

Absence of an Energetically Viable Pathway for Triplet 1,2 Hydrogen Shifts. A Theoretical Study of the Vinylidene–Acetylene Isomerization

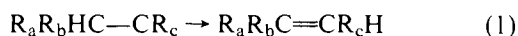
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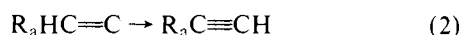
Abstract: Ab initio molecular electronic structure theory has been applied to the simplest triplet 1,2 hydrogen shift, the isomerization of vinylidene CCH_2 to acetylene $HCCH$. Both double ζ (DZ) and double ζ plus polarization (DZ + p) basis sets have been used, and electron correlation was explicitly considered via configuration interaction (CI) including all single and double excitations. One of the most interesting results is that the lowest energy transition state is decidedly *nonplanar* and connects 3B_2 vinylidene with the lowest triplet state of cis, as well as with the energetically higher trans 3B_u isomer, of acetylene. The classical barrier height for this process is ~ 55 kcal, suggesting a long lifetime for triplet carbenes and nitrenes, at least with respect to their 1,2 hydrogen shifts.

Introduction

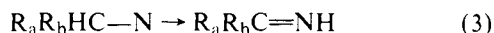
The 1,2 hydrogen shift, typified by the carbene reaction



is thought to be one of the most important routes for the disappearance of carbenes.¹ The analogous vinylidene and nitrene² reactions, also important, are of the forms



and



Since carbenes, vinylidenes, and nitrenes may have singlet or triplet ground electronic states,³ there are at least two potential energy surfaces which are important for each of these reactions.

To date, most attention has been directed toward the singlet rearrangements, which are now on a fairly firm theoretical foundation.⁴ To be specific, fairly small barriers (activation energies), of the order of 0–15 kcal, are anticipated. The methylcarbene rearrangement



has been the subject of several studies,^{5,6} and a definitive treatment of the naked vinylidene isomerization



has been reported.⁴ For the latter reaction a barrier of ~ 8 kcal was predicted, and, by comparison at a much simpler level⁶ of theory, the activation energy for eq 4 appears to be comparable.

The purpose of the present communication is to report very high barriers for the triplet 1,2 hydrogen shifts. This means, in essence, that the 1,2 hydrogen shift does not occur *at all* on the triplet potential energy surface. Thus, if a carbene, vinylidene, or nitrene finds itself in its lowest triplet state, a triplet–singlet transition must precede the 1,2 hydrogen shift. In the case of cold triplet ground-state molecules, like CH_3CH ⁷ and CH_3N ,⁸ there will be extremely long lifetimes with respect to unimolecular rearrangement.

It must be noted that ours is not the first inkling that triplet 1,2 hydrogen shifts have large activation energies. Although never stated explicitly, Zimmerman's MO following analysis⁹ of carbene shifts clearly implies the existence of large barriers for the triplet rearrangements. The only previous quantitative theoretical study of this problem is that of Altmann, Csizmadia, and Yates¹⁰ concerning the triplet methylcarbene rear-

rangement. Using a double ζ (DZ) basis set and self consistent field theory, they searched for the transition state structure using a sensibly composed, but nevertheless fairly restricted, one-dimensional coordinate system. Although there are obvious limitations to their approach, Csizmadia's predicted barrier height of 87.8 kcal is so high that it seems likely that the triplet barrier for reaction 4 is indeed large.

Equilibrium Geometries and Transition States

Here we present a definitive theoretical study of the triplet vinylidene isomerization (eq 5). The study began with the same DZ basis set¹¹ used by Csizmadia¹⁰ in his methylcarbene studies. At the SCF level of theory, the structure of the 3B_2 ground state was first optimized, yielding $r(C=C) = 1.324$ Å, $\theta(HCH) = 117.6^\circ$, $r(C-H) = 1.076$ Å. The predicted C=C distance is in fair agreement with the value of 1.36 Å reported by Davis, Goddard, and Harding¹² in their recent study of the electronic spectrum of vinylidene.

As a second step, the constrained planar transition state geometry was determined at the DZ SCF level of theory. The saddle-pointed geometry thus obtained is given in Figure 1, where it is seen that the two carbon atoms and the migrating hydrogen form a nearly equilateral triangle. In this sense the transition state may be considered about halfway between reactants and products. Further comparisons require that we also predict the structure of the product excited state of acetylene, and this equilibrium geometry is also included in Figure 1. Perhaps the most interesting result seen there is that the transition state C–C separation is actually *shorter* than either the reactant or product molecules. It is also noteworthy that the transition state HCC bond angle (of the H atom that does not migrate) is not intermediate between the vinylidene and acetylene values.

In the course of characterizing this constrained transition state, nonplanar excursions of the migrating hydrogen atom led to notably lower total energies. This in turn led to the discovery that the true transition state is far from planar. As seen in Figure 2, the migrating H atom lies in a plane (with the two carbon atoms) that is nearly perpendicular to the original plane of the vinylidene. Perhaps even more surprising is the fact that this true transition state connects not only the lowest trans state of acetylene but also the cis 3B_2 state with vinylidene. This transition is, however, in some ways more "conventional" since the C–C separation, 1.425 Å, is much greater than for either 3B_2 vinylidene, 1.324 Å, or 3B_2 acetylene, 1.338 Å. In addition the HCC angle for this transition state is intermediate between reactant and product. Finally it should be mentioned that, although a low-symmetry transition state may seem unex-

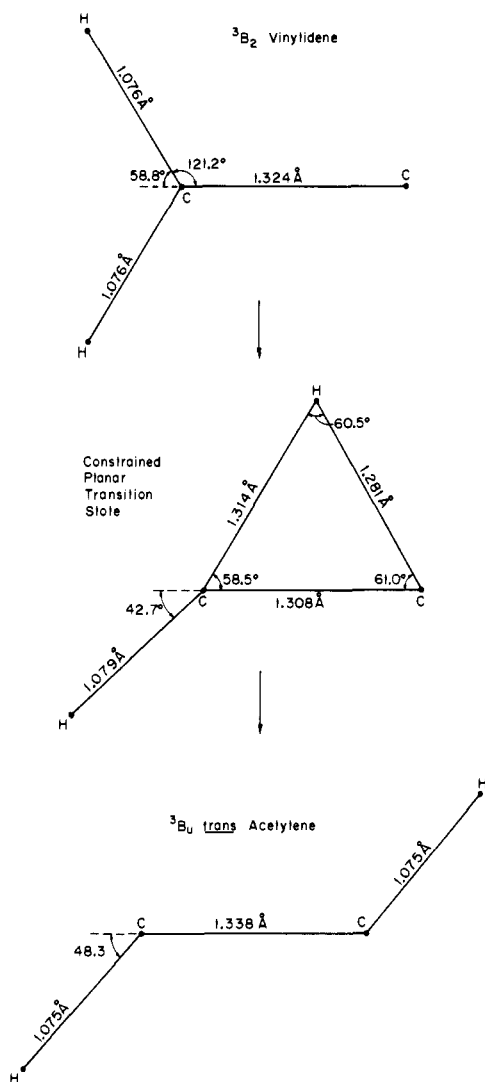


Figure 1. Structures for the reactant triplet vinylidene, constrained planar transition state, and product triplet *trans*-acetylene species.

pected, Dewar and co-workers^{13a} have recently reported a number of these using the MINDO method.

In at least one respect, it is not surprising that the nonplanar transition state connects triplet vinylidene with the *cis* 3B_2 state of acetylene. Namely, the *cis* 3B_2 and *trans* 3B_u states are just different local minima on the *same* potential energy surface, the lowest triplet surface for C_2H_2 . The 3B_2 vinylidene equilibrium geometry is a third distinct minimum on this same triplet potential surface. The *cis* 3B_2 and *trans* 3B_u triplet isomers of acetylene are related by a rotation by 180° about the C-C axis, and Demoulin^{13b} has reported a large barrier (>25 kcal) for this 3B_u - 3B_2 rotation.

Energetics

The present energetic results are summarized in Table I. There we see that the level of theory described above—DZ SCF—predicts a barrier of 91.6 kcal for the constrained planar transition state (Figure 1) and 71.6 kcal for the true nonplanar transition state (Figure 2). Thus the nonplanar excursion has an effect of ~20 kcal on the predicted barrier. Since polarization functions are often¹⁴ more important for cyclic (i.e., like the transition states reported here) than for open structures, a set of d functions (orbital exponent $\alpha = 0.8$) on each carbon atom was appended to the DZ basis, yielding our DZ + d set. At the SCF level, this DZ + d basis yields planar and nonplanar barriers of 83.0 and 62.0 kcal. Finally, p functions

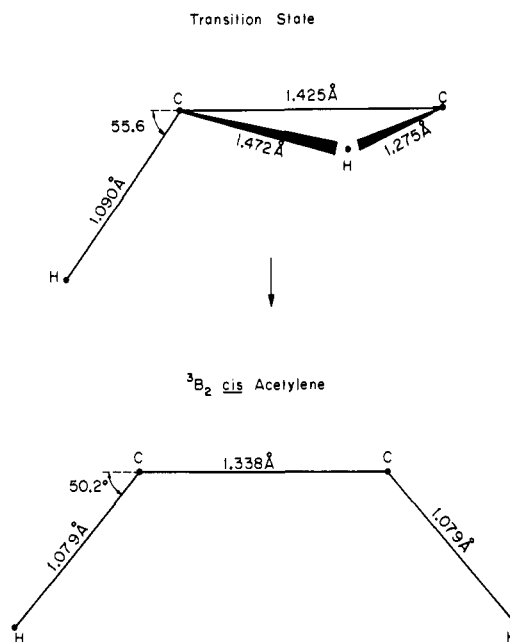


Figure 2. Theoretical structures for the nonplanar transition state and product triplet *cis*-acetylene. The migrating hydrogen atom forms a plane with the two carbon atoms, and this plane makes an angle of 78.8° with the plane of the original vinylidene. The reactant molecule for this simple unimolecular process is 3B_2 vinylidene, which is pictured in Figure 1.

($\alpha = 1.0$) on each hydrogen atom were added to yield our final DZ + p basis set. Using the structural parameters predicted above, this DZ + p basis yields planar and nonplanar barriers of 80.2 and 60.5 kcal/mol at the SCF level. Thus it is seen that polarization functions lower the relative energies of the two transition states by 11.4 and 11.1 kcal, respectively.

For the singlet vinylidene isomerization,⁴ the effect of electron correlation is to lower the predicted barrier by 6.1 kcal, from 14.7 to 8.6 kcal when the DZ + p basis is used. Therefore it seemed critical to examine correlation effects for the triplet isomerization. This was accomplished using the direct CI method of Roos,¹⁶ which has been formulated by Lucchese¹⁷ for triplet spin states and implemented as part of the BERKELEY system of minicomputer-based programs.¹⁸

With the DZ basis it was possible to include all Hartree-Fock interacting¹⁹ (i.e., having nonzero matrix elements with the respective SCF reference configurations) singly and doubly excited configurations. For the five different geometries studied, this procedure yields the following numbers of configurations: vinylidene, 3104 3B_2 ; planar transition state, 5892 ${}^3A'$; nonplanar transition state, 9540 3A ; *trans*-acetylene, 2976 3B_u ; *cis*-acetylene, 2976 3B_2 .

With the double ζ plus polarization basis set it was necessary to delete core correlation effects from the CI calculations. Since these were shown to be negligible here (core correlation effects change the planar barrier height by less than 0.1 kcal with the DZ basis set) and for related problems,²⁰ this deletion seems quite justifiable. Therefore the two lowest occupied SCF orbitals were held doubly occupied in all configurations and the two highest virtual orbitals deleted from the CI basis. In this manner, 5155, 10147, 16530, 5115, and 5115 configurations were included, respectively, for vinylidene, the planar transition state, the nonplanar transition state, *trans*-acetylene, and *cis*-acetylene.

The reason for our adopting the DZ + d basis set was that the nonplanar DZ + p CI calculation described above, 16530 configurations, proved to be slightly beyond the current capabilities of our minicomputer system.^{17,18} However, the DZ + d CI includes only 10851 configurations, and should include

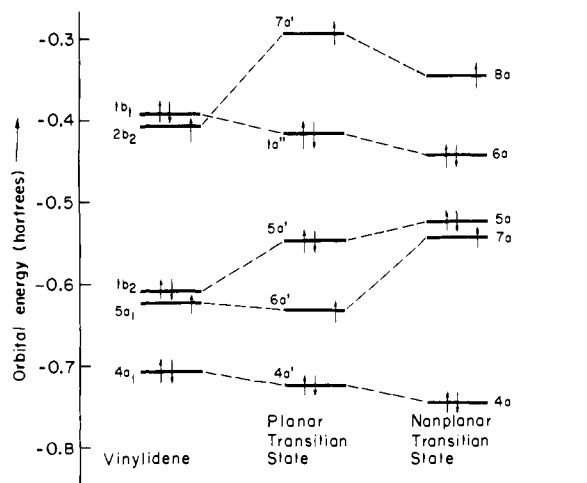


Figure 3. Ab initio orbital energies for the lowest triplet state of vinylidene, the constrained planar transition state, and the true (nonplanar) transition state.

the major part of the correlation effects due to polarization functions.

From Table I it is seen that the DZ CI barrier for the constrained planar transition state is 80.1 kcal, a reduction of 11.5 kcal from the original DZ SCF result. However, it is somewhat surprising that the nonplanar transition state is lowered by only 1.4 kcal, to 70.2 kcal. Thus while the planar transition state lies a full 20 kcal above the true transition state at the DZ SCF level, this difference is reduced to 10 kcal with DZ CI.

The same trend is seen in the DZ + d results. That is, the energy of the planar transition state is 21 kcal above that found at the nonplanar saddle point. However, this difference is reduced to 11.5 kcal at the CI level. Thus it is clear that in this

particular case, the effect of electron correlation is to "flatten out" the potential surface in the region of the transition state.

Although we were unable to complete the DZ + p CI calculation on the nonplanar transition state, it is rather easy to estimate the predicted barrier as 57 kcal. This result can in turn be corrected for the effects of higher excitations (unlinked clusters) using Davidson's correction.²¹ Using the DZ + d CI results, the Davidson formula predicts unlinked clusters to be 1.1 kcal more important for the transition state than for vinylidene. Thus a "final" value of 56 kcal is predicted for the classical barrier. Although the use of a larger basis set and more extensive level of CI will probably lower this predicted barrier further, we suspect that the exact classical barrier is no less than 50 kcal/mol.

Electronic Structure Considerations

We have in a sense confirmed the suggestion, implicit in Zimmerman's treatment,⁹ that the planar transition state (at least) has a large barrier. However, it remains to be understood why the nonplanar transition state is more than 10 kcal more favorable. To discuss this point we have sketched, in Figure 3, the orbital energies for the reactant 3B_2 vinylidene and for the constrained and unconstrained transition states. It may surprise the reader that the singly occupied molecular orbitals are not highest among the occupied SCF orbitals. This is not due to errors in labeling but rather to the fact that the total energy is *not* the sum of the orbital energies, each of which may be associated with an ionization potential via Koopmans' theorem.

The source of the high barrier for the planar transition state is the $7a'$ orbital, which is essentially an antisymmetric combination of the in-plane carbon p orbitals directed perpendicular to the C-C axis. The lowering of this $7a'$ orbital energy as one goes to the $8a$ orbital of the nonplanar transition state

Table I. Energetic Summary of Theoretical Results for the Triplet Isomerization of Vinylidene to Acetylene

	double ζ SCF	double ζ CI	double ζ plus d SCF	double ζ plus d CI	double ζ plus polariza- tion SCF	double ζ plus polariza- tion CI
3B_2 vinylidene						
total energy, hartrees	-76.697 92	-76.875 77	-76.723 64	-76.936 59	-76.728 56	-76.954 22
rel energy, kcal	0.0	0.0	0.0	0.0	0.0	0.0
planar transition state (see Figure 1)						
total energy, hartrees	-76.551 98	-76.748 09	-76.591 36	-76.824 05	-76.600 74	-76.844 71
rel energy, kcal	91.6	80.1	83.0	70.6	80.2	68.7
nonplanar transition state (see Figure 2)						
total energy, hartrees	-76.583 75	-76.763 92	-76.624 82	-76.842 47	-76.632 20	
rel energy, kcal	71.6	70.2	62.0	59.1	60.5	
<i>trans</i> -acetylene						
total energy, hartrees	-76.686 70	-76.860 68			-76.720 36	-76.943 30
rel energy, kcal	7.0	9.5			5.1	6.9
<i>cis</i> -acetylene						
total energy, hartrees	-76.697 90	-76.872 51			-76.732 17	-76.956 17
rel energy, kcal	0.0	2.0			-2.3	-1.2

Table II. Electronic Structure Changes Accompanying the Triplet Vinylidene Isomerization^a

Mulliken populations	3B_2 vinylidene	planar transition state	nonplanar transition state	<i>trans</i> 3B_u acetylene	<i>cis</i> 3B_2 acetylene
C ₁	-0.27	-0.28	-0.03	-0.16	-0.14
H ₁	+0.15	+0.17	+0.15	+0.16	+0.14
H ₂	+0.15	+0.25	+0.11	+0.16	+0.14
C ₂	-0.03	-0.13	-0.23	-0.16	-0.14
dipole moment, D	0.48	0.48	2.93	0.00	1.30

^a C₁ is the methylene carbon of vinylidene and H₂ is the migrating H atom.

may be taken as the primary reason for the smaller nonplanar barrier height. However, this picture is somewhat simplistic, even though the sum of the valence shell orbital energies is less for the nonplanar than for the planar transition state. The overly simplistic nature of this "one-orbital" model is most readily seen by the fact that the other singly occupied orbital, the $6a'$ orbital, is markedly raised in going from planar to nonplanar geometries. This in turn, however, is more than compensated by the stabilization of the doubly occupied $1a''$ orbital.

In Table II are displayed Mulliken populations and dipole moments for triplet vinylidene, the planar and nonplanar transition states, and *cis*- and *trans*-acetylene. These results were obtained from the DZ + p SCF wave functions. Both triplet vinylidene itself and the constrained planar transition state have rather small dipole moments, namely, 0.48 D. However, the true, nonplanar transition state is strongly polar, with a dipole moment of 2.93. The latter value is more than twice as large as that predicted for the lowest *cis* triplet state, the 3B_2 state, of acetylene. The Mulliken populations suggest that the polarity of the transition state is primarily due to the large difference in electron densities about the two carbon atoms. This is confirmed by the fact that the component of the dipole moment along the C-C axis is 2.77 D.

Finally, some very qualitative remarks concerning the planar and nonplanar transition states are in order. The present structural results suggest the following interpretation: in the planar transition state the C-C π bond and the hybridization at the C atoms are conserved; the migration of the H atom is accompanied by an almost complete cleavage of the CH bond, since the antibonding $7a'$ orbital is singly occupied. In the nonplanar transition state the C-C π bond is broken, the hybridization at the methylene carbon is changed, and the H atom migrates via a CCH three-center bond to the terminal carbon.

Concluding Remarks

Perhaps the most important conclusion of this theoretical study is that the accurate characterization of transition state structures and energetics can be very demanding. In the present case the most obvious transition state structure is planar and a convenient level of theory to apply is the double ζ (DZ) self consistent field (SCF) approach. Using this approach a very large barrier of 91 kcal is predicted. However, by simultaneously allowing nonplanar transition state geometries to be

considered, going to a basis set including polarization functions, and variationally incorporating the effects of electron correlation, a drastically lower barrier, ~ 55 kcal, is predicted. Nevertheless this barrier is still large, much greater than the 8 kcal predicted⁴ for the analogous singlet vinylidene isomerization. Since the zero point vibrational energy associated with the transition state is certainly less than that of triplet vinylidene, a further lowering of perhaps 5 kcal leads to a prediction of ~ 50 kcal for the activation energy. Thus we conclude that triplet diradicals will be quite stable with respect to 1,2 hydrogen shifts.

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