configuration C in this system is to diminish the magnitude of the 1A_1 - 3B_1 splitting relative to a HF-level splitting.

On the basis of semiempirical MINDO/2 calculations, Bodor et al.³¹ predicted that the 3B_2 state of **2** lies 20.5 kcal/mol above the 1A_1 ground state, a result qualitatively confirmed in the work of Dykstra and Schaefer,³⁴ who obtained a singlet-triplet splitting of 32.4 kcal/mol with their self-consistent electron pair (SCEP) method, which includes a modest treatment of electron correlation. Our MBPT results are in good agreement with the generalized valence bond (GVB) study of Davis, Goddard, and Harding,³³ which, with careful account of correlation effects in both the 1A_1 and 3B_2 states, yielded a singlet-triplet splitting of 45.9 kcal/mol for **2** at slightly different state geometries from those we selected. The larger magnitude of the HF level singlet-triplet splitting in **2** reported by these authors (i.e., 31.0³³ and 27.2 kcal/mol³⁴ vs. our corresponding value of 15.7 kcal/mol) can be attributed to their use of a restricted Hartree-Fock (RHF) rather than a UHF triplet. The UHF necessarily yields a lower triplet energy than the RHF, thereby stabilizing the 3B_2 HF state relative to the 1A_1 HF state. Since the triplet is above the singlet in **2**, the use of a UHF triplet gives rise to a smaller singlet-triplet splitting at the HF level.

C. Vinylidene carbene. The dominant valence configurations of **3** analogous to A-C of **1** and D-F of **2** are shown in H-J. Carbene **3** also has an important group of valence configurations K-O arising from excitations out of the b_1 and b_2 bonding



π orbitals of H-J. It is easily seen that configuration K, a $b_2^2 \rightarrow b_1^2$ (i.e., HOMO \rightarrow LUMO) excitation of the singlet configuration I, is analogous to configuration G in carbene **2**. However, the configurations L-O of **3** have no counterparts in either **1** or **2**. The contributions of configurations H-O to the lowest singlet and triplet states of **3** are given by



$$|^3B_1\rangle_{H_2CCC} \approx C_H[\text{core}] a_1 b_1^2 b_2^2 b_1' + C_O[\text{core}] a_1 b_2^2 b_1'^2 b_1'' \quad (9)$$

$$|^1A_1\rangle_{H_2CCC} \approx C_1[\text{core}] a_1^2 b_1^2 b_2^2 + C_J[\text{core}] b_1^2 b_2^2 b_1'^2 + C_K[\text{core}] a_1^2 b_1^2 b_1'^2 + C_L[\text{core}] a_1^2 b_2^2 b_1'^2 + C_M[\text{core}] a_1^2 b_2^2 b_1''^2 + C_N[\text{core}] b_2^2 b_1''^2 b_1'''^2 \quad (10)$$

where $|C_H|^2 + |C_O|^2 \approx 1$ and $|C_1|^2 + |C_J|^2 + |C_K|^2 + |C_L|^2 + |C_M|^2 + |C_N|^2 \approx 1$ in eq 9 and 10.

The core electrons in **3** occupy three a_1 carbon $1s$ orbitals, two a_1 C-C σ bonding orbitals, and two C-H bonding orbitals with a_1 and b_2 symmetry. In addition to the usual a_1 σ and b_1' π nonbonding orbitals, the valence region of this carbene includes a b_1 π bond between the methylene and center carbon atoms, a b_2 π bond between the center and terminal carbon atoms, a b_1'' π orbital with bonding character between the center and terminal carbon atoms, and a nonbonding b_1''' π orbital localized on the methylene carbon. As in carbene **2**, the a_1 σ valence nonbonding orbital of **3** exhibits sp hybrid character in the triplet state and $s^2 p^{\ll 1}$ character in the singlet, but the b_1' π nonbonding orbital is again perpendicular to the molecular plane, as in carbene **1**. Both of these nonbonding orbitals are localized on the terminal carbon atom of carbene **3** in our simple MO pictures H-J, which are analogous to the basic configurations A-C in carbene **1**. In this system, however, we must consider intravalence correlation between the electrons in the bonding and nonbonding π orbitals of b_1 symmetry, as indicated by the presence of configurations L-O. This important correlation effect has no direct analogue in either carbene **1** or **2**. While the b_2 π nonbonding valence orbital in carbene **2** can in principle correlate with the b_2 C-H bond, this core-valence hyperconjugative correlation is not expected to be as important as the intravalence correlation we find in **3**. Theoretical studies of correlation in the analogous formaldehyde oxygen b_2 π orbital⁵³ support our prediction of a small b_2 core-valence correlation contribution in carbene **2**.

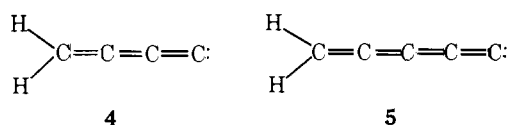
We consider now the effects of this intravalence b_1 π electron correlation on the states of **3**. In the 3B_1 state of **3**, it is seen that the electron in the b_1 valence nonbonding π orbital can correlate with the b_1 valence bonding electron pair to give a diradical triplet configuration O (i.e., $H_2\dot{C}-C\equiv\dot{C}$). This accounts for some lowering of the 3B_1 state energy relative to that of the 1A_1 state. However, the 1A_1 state, inherently a highly correlated state in all carbenes, becomes even more highly correlated in **3** owing to b_1 nonbonding orbital delocalization. In addition to configurations I and J, which have analogues in both **1** and **2**, and K, the analogue of G in **2**, three more configurations, L, the $b_1^2 \rightarrow b_1'^2$ excitation of I, and the two zwitterionic configurations, M and N (i.e., $H_2C^+-C\equiv C^-$ and $H_2C^--C\equiv C^+$), analogues of the triplet configuration O, appear in **3** as a result of correlation of the b_1 π electrons. Configuration L, an important valence configuration in singlet **3**, has no similar counterpart in the triplet. Thus, the b_1 intravalence correlation in **3** preferentially stabilizes the 1A_1 state over the 3B_1 state.

From these considerations, together with the predominantly s character of the a_1 σ nonbonding orbital, a singlet ground state is predicted for **3**. Hartzler's experimental results suggest a singlet ground state for $(CH_3)_2CCC$, the methyl-substituted analogue of **3**.^{3,54} Our HF-level calculations, in which the 1A_1 state is assumed to be configuration I and the 3B_1 state is assumed to be configuration H, show that the 3B_1 state lies only 2.4 kcal/mol above the 1A_1 ground state. With correlation, the splitting increases to 48.7 kcal/mol, indicating a differential correlation increase of 46.3 kcal/mol for the 1A_1 state. As expected, the increase in the correlation energy of the 1A_1 state, which arises from including the effects of the electron pair delocalization configurations J-N, is greater in magnitude than the 3B_1 correlation energy increase due to configuration O, which describes the delocalization of the lone b_1 electron in this

triplet (see Table IV).

It is interesting to note that Hehre et al. find the singlet state of **3** to lie above the triplet at the single-configuration HF level.³⁵ As basis set quality is improved, however, the magnitude of the singlet–triplet splitting reported by these authors decreases from -25.6 kcal/mol (STO-3G basis) by only -1.5 kcal/mol (6-31G* basis including d-type polarization functions).³⁵ These calculations illustrate that improvements to the basis set, particularly provisions for d-type polarization flexibility, bring about a significant preferential stabilization of the lowest singlet over the lowest triplet in **3**, a pattern also seen in theoretical studies of **1** and **2**. Similarly, our preliminary HF test calculations on **3** employing a nonpolarized basis set also placed the triplet beneath the singlet by -4.8 kcal/mol. Since basis set augmentation and treatment of correlation, the two major ways to improve the quality of an ab initio theoretical study, both favor the singlet ground state, it is expected that any more complete study of **3** will confirm our predicted state ordering for this system. However, it should be kept in mind that our basis set for **3**, which contains d functions only on the carbene carbon, is slightly biased against the $^3B_{1,2}$ state. Our theoretical results for carbene **3** are summarized in Table III.

D. Trends and Predictions. Listed in Table IV are the 1A_1 and $^3B_{1,2}$ correlation energies, correlation energy differences, and uncorrelated and correlated energy splittings for carbenes **1**, **2**, and **3**. From the second and third columns of this table, we see that the magnitude of the correlation energy of both the 1A_1 and $^3B_{1,2}$ states increases as the complexity of the carbene species increases. In addition, the figures in the fourth column of the table indicate that the 1A_1 – $^3B_{1,2}$ correlation energy difference increases with increasing carbene size (i.e., the correlation energy increase of the 1A_1 state is proportionately larger than the increase of the $^3B_{1,2}$ correlation energy as the carbene system itself becomes larger). This trend reflects the proliferation of singlet valence configurations as carbene size increases. At the HF level, however, the splitting between the 1A_1 and $^3B_{1,2}$ state diminishes in magnitude going from **2** to **3**; the $^3B_{1,2}$ HF state is consequently stabilized relative to the 1A_1 HF state in the larger unsaturated carbenes. Since the singlet state is more correlated than the triplet, a single-configuration approximation will always describe the triplet more accurately than the singlet. The latter trend would of course be expected to continue for extended unsaturated carbenes such as **4** and **5**, where increased nonbonding orbital delocalization would enhance the $^3B_{1,2}$ HF state energy stabilization



(i.e., as carbene size increases, a single configuration represents a proportionately smaller component of the true correlated singlet than the true triplet. Consider the number of singlet and triplet valence configurations required for carbenes **1**–**3**: **1**, 2S–1T; **2**, 3S–1T; **3**, 6S–2T). In fact, a HF single-configuration prediction of triplet ground states for **4** and **5** is suggested by the trend shown in the first column of Table IV.

The above HF- and correlated-level trends imply that stabilization of the 1A_1 state due to greater s hybrid character of the doubly occupied nonbonding a_1 σ orbital becomes proportionately less important as carbene complexity increases, allowing other features of electronic structure, particularly electron correlation and nonbonding π orbital delocalization, to dominate. Since the 1A_1 state is inherently a more correlated state than the $^3B_{1,2}$ state, we expect the large correlation and delocalization contributions arising from a more complex system to amplify the basic differences in the two states, thereby giving preferential stabilization to the 1A_1 state, as

suggested by the trend in the fourth column of Table IV. Again, this follows from our observation that the number of configurations required to describe the singlet well increases more rapidly with carbene size than the number required for an equivalent treatment of the triplet. On the basis of these trends, we predict singlet ground states for carbenes **4** and **5**, since the strong correlation effects and $\sigma^2 \rightarrow \pi^2$, $\pi^2 \rightarrow \pi^2$ delocalization influences in these systems would be expected to pull the 1A_1 states beneath the triplet states, counteracting the “artificial” trend of $^3B_{1,2}$ state stabilization at the HF level and the weak delocalization stabilization effect of the single nonbonding $^3B_{1,2}$ π electron at the correlated level. Finally, it should be noted that given an extended valence π region, the lowest 3A_2 states of **4** and **5**, which can be thought to rise from $b_{1,2}$ valence occupancy, may approach in energetic stability the corresponding $^3B_{1,2}$ states of these species.

Our results also show that carbene carbon d functions must be present in basis sets for **2** and **3** to ensure accurate theoretical description of the low-lying states of these species. We find that the carbene carbon d functions preferentially stabilize the 1A_1 states of **2** and **3**. This effect is well documented in recent theoretical studies on carbene **1**. For example, the erroneously large methylene (carbene **1**) 1A_1 – 3B_1 splitting of -22.2 kcal/mol, computed by O’Neil, Schaefer, and Bender using the nonpolarized (4s2p/2s) basis together with multiconfiguration state descriptions,¹¹ shows that even the multiconfiguration approach cannot completely compensate for a lack of basis set polarization flexibility. In the work of Meadows and Schaefer²⁵ and Bauschlicher and Shavitt²⁹ on **1**, however, simple one- and two-configuration state descriptions, used in conjunction with excellent polarized HF-limit basis sets, gave the correct 1A_1 – 3B_1 splitting of ~ -11 kcal/mol. Thus, it is not surprising to find that adequate theoretical description of the more correlated singlet states of unsaturated carbene systems requires a corresponding polarization flexibility in the basis. Without such flexibility, we find that even the state ordering in **3** is reversed at the HF level.

Conclusion

Our ab initio calculations predict a triplet ground state for methylene (**1**) and singlet ground states for both vinylidene (**2**) and vinylidenecarbene (**3**). The lowest excited state in each of these unsaturated carbene systems is found to have triplet spin multiplicity. Singlet–triplet energy splittings of -13.1 , 51.1 , and 48.7 kcal/mol were computed for **1**, **2**, and **3**, respectively. The greater s character of the nonbonding a_1 σ orbital on the terminal carbon and correlation effects arising from $\sigma^2 \rightarrow \pi^2$ and $\pi^2 \rightarrow \pi^2$ configuration interaction of the valence electrons are identified as important factors in the stabilization of the singlet states of unsaturated carbenes. Preferential stabilization of the singlet state in carbene **3** due to b_1 π orbital delocalization is discussed and its implications are noted for extended unsaturated carbenes. Singlet ground states are predicted for the extended unsaturated carbenes $\text{H}_2\text{CCCC:}$ (**4**) and $\text{H}_2\text{CCCCC:}$ (**5**) on the basis of singlet state correlation stabilization trends observed in carbenes **2** and **3**. The importance of carbon d-type polarization functions in unsaturated carbene basis sets is demonstrated. We find that this d function polarization flexibility preferentially stabilizes the singlet state, as in methylene.

Acknowledgment. The reviewers’ comments and suggestions are gratefully acknowledged. J.W.K. wishes to thank Professor Peter J. Stang for many stimulating discussions and for making available a preprint copy of his review article on unsaturated carbenes.

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A Molecular Orbital Study of Protonation. 5. Equilibrium Structures and Energies of Ions R_2COH^+

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Abstract: Ab initio SCF calculations have been performed to determine the relative proton affinities of the carbonyl bases R_2CO and the structures of the ions R_2COH^+ , with R one of the isoelectronic saturated groups CH_3 , NH_2 , OH , and F . The predicted order of proton affinity with respect to R is $NH_2 > CH_3 > OH > H > F$, which is the same order predicted for the monosubstituted carbonyl bases $RCHO$. Replacement of the hydrogen atom in $RCHO$ by a second R group causes a further change in the proton affinity of the base in the same direction as observed upon substitution of the first R group, although the effect of two substituents is less than additive except in F_2CO . Protonation of carbonyl bases leads to an increase in the C-O bond distance and a decrease in the bond distance between the carbonyl carbon and the substituent, the magnitude of which depends on the substituent. Protonation also causes changes in the bond angles about the carbonyl carbon which are essentially independent of the nature of the substituent, but strongly dependent on the position of the proton relative to the two substituents. Changes in bond lengths and bond angles and in the electron distribution upon protonation of the bases R_2CO are similar to the changes which occur upon protonation of the bases $RCHO$. From the computed results, a model for the protonation of carbonyl bases is proposed.

Introduction

In part 3 of this series,¹ the relative proton affinities of the bases $RCHO$ were computed, and an analysis was made of substituent effects on proton affinities. In that study, the equilibrium structures of the relaxed ions $RCHOH^+$ were

determined, and comparisons between the structures of these ions and the structures of the corresponding bases $RCHO$ provided insight into the geometry changes due to protonation. That study has now been extended to the disubstituted carbonyls R_2CO , with R comprising the isoelectronic saturated