though the triplet-state configuration has a lower MS-Xα energy, the difference between it and the singlet state is too small to be confident of this ordering. The observed singlet ground state is therefore not inconsistent with the calculated results. In the 5− structure, the extra electron goes into the same HOMO and there is almost no change in the orbital spectrum. This is in agreement with the observed $S = {}^1/_2$ ground state as well as the fact that the absorption spectrum is nearly the same as that of the 4− structure. The Hellmann–Feynman force on a cobalt atom differs by only a small amount in the two structures, implying similarly sized structures as is observed in experiment. However, the 5− structure is predicted to be slightly smaller, in contradiction to the crystal data.

Two models were used to extrapolate from the clusters to the mineral cobalt pentlandite. The first was the anion $[Co_8S_6(SH)_8]^{6-}$, in which the cobalt atoms have the same formal charge as in pentlandite. The extra electron goes to fill the highest occupied $12e_u$ level of the 5− structure, and the orbital spectrum is similar to the 4− and 5− clusters. However, the additional electron charge leads to an increase in the inward Hellmann–Feynman force on the cobalt atoms, implying that this oxidation state would tend to be smaller in size. This could be a contribution to the decreased size of the Co_8S_6 core in pentlandite, but does not appear to be the dominant one. Calculations on the $[Co_8(SH)_6(SH)_8]^{2+}$ cluster, in which the extra coordination in the extended material is imitated by additional hydrogen ligands, were also performed. With the 4− cluster as a reference, there is a shifting about of the frontier orbitals, with a stabilization and occupation of what would correspond to the $5e_g$ LUMO of the octahedral cluster. There is also a significant increase in the inward Hellmann–Feynman force on the cobalt atoms relative to the 4− cluster, which is about 4 times that of the 6− cluster. Burdett and Miller also observed such a stabilization in going from the Co_8S_8 to the Co_9S_8 crystal, which corresponds to adding ligands to the bridging sulfurs of the Co_8S_8 material. Their interpretation was that this orbital increases the direct metal–metal interactions to cause the shrinkage. However, it was found here that, although these newly occupied orbitals make a sizable contribution to the increase in the Hellmann–Feynman force, the contribution is nearly identical with that of the orbitals they replace. The decrease in size is therefore due to a subtle combination of effects from the redistribution of the electron charge in the molecule and cannot be associated with only one or a few orbitals. It is clear, though, that the dominant effect on the size of the core is due to extra coordination on the bridging sulfurs.

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Vinylidene: The Final Chapter?

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Abstract: Ab initio molecular electronic structure theory is used to study the electronic ground state vinylidene–acetylene isomerization. Vinylidene, acetylene, and the transition state connecting them are located at various levels of theory, including correlated levels, and with large basis sets. The highest level and basis set with which geometry optimizations are performed is the CCSD level with the TZ+2P basis set. These structures are characterized by harmonic vibrational analyses as minima or transition states. Single-point energies also are computed at higher levels of theory, the highest being CCSD/QZ+3P, for all three structures. The effects of carbon atom f functions and hydrogen atom d functions are also explicitly considered. A *classical* barrier to isomerization from vinylidene to acetylene of ~3 kcal/mol is found. The ΔE for isomerization is predicted to be ~43 kcal/mol.

Introduction

Vinylidene, the simplest unsaturated carbene, plays an important role in organic chemistry.[1,2] As a proposed intermediate in many chemical reactions, it has been studied extensively, both experimentally and theoretically. The fundamental issue addressed in these studies has been whether or not vinylidene actually exists as a bound molecule. It has long been established that, *if* vinylidene indeed exists, its lifetime is very short.[3-7] Consequently, it was long believed to be extremely difficult, if not impossible, to observe vinylidene either chemically or spectroscopically.

Some recent experiments have prompted the proposal of vinylidene as an intermediate in chemical reactions[8,9] while others have provided evidence of vinylidene's participation in chemical reactions.[10,11] Field and co-workers[12,13] have very recently observed features diagnostic of vinylidene in the high resolution stimulated emission pumping spectrum of acetylene. By spectral cross correlation and information extracted from the spectrum, they determined an upper bound of 44.4 kcal/mol for the vinylidene zero-point level relative to that of acetylene. However, they were unable to determine the height of the barrier to isomerization of vinylidene to acetylene or even whether or not a barrier exists. Holme and Levine[14] subsequently performed classical trajectory and quantum algebraic computations in order to define the detailed dynamics that produce the spectral structures observed in the stimulated emission pumping spectrum of acetylene. Li-

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neberger and co-workers[15,16] have actually observed the X $^1A_1$ ground state of vinylidene (and also, in 1989, the a^3B_2 and b^3A_2 states) in the ultraviolet photoelectron spectra of X $^2B_2$ H_2CC^-, X $^2B_2$ D_2CC^-, and X $^2A_1$ $HDCC^-$. They have determined a strict lower bound to the lifetime of vinylidene of 0.027 ps when only lifetime broadening is considered, but they estimate the lifetime to be 0.04–0.20 ps on the basis of a simulation of the line shapes including rotational broadening. Their vibrational analysis has yielded fundamental vibrational frequencies of 3025 ± 30 cm^{-1} for the CH symmetric stretch, 1635 ± 10 cm^{-1} for the CC stretch, and 1165 ± 10 cm^{-1} for the CH_2 scissors. The acetylene–vinylidene isomerization energy is concluded to be 44 ± 4 kcal/mol. The negative ion photoelectron spectroscopic and gas-phase proton transfer kinetic studies of Ervin et al.[17] yielded a result of 47.4 ± 4.0 kcal/mol for the acetylene–vinylidene isomerization energy. They also determined, among other things, the electron affinity of the vinylidene radical. The acetylene–vinylidene isomerization energy values determined in these three studies are in serious disagreement with the value of 66 kcal/mol determined by Benson[18] from bond additivity arguments, yet they are in excellent agreement with each other. They also are consistent with values obtained by theory.[19-25]

There have been numerous theoretical investigations of the vinylidene–acetylene isomerization. A partial survey of these studies[21-25] yields predictions of the classical barrier height ranging from 3.3 to 8.1 kcal/mol. One of the first reliable theoretical studies of this isomerization was that of Dykstra and Schaefer.[26] With the self-consistent electron pairs (SCEP) method and a double-ζ plus polarization (DZP) basis set, they found a barrier to rearrangement of 8.6 kcal/mol. Improvements in both basis set and correlation[27] resulted in a barrier of 6.4 kcal/mol. Corrections to this value led to a "best estimate" of 4 kcal/mol for the classical barrier height and 2.2 kcal/mol for the zero-point corrected barrier height. Further improvements in the basis set[28] did not change the results significantly, leading to an ab initio classical barrier height of 6.3 kcal/mol. Additional corrections resulted in a best estimate of 2–4 kcal/mol for the classical barrier height. The conclusion of these studies was that vinylidene does indeed exist as a bound molecule. However, another important series of theoretical studies of this isomerization arrived at quite a different conclusion. The Moller–Plesset perturbation theory studies of the Pople group[29,30] resulted in a value of 0.9 kcal/mol for the zero-point corrected barrier to isomerization of vinylidene to acetylene. Significant reductions in the barrier height with basis set extension and various corrections prompted the following speculation: "It is quite possible that further refinement of the theory would entirely eliminate the activation barrier for rearrangement."[30] Although the conclusion drawn from these studies was that vinylidene is either a very shallow minimum or a saddle point on the potential surface, the following is stated: "Vinylidene should rather be considered as the effective transition structure for the degenerate rearrangement on the C_2H_2 surface in which the hydrogen nuclei of acetylene change places."[30]

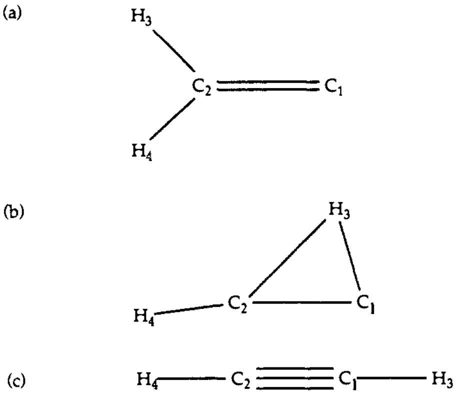

Figure 1. The nuclear configurations of (a) vinylidene, (b) transition state, and (c) acetylene.

Although there is growing experimental evidence for the existence of vinylidene, the issue of whether or not vinylidene indeed exists as a bound molecule has yet to be completely resolved. Hence, the goal of the present study is to reexamine this problem at a high level of theory. Very large basis sets and extensive treatment of electron correlation are used to locate vinylidene, acetylene, and the transition state connecting them. Vibrational analyses are performed to verify the nature of all three of these stationary points. Zero-point vibrational corrections to the energies for vinylidene and the transition state are found. The barrier for rearrangement of vinylidene to acetylene and the acetylene–vinylidene isomerization energy are examined.

Theoretical Methods

Four different basis sets were used in this study. The first, of double-ζ plus polarization quality, is the Huzinaga–Dunning contracted Gaussian basis[31,32] C(9s5p/4s2p), H(9s/4s) augmented with a set of (six) d functions on C (α = 0.75) and a set of p functions on H (α = 0.75), designated DZP. The second, TZ+2P, is the Huzinaga–Dunning[31,33] C(10s6p/5s3p), H(5s/3s) augmented with two sets of d functions on C (α = 1.50, 0.35) and two sets of p functions on H (α = 1.50, 0.35). The QZ+3P basis set consists of Van Duijneveldt's[34] C(11s7p/6s4p), H(7s/4s) basis augmented with three sets of d functions on C (α = 1.85, 0.65, 0.23) and two sets of p functions on H (α = 1.26, 0.36). The final basis set, TZ+2P+f, consists of the TZ+2P basis augmented with a set of f functions on C (α = 0.80) and d functions on H (α = 1.0). The use of seven-component f functions and five-component d functions was employed throughout the TZ+2P+f basis as opposed to ten f-like functions and six d-like functions.

The self-consistent-field (SCF) method is employed in this study, while the effects of electron correlation are taken into account with the configuration interaction (CI) method and the coupled cluster (CC) method. In the configuration interaction method we consider configurations generated by all single and double excitations relative to the SCF reference configuration (CISD). Restrictions applied here are that the two lowest SCF molecular orbitals (carbon 1s-like) are kept doubly occupied in all configurations while the two highest SCF virtual molecular orbitals are deleted. Davidson's correction to the energy for unlinked quadruple excitations[35,36] has also been considered. In the coupled cluster method we consider all configurations generated by all single and double excitations relative to the SCF reference configuration (CCSD).[37] In the CCSD studies all SCF molecular orbitals are included.

The structures of vinylidene, acetylene, and the transition state connecting them are optimized at the SCF and CISD levels with the DZP, TZ+2P, TZ+2P+f, and QZ+3P basis sets; at the CCSD level with the DZP and TZ+2P basis sets; and at the CCSDT-1 level with the DZP basis set. Analytic first derivative methods are used in these optimiza-

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Table I. Predicted Molecular Structures[a]

	SCF			CISD			CCSD	
	DZP	TZ+2P	QZ+3P	DZP	TZ+2P	QZ+3P	DZP	TZ+2P
vinylidene								
r_{12}	1.2993	1.2857	1.2860	1.3159	1.2957	1.2961	1.3216	1.3003
r_{23}	1.0804	1.0751	1.0758	1.0879	1.0791	1.0799	1.0903	1.0814
θ_{324}	120.2	120.5	120.5	119.7	120.2	120.2	119.5	120.0
transition state								
r_{12}	1.2429	1.2303	1.2295	1.2631	1.2444	1.2436	1.2709	1.2509
r_{23}	1.4674	1.4498	1.4588	1.4286	1.4104	1.4209	1.4003	1.3862
r_{24}	1.0679	1.0597	1.0602	1.0770	1.0651	1.0664	1.0801	1.0672
θ_{123}	50.5	51.2	50.8	52.0	52.7	52.1	53.2	53.9
θ_{124}	180.5	180.3	180.5	179.1	179.0	179.4	178.7	178.6
acetylene								
r_{12}	1.1912	1.1798	1.1796	1.2131	1.1955	1.1956	1.2198	1.2010
r_{13}	1.0616	1.0537	1.0542	1.0691	1.0581	1.0593	1.0720	1.0605

[a] Bond distances in angstroms and bond angles in degrees.

tions.[38-44] Harmonic vibrational frequencies are determined for all of the above-mentioned optimized structures except those optimized with the TZ+2P+f basis set and those found at the CCSDT-1 level. At the SCF level, vibrational frequencies have been evaluated by analytic second derivative methods,[45-47] and at the CISD and CCSD levels they are found by finite central differences of analytic gradients. The following single point energy calculations for all three structures are also performed: CCSD with the TZ+2P+f basis at the CCSD/TZ+2P optimized structure and with the QZ+3P basis at the CISD/QZ+3P optimized structure [the two lowest SCF molecular orbitals (carbon 1s-like) are kept doubly occupied in all configurations while the two highest SCF virtual molecular orbitals are deleted for these energy points]; and CCSDT-1 with the TZ+2P basis at the CCSD/TZ+2P optimized structure.

Results and Discussion

Molecular Structures. The nuclear arrangements of all three molecules appear in Figure 1. The geometries predicted for all three molecules at all levels of theory appear in Table I. As expected, the bond lengths for all three structures and all three levels of theory decrease with increasing size of the basis set. In addition, the bond lengths of all three structures found with a given basis set increase with increasingly comprehensive treatment of electron correlation. At the SCF and CISD levels of theory, there is negligible change in the geometries of all three structures in progressing from the TZ+2P basis to the QZ+3P basis. Furthermore, for the TZ+2P basis (the largest basis with which geometry optimizations were performed at all levels of theory), there is very little change in the geometries from the CISD to the CCSD level, that is, in going from one correlated level to another which more accurately accounts for electron correlation.

The structures determined at the CCSDT-1/DZP level follow: for vinylidene, r_{12} = 1.325 Å, r_{23} = 1.092 Å, and θ_{324} = 119.2°; for the transition state, r_{12} = 1.279 Å, r_{23} = 1.392 Å, r_{24} = 1.082 Å, θ_{123} = 53.8°, and θ_{124} = 178.1°; and for acetylene, r_{12} = 1.226 Å and r_{13} = 1.073 Å. With the exception of the r_{23} bond length of the transition state, all of the bond lengths increase upon going from the CCSD/DZP to the CCSDT-1/DZP level. It should be noted that this bond in the transition state is between C_2 and the migrating hydrogen atom, and as such we would expect to encounter the most uncertainty (with respect to the determination of the other bond lengths involved in this study) in its determination. The bond lengths agree quite well in all cases with the values determined at the CCSD/DZP level, the largest deviation being 0.009 Å for the r_{23} bond length in the transition state. The bond angles are also in very good agreement. Thus, it can be seen that there is very little change in the geometries upon going from structures optimized at the CCSD to the CCSDT-1 level of theory. As a result of these observations, we would expect insignificant changes in the geometries of all three structures upon extending the basis set beyond TZ+2P or increasing the accounting of electron correlation beyond CCSD.

The geometrical parameters for acetylene found at the CCSD/TZ+2P level are highly consistent with those found by experiment. Specifically, the predicted value of the CC bond length is 0.002 Å shorter than the experimental value of 1.203 Å, and the predicted value of the CH bond length is 0.001 Å shorter than the experimental value of 1.061 Å.[48] The vinylidene CC bond length predicted by theory (1.30 Å) is consistent with that of a short formal CC double bond. As expected, the CC bond length predicted by theory for the transition state is intermediate between those of acetylene and vinylidene, and hence intermediate between those of a formal CC triple bond and a formal CC double bond.

It is interesting to note that the predicted geometrical structure of the transition state more closely resembles that of acetylene than vinylidene. This is most easily seen by noting that the angle formed by the two carbon atoms and the non-migrating hydrogen atom is very nearly linear and that the migrating hydrogen atom is closer to the carbon atom to which it is migrating than it is to the carbon atom from which it originated. This is in violation of Hammond's postulate[49] which states that, for an exothermic reaction, the transition state should more closely resemble the reactant than the product.

Vibrational Frequencies. The predicted harmonic vibrational frequencies for vinylidene and the transition state appear in Table II and those for monodeuterium- and dideuterium-substituted vinylidene appear in Table III. It should be noted that these are *harmonic* frequencies and as such do not account for anharmonicity. Errors in the predicted harmonic vibrational frequencies with respect to the true anharmonic vibrational frequencies are expected to be ~10–15% at the SCF level, ~7–10% at the CISD level, and ~5–7% at the CCSD level. Comparison of the predicted frequencies for the vinylidene CH symmetric stretch, CC stretch, and CH_2 scissors with those found by Lineberger and co-workers[15] (3025 ± 30 cm^{-1} for the CH symmetric stretch, 1635 ± 10 cm^{-1} for the CC stretch, and 1165 ± 10 cm^{-1} for the CH_2 scissors) is possible. Taking the above-mentioned expected errors into account, it can be seen that the CCSD/TZ+2P predicted frequencies agree quite well with the corresponding values determined by

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Table II. Harmonic Vibrational Frequencies (cm^{-1})

	assignment	DZP	TZ+2P	QZ+3P
	SCF			
vinylidene	CH asym str	3399	3380	3362
	CH sym str	3303	3288	3272
	CC str	1812	1821	1815
	HCH bend	1354	1358	1357
	C_1 oop	906	908	908
	HCH rock	542	536	534
transition state	C_2H_4 str	3555	3545	3531
	C_2H_3 str	2766	2708	2737
	CC str	1964	1973	1973
	HCH bend	1021	1020	1026
	H_4 oop	618	623	622
	$C_1C_2H_3$ bend	1012i	1009i	1011i
	CISD			
vinylidene	CH asym str	3326	3302	3283
	CH sym str	3225	3206	3189
	CC str	1707	1723	1721
	HCH bend	1278	1269	1277
	C_1 oop	775	788	789
	HCH rock	431	399	424
transition state	C_2H_4 str	3442	3435	3416
	C_2H_3	2687	2606	2652
	CC str	1871	1885	1887
	HCH bend	934	923	908
	H_4 oop	572	572	526
	$C_1C_2H_3$ bend	1007i	1007i	998i
	CCSD			
				expt[16]
vinylidene	CH asym str	3291	3255	
	CH sym str	3189	3160	3025
	CC str	1670	1685	1635
	HCH bend	1262	1246	1165
	C_1 oop	750	765	
	HCH rock	428	386	320
transition state	C_2H_4 str	3392	3386	
	C_2H_3 str	2616	2524	
	CC str	1821	1838	
	HCH bend	906	906	
	H_4 oop	547	571	
	$C_1C_2H_3$ bend	976i	971i	

Table III. Substituted Vinylidene Harmonic Vibrational Frequencies (cm^{-1})

	assignment	DZP	TZ+2P	QZ+3P
	SCF			
HDC_2	CH str	3354	3337	3320
	CD str	2473	2461	2448
	CC str	1777	1785	1779
	DCH bend	1199	1203	1202
	C_1 oop	819	821	821
	DCH rock	469	463	462
D_2C_2	CD asym str	2526	2511	2498
	CD sym str	2428	2418	2407
	CC str	1743	1750	1744
	DCD bend	995	998	997
	C_1 oop	722	723	723
	DCD rock	428	423	422
	CISD			
HDC_2	CH str	3279	3257	3239
	CD str	2414	2398	2386
	CC str	1676	1692	1690
	DCH bend	1130	1120	1128
	C_1 oop	701	713	713
	DCH rock	373	346	367
D_2C_2	CD asym str	2471	2452	2438
	CD sym str	2365	2352	2341
	CC str	1646	1662	1659
	DCD bend	939	931	937
	C_1 oop	617	628	628
	DCD rock	340	315	335
	CCSD			
				expt[16]
HDC_2	CH str	3243	3210	2995
	CD str	2388	2364	2265
	CC str	1639	1655	1610
	DCH bend	1116	1100	1025
	C_1 oop	678	692	
	DCH rock	371	335	275
D_2C_2	CD asym str	2446	2417	
	CD sym str	2338	2318	2190
	CC str	1609	1626	1590
	DCD bend	928	915	865
	C_1 oop	597	610	
	DCD rock	338	305	250

experiment. The monodeuterium- and dideuterium-substituted frequencies of vinylidene also agree well with those found in the Lineberger experimental study. The frequency shift values found in the Lineberger study are the following: for H_2C_2 to D_2C_2, a CH stretch shift of -835 cm^{-1}, a CC stretch shift of -45 cm^{-1}, and a H(D)CH(D) scissors shift of -300 cm^{-1}; and for H_2C_2 to HDC_2, a CC stretch shift of -25 cm^{-1}. The frequency shift values found in the present study are the following: for H_2C_2 to D_2C_2, a CH stretch shift of -842 cm^{-1}, a CC stretch shift of -59 cm^{-1}, and a H(D)CH(D) scissors shift of -331 cm^{-1}; and for H_2C_2 to HDC_2, a CC stretch shift of -30 cm^{-1}.

The structure referred to as the "transition state" has been confirmed by vibrational analyses at all levels of theory to be a true transition state with a single imaginary frequency. The reaction coordinate corresponds to the $C_1C_2H_3$ bend (see Figure 1). Furthermore, vinylidene has been confirmed to be a minimum, having all real frequencies, at all levels of theory. The fact that the values of the imaginary frequency of the transition state and the smallest frequency of vinylidene have essentially converged at high levels of theory indicates that the nature of these two stationary points will not be changed by further expansion of the basis set or a more extensive treatment of correlation—that is, vinylidene will remain a minimum and the "transition state" will remain a true transition state.

The predicted vibrational frequencies were used to compute zero-point vibrational corrections to the energies of vinylidene and the transition state. The zero-point corrections to the energies were taken as the sum of the real harmonic vibrational frequencies divided by two.

Energetics. The predicted barriers to rearrangement from vinylidene to acetylene, along with their corresponding zero-point vibrational corrections, appear in Table IV. The values of Davidson's correction to the CISD predicted barriers are also included. At each level of theory, the predicted classical barriers to rearrangement appear to have converged to within 0.5 kcal/mol with increasing basis set with the exception of the bases containing f functions. They also have converged to within 1.0 kcal/mol in progressing from the CISD to the CCSD level within a given basis set. The zero-point vibrational corrections (within the harmonic approximation) to the barriers have converged at all levels of theory and all basis sets, as have the Davidson corrections to the barriers for the CISD level of theory. Hence, the values obtained for the zero-point corrected barriers to rearrangement have converged to within 0.4 kcal/mol at each level of theory with increasing basis set and to within 0.2 kcal/mol in going from the CISD level to the CCSD level within a given basis set. We would therefore expect that further extension of the basis set and more extensive treatment of electron correlation would further decrease the barrier height, but would not eliminate it entirely. The single point energy calculations (see Table V) corroborate this expectation. An extension of the basis set from TZ+2P to QZ+3P at the CCSD level of theory yields no change (to within 0.1 kcal/mol) in the barrier. The effect of f functions on carbon and d functions on hydrogen can be inferred from our results via two approaches. First, the addition of f functions on carbon and d functions on hydrogen to the TZ+2P basis set, that is, the TZ+2P+f basis set, results in a lowering of the CISD Davidson corrected barrier by 1.9 kcal/mol. Second, a single point energy calculation at the CCSD/TZ+2P+f level of theory at the CCSD/TZ+2P optimized structure leads to a lowering of the classical barrier by 1.5 kcal/mol with respect to that found at the CCSD/TZ+2P Level. Either

Table IV. Barriers to Rearrangement (kcal/mol) for the Vinylidene–Acetylene Reaction

	DZP	TZ+2P	TZ+2P+f	QZ+3P
		SCF		
classical barrier	14.1	13.4	12.5	12.9
zero pt corr	−2.0	−2.0		−1.9
E_a	12.1	11.4		11.0
		CISD		
classical barrier	7.5	7.1	5.3	6.7
zero pt corr	−1.8	−1.8		−1.8
Davidson corr	−0.9	−0.8	−0.9	−0.8
E_a	4.8	4.5		4.1
		CCSD		
classical barrier	6.6	6.1		
zero pt corr	−1.9	−1.8		
E_a	4.7	4.3		
		CCSDT-1		
classical barrier	4.9			

[a] At each level of theory, the geometries of both vinylidene and the transition state have been rigorously optimized.

Table V. Single-Point Energies at High Levels of Theory

	classical barrier to rearrangement, kcal/mol	classical exothermicity for isomerization, kcal/mol
CCSD/TZ+2P+f//CCSD/TZ+2P	4.6	44.0
CCSD/QZ+3P//CISD/QZ+3P	6.1	40.6
CCSDT-1/TZ+2P//CCSD/TZ+2P	4.6	43.5

of these values could be considered to be an estimation of the effect of f functions upon the barrier to rearrangement. However, we would consider the value of 1.5 kcal/mol to be the better estimate as it is determined at the higher level of theory, and we would not expect that neglect of geometry optimization would have much of an effect at this level of theory. The effect of triple substitutions upon the barrier height can also be considered from two perspectives. First, the effect of the inclusion of linearized triple excitations for the DZP optimized structures upon the classical barrier height is to lower it by 1.7 kcal/mol. Second, a single point energy calculation at the CCSDT-1/TZ+2P level of theory at the CCSD/TZ+2P optimized structure leads to a lowering of the classical barrier of 1.5 kcal/mol with respect to that found at the CCSD/TZ+2P level. Either of these values could be taken as an estimate of the effect of triple excitations upon the barrier height. Hence, a comparison of the results of the optimized structure values and these single point energy calculations show that further extension of the basis set and a more comprehensive treatment of correlation do indeed lead to a lowering of the barrier but do not eliminate it entirely.

The ab initio barriers to rearrangement predicted in this study may be compared with estimated barriers derived from the experiments of Lineberger and co-workers.[16] On the basis of their observation of vibrational levels in the CH_2 rock mode, they state that vinylidene must indeed exist as a minimum on the potential energy surface and that the barrier to rearrangement must be at least as deep as the observed 2 ← 0 CH_2 rock transition frequency of 1.3 kcal/mol. They further infer from a comparison of experimental and theoretical results an estimate of 2 kcal/mol for the barrier to rearrangement of vinylidene to acetylene. This value is consistent with our predicted barrier heights when adjustments based upon further basis set expansion and a more extensive treatment of electron correlation are considered.

It is important to examine the results of the Moller–Plesset perturbation theory studies of Pople and co-workers[29,30] and attempt to determine the reason for the slight disagreement between those studies and the present one. The barrier to rearrangement reported in the Moller–Plesset studies is from fourth-order Moller–Plesset (MP4) single point calculations with a 6-311G** basis performed at molecular geometries obtained at the second-order Moller–Plesset (MP2) level with a 6-31G* basis set.

Table VI. ΔE for the Vinylidene–Acetylene Isomerization (kcal/mol)

	DZP	TZ+2P	TZ+2P+f	QZ+3P
		SCF		
ΔE	33.8	35.0	36.1	34.9
		CISD		
ΔE	39.5	41.8	43.6	40.5
Davidson corr	0.2	0.2	0.3	0.0
ΔE_{corr}	39.7	42.0	43.9	40.5
		CCSD		
ΔE	40.4	43.0		
		CCSDT-1		
ΔE	41.4			

Zero-point vibrational corrections to the energies were determined from force constants obtained at the Hartree–Fock (HF) level with a 6-31G* basis set. The use of the 6-311G** basis in the single point calculations appears not to be a significant source of disagreement. The barriers to rearrangement determined in the present study do not vary appreciably in going from the DZP to the TZ+2P or QZ+3P basis sets. Thus, extending the basis set beyond 6-311G** would not be expected to alter the barrier significantly. The fact that the zero-point corrections applied in these Moller–Plesset studies were obtained from frequencies determined at the HF/6-31G* level should not be considered a source of disagreement. In fact, the present study shows that zero-point corrections determined from frequencies obtained at higher levels of theory are even larger than those applied in these Moller–Plesset studies and would have resulted in an even smaller barrier to rearrangement. The effect of triple substitutions in the Moller–Plesset studies was to lower the barrier height 2.5 kcal/mol. The CCSDT-1 single point calculations performed in the present study indicate a smaller lowering of the barrier, ~1.5 kcal/mol, and the CCSDT-1 optimizations with the DZP basis set indicate a lowering of ~1.7 kcal/mol, due to linearized triple excitations in addition to the disconnected triples accounted for in CCSD. The use of geometrical structures optimized at the MP2/6-31G* level of theory could possibly be a source of disagreement. The MP2/6-31G* optimized structures of vinylidene and the transition state differ from the structures optimized at our highest level of theory, CCSD/TZ+2P, by 0.007 Å in the CC bond lengths and 0.007–0.008 Å in the CH bond lengths, the H atom here being non-migrating. The transition-state difference between the bond lengths is much greater for the bond between the C_2 atom and the migrating H atom, that is, 0.027 Å. All of the MP2/6-31G* bond lengths are longer than the CCSD/TZ+2P bond lengths. Hence, there appear to be several possible sources of disagreement between the two studies, each accounting for a small part of the overall discrepancy, but no one apparent source accounting for the whole of the disagreement between the two sets of studies.

The predicted acetylene–vinylidene isomerization energy values appear in Table VI. The convergence of these values within basis set and method is quite good. The Davidson correction to the CISD level isomerization energy values proves to be insignificant for all basis sets. Although zero-point vibrational corrections to these isomerization energy values were not taken into account, they would be expected to lower the values by ~1.4 kcal/mol. The isomerization energies predicted in this study, the best result being the CCSD/TZ+2P value of 43.0 kcal/mol, are in excellent agreement with the experimental value of 44 ± 4 kcal/mol found by Lineberger and co-workers[16] and with the upper bound to the isomerization energy of 44.4 kcal/mol determined by Field and co-workers.[13] As mentioned in the introduction, all of these values differ significantly from the value of 66 kcal/mol determined by Benson[18] from bond additivity arguments.

Conclusion

The results of this study indicate that vinylidene does indeed exist as a bound molecule. Vibrational analyses have confirmed that vinylidene is a minimum and that there exists a true transition state on the potential energy surface. It is clear that a more accurate accounting of electron correlation and an extension of the basis sets beyond those that we have used in explicit geometry optimizations would result in an additional lowering of the barrier. Specifically, we would expect that the effects of triple substitutions and f functions would lead to a lowering of the barrier. On the basis of a comparison of the classical barriers determined at the optimized levels with those found with the single point calculations, we would expect a lowering of the classical barrier with respect to our "best" optimized level, CCSD/TZ+2P, due to these effects of ~3.0–3.2 kcal/mol. This leads to a best estimate of ~3.0 kcal/mol for the classical barrier to rearrangement of vinylidene to acetylene. Although the augmentation of the basis with additional sets of f functions beyond the one set used in this study may lead to an additional lowering of the barrier, the combined effect of additional f functions and triple substitutions will likely be partially cancelled, as CCSDT-1 tends to overestimate the true effect of triple substitutions. Thus, we do not expect that the classical barrier will vanish.

Finally we return to the question raised in the title of this paper. Specifically, is this the "Final Chapter" for vinylidene? With respect to the existence/nonexistence of $H_2C{=}C$: as a genuine minimum on the ground-state acetylene potential energy hypersurface, our answer to this question is "Yes". Vinylidene is a genuine minimum. With respect to other important chemical questions, we have just begun to scratch the surface for vinylidene. The precise value of the classical barrier remains uncertain, although we doubt that it will fall much below 2 kcal/mol. Theoretical questions pertaining to the dynamical aspects of this elementary reaction should continue to be of great interest. And, of course, a variety of new gas-phase experiments will be critical to unfolding the properties of vinylidene, the simplest unsaturated carbene.

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Resolution of a Long-Standing Problem in Elemental Sulfur Chemistry: A Theoretical Study of Tetrasulfur

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Abstract: Theoretical studies of the potential energy surface of a poorly understood allotrope of elemental sulfur, S_4, have been performed with use of ab initio electronic structure theory. Eleven different isomers have been considered. Singlet states have been studied with SCF, two-configuration SCF (TCSCF), CISD (single and double excitation configuration interaction), and TC-CISD levels of theory, and selected triplet states have also been investigated with SCF and CISD theory. A few studies have also been performed on the most stable isomers with MR (multi-reference)-CISD, CCSD (coupled cluster theory with single and double substitutions), and CCSDT-1 (CCSD with linearized triple substitutions) methods. Two basis sets, of double-ζ plus polarization (DZP) and triple-ζ plus double polarization (TZ2P) quality, respectively, have been used. The effects of f-functions on the S–S bond have been investigated with S_2 as an example with a TZ2P+f basis set. Harmonic vibrational frequencies, infrared, and some Raman intensities have been evaluated, as have the ionization energies and the lowest energy electronic transitions for the most stable isomers. Experimental data for these properties are compared with our theoretical results. The global minimum of S_4 is predicted to have a singlet cis planar structure (C_{2v} symmetry); there are several low-lying states, of which the closest to the global minimum are a singlet trans isomer ($\approx$10 kcal mol^{-1} above the cis), followed by triplet trans and helical isomers that are almost degenerate, and a singlet four-membered puckered ring and branched three-membered ring isomers that are also almost degenerate. We have been able to assign most of the vibrational spectra previously attributed to S_4 to fundamentals of the cis and trans singlet isomers, and the electronic absorptions assigned to two isomers of S_4 match satisfactorily with the theoretically predicted transition energies for these isomers.

Introduction

Of all the elements, it is sulfur that has by far the most extensive, complex, and interesting allotropy,[1] an allotropy that is dominated by rings. The astonishing temperature variation in the color and viscosity of liquid sulfur has attracted much attention, and while the molecular changes that give rise to these variations are not established in detail, it seems clear that some very large S_n molecules must be involved. Sulfur vapor is a complicated mixture; all S_n in the range $2 \leq n \leq 10$ have been detected, but surprisingly little is known about several of the smaller S_n molecules, no doubt because they cannot be prepared in a "pure" state. Despite much effort over recent years, which has included the use of most components in the spectroscopic arsenal and several theoretical studies, there is no consensus as to the electronic or geometrical structure of S_4 in its most stable form. No fewer than *six* different isomers have been reported to be the global minimum by various authors! This startling lack of unanimity for such a small molecule, one of the basic allotropic forms of one of the best-studied elements, reflects rather poorly on our structural knowledge and understanding of fundamental bonding principles. In an attempt to overcome at least some of these difficulties, we have undertaken an extensive theoretical study of S_4. In addition

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