

An ab Initio Study of Substituent Effects in [1,3]-Hydrogen Shifts

Charles E. Hudson* and David J. McAdoo

Marine Biomedical Institute, The University of Texas Medical Branch, Galveston Texas 77555-1043

cehudson@utmb.edu

Received September 30, 2002

Reports in the literature place the TS for the [1,3]-H shift in propene comparable to or higher in energy than loss of the allylic H. However, [1,3]-H shifts have been repeatedly observed experimentally in enolates. We used GAUSSIAN 98 to examine the origin of this apparent contradiction. We found the first TS for an antarafacial [1,3]-H shift that is clearly lower in energy than simple dissociation of the migrating H. This occurs in the [1,3]-H shift in the acetone enolate. Symmetrical substituents (H, O⁻, ethynyl) have TSs with C₂ symmetry, implying that they, and probably most [1,3]-H shift TSs, are antarafacial. Conjugating substituents at C2 lower the energy of [1,3]-H shifts and raise the energy of dissociation by loss of a hydrogen atom from C3, increasing the likelihood of the former type of reaction. Strongly electron-donating and electron-withdrawing substituents are more effective than neutral substituents in lowering the energy requirement of [1,3] shifts. Our best calculations predict that a [1,3]-H shift is lower in energy than dissociation by loss of the H by 27.8 kJ/mol in 2-methyl-1-butene-3-yne, by 36.8 kJ/mol in isoprene, by 55.9 kJ/mol in 2-aminopropene, by 114.5 kJ/mol in the acetone enolate, and by 120.8 kJ/mol in the 1-methylacryloyl cation. Thus, there is a chance of experimental observation of [1,3] shifts in conjugated alkenes and related species.

Introduction

In 1965, Woodward and Hoffmann (W&H) published their famous trilogy of papers dealing with reactions whose paths are determined by the symmetries of the orbitals involved.¹ In their paper dealing with sigmatropic reactions, W&H predicted that [1,3]-hydrogen shifts would be antarafacial.^{1c} The seminal publications¹ were followed by a period of intense experimental testing of the predictions. For the most part, the predictions were confirmed.² However, the [1,3]-H shift remained experimentally elusive. It was clear from the outset that if the TS for a [1,3]-H shift is indeed antarafacial, it must be high in energy, not only because of the angle strain inherent in the four-membered ring involved but also because of disruption of π -bonding between the atoms of the double bond. In this work, we examine the effect of a conjugating substituent at the 2-position of [1,3]-H shifts because we suspect that they control the critical energies for the reactions and therefore whether the reactions may occur.

Because it is the simplest system in which the reaction of interest can in principle occur, previous theoretical work focused on propene.³⁻⁷ Most calculations have

indicated that the [1,3]-H shift should be comparable to or higher in energy than dissociation by loss of a hydrogen atom. This implies that, if such a shift is to take place in neutral propene, it would be by a stepwise mechanism and should not occur at all in the high vacuum of a mass spectrometer where the [1,3] shifts in enolates were discovered. In the following studies in which dissociation was not expressly characterized,^{3,5,6} propene's experimental dissociation energy for H loss of 359 kJ/mol forms a useful point of reference.⁸ Bouma, Vincent, and Radom computed the activation energy of the [1,3]-H shift in propene to be 381 kJ/mol by successive [1,2] shifts and 467–481 kJ/mol by the allowed antarafacial TS.³ Bernardi et al. found the antarafacial TS to be 33–118 kJ/mol higher in energy than the dissociation products, allyl radical + H.⁴ Hess, Schaad, and Pancir concluded that the [1,3] shift in propene requires 377–452 kJ/mol.⁵ Dormans and Buck⁶ computed transition state energies for the [1,3]-H shift in propene for suprafacial (C_s), antarafacial (C₂), and highly symmetrical (C_{2v}) processes. At nearly every level of theory, the antarafacial process was the lowest in energy. The computed activation energy for the antarafacial process was 369–467 kJ/mol, with the highest level calculation giving the lowest energy.⁶ Houk, Li, and Evanseck found

(1) (a) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 395–397. (b) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 2046–2048. (c) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511–2513.

(2) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 827–837.

(3) Bouma, W. J.; Vincent, M. A.; Radom, L. *Int. J. Quantum Chem.* **1978**, *14*, 767–777.

(4) Bernardi, F.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1984**, *106*, 1198–1202.

(5) Hess, B. A., Jr.; Schaad, L. J.; Pancir, J. *J. Am. Chem. Soc.* **1985**, *107*, 149–154.

(6) Dormans, G. J. M.; Buck, H. M. *J. Mol. Struct. (THEOCHEM)* **1986**, *136*, 121–138.

(7) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed.* **1992**, *31*, 682–708.

(8) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, G. W. *J. Phys. Chem. Ref. Data* Supplement No. 1, **1988**, *17*, 114, 117, 616.

the C_2 antarafacial TS for the [1,3] shift in propene. They stressed the similarity of both the energy and the C–C bond length to those of the dissociation products, an allyl radical and a hydrogen atom.⁷ Thus, many computations indicate that the activation energy of the [1,3] sigmatropic H shift in propene is either about the same as or higher than that for dissociation by loss of H. Therefore, the dissociation is likely to occur in preference to the [1,3] shift.

In contrast to the theoretical work on propene that indicates that a concerted [1,3]-H shift should not occur, enolate anions generated in a mass spectrometer do undergo these shifts.^{9,10} Hayes, Sheldon, and Bowie (HSB), in a study of the collision-induced dissociations of the anion derived from 4-hydroxy-3-pentene-2-one (acetylacetone), concluded that a [1,3]-H shift preceded the loss of ketene, which is the principal dissociation.⁹ HSB's ab initio calculations predicted a barrier of about 370 kJ/mol for the rearrangement. The energy required for hydrogen atom loss, which is the second most abundant dissociation, was not computed. HSB assumed a TS of C_2 symmetry for the [1,3]-H shift of the acetone enolate and computed an activation energy of 324–370 kJ/mol for it. HSB's [1,3] shift TSs would be accessible if dissociation by hydrogen atom losses in the enolates they considered were a little higher in energy than H loss in propene. However, HSB did not identify their TS for the [1,3]-H shift in the acetone enolate as antarafacial, and the C_2 axis of symmetry of this TS was assumed rather than demonstrated. Sannes and Braumann (S&B), in a study of laser-induced dissociations of enolates, also concluded that [1,3]-H shifts do occur in these ions.¹⁰ S&B also performed semiempirical calculations on the acetone enolate system, but they assumed that only suprafacial shifts were possible.¹⁰ We wanted to clarify why a reaction that should not occur at all in propene should be so readily observable in enolates.

Methods

We used GAUSSIAN 98W¹¹ to compute the energies of the H atom loss dissociation products and the activation energies for [1,3]-H shifts in propene, the acetone enolate, 2-methyl-1,3-butadiene (isoprene), 2-methyl-1-butene-3-yne, the 1-methylacryloyl cation, and 2-aminopropene. We found [1,3]-H shift TS candidates by constraining the migrating hydrogen (H_t) to be equidistant from the reaction termini at the B3LYP/6-31G* level. The initial guesses were otherwise unsymmetrical but close to C_{2v} , except in the case of the isoprene TS, where the vinyl group destroys the possibility of symmetry. We used the resulting geometry to start the TS finding run

(9) Hayes, R. N.; Sheldon, J. C.; Bowie, J. H. *Int. J. Mass Spectrom. Ion Processes* **1986**, *71*, 233–243.

(10) Sannes, K. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1995**, *117*, 10088–10092.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(B3LYP/6-31G*) with the constraint to equal bond lengths removed with the command OPT = (Z-MATRIX, TS, TIGHT, CALCALL), which showed that each point thus located was a true TS with a single negative eigenvalue of the force constant matrix. This gave force constants for further optimizations, and provided the ZPVEs. TSs were then found at other levels of theory using the force constants thus calculated. In the case of the [1,3]-H shift TS in 2-aminopropene, the TS finding routine stepped into a region of the wrong curvature at the QCISD level. A QCISD TS candidate was found by optimizing the structure at the QCISD level with constraint to equal C–H bond lengths followed by optimization to the TS with the constraint removed using Hartree–Fock force constants. In the case of the CO^+ substituent, the structure with equal C–H bond lengths is a stable structure rather than a TS. The TS candidate for the CO^+ substituent was found by a relaxed scan of the C1–H_t distance. All ZPVEs were scaled by 0.9806.¹² IRC calculations were performed at the B3LYP/6-31G* level using force constants calculated at the same level of theory.

Some W&H processes have transition states with considerable diradical character,¹³ with a near-degeneracy occurring in the two highest occupied MOs. In those cases, it is necessary to take nondynamical correlation into account. Accordingly, we performed CASSCF calculations on the [1,3]-H shifts in the acetone enolate and in propene via the triplets. For a description of our CASSCF methods, please refer to Supporting Information.

Results and Discussion

We find that the [1,3]-H shift in the acetone enolate is antarafacial; this is the first clear-cut example of an antarafacial [1,3]-H shift in a system in which the shift is lower in energy than dissociation by loss of the migrating H. Our evidence for the antarafacial nature of this process is twofold: the TS has C_2 symmetry, and IRC calculations show that H_t reaches and departs from the TS in opposite directions. Figure 1a illustrates the C_2 axis, and Figure 1b gives the optimized parameters for this TS. Figure 2 shows how the $H_tC1C2C3$ dihedral angle varies along the reaction coordinate. IRC calculations show that propene behaves similarly to the acetone enolate in its [1,3]-H shift.

Our calculations (Table 1) demonstrate unequivocally that the O^- substituent on C2 in the acetone enolate strongly stabilizes the TS for [1,3]-H shift. The lowest barrier to the [1,3] shift computed by any of our methods for propene is 341.2 kJ/mol, while the highest barrier we computed to the [1,3] shift in the acetone enolate is 272.1 kJ/mol. This minimum difference of 69.1 kJ/mol expands to 89.8 kJ/mol when comparable methods are used. The calculations show that conjugating substituents at C2 generally facilitate [1,3]-H shifts.

It is thought by some that multiconfiguration SCF (MC-SCF), in this work represented by the CASSCF calculations (F, G, H, and I in Table 1), is essential for understanding [1,3] shifts because of a near-degeneracy in occupied and unoccupied orbitals that occurs in the TS for these shifts.¹³ However, our calculations [CAS-(4,4)/6-311G**] on the propene rearrangement cast doubt on this belief. The triplet lies 275.5 kJ/mol above the singlet at the geometry of the singlet TS. For the TS for the [1,3]-H shift in the acetone enolate, the singlet–

(12) Scott, A. P.; Radom, L. *J. Chem. Phys.* **1996**, *100*, 16502–13.

(13) (a) Davidson, E. R.; Gajewskii, J. J.; Shook, C. A.; Cohen, T. J. *Am. Chem. Soc.* **1995**, *117*, 8495–501. (b) Davidson, E. R.; Gajewskii, J. J. *J. Am. Chem. Soc.* **1997**, *119*, 10543–44.

TABLE 1. Computed Energetics^a of [1,3]-H Shift and H Loss

substituent process ^b method ^c	H		O ⁻		C ₂ H		CH=CH ₂		NH ₂		CO ⁺	
	S	L	S	L	S	L	S	L	S	L	S	L
experimental		359.										
A//A	335.4	355.9	245.6	364.3	321.7	361.4	322.0	366.9	290.2	362.6	236.6	378.3
B//B	355.9	351.9	247.1	365.3	348.2	356.6	345.8		317.7	358.6	257.7	369.8
C//B	342.7	355.9	237.8	367.0	333.9	361.7	331.8		306.3	362.2	254.5	375.3
D//B	354.4	-	260.6	364.2								
C + D - B	341.2		251.3	365.8								
E//B	355.3	353.1										
C + E - B	342.1	357.1										
F//F	385.7											
G//F	376.4											
H//H			272.1									
I//H			268.1									
J//J							357.4	364.4				
K//J							344.9	368.6				

^a In kJ/mol, corrected for ZPVE. ^b S = [1,3]-H shift TS; L = H loss. ^c A = B3LYP/6-311G**, B = QCISD/6-311G**, C = QCISD(T)/6-311G**, D = QCISD/6-311+G(3df,2p), E = QCISD/6-311+G(3d,2p), F = CAS(4,4)/6-311G**, G = CAS(4,4) MP2/6-311G**, H = CAS(6,5)/6-311G**, I = CAS(6,5) MP2/6-311G**, J = QCISD/6-31G**, K = QCISD(T)/6-31G**.

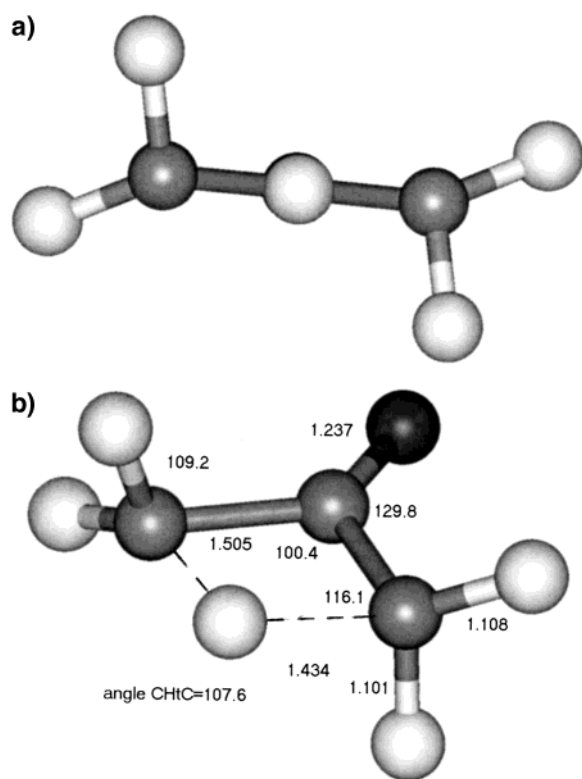


FIGURE 1. (a) View along the C₂-axis of the [1,3] H-shift TS in the acetone enolate. (b) TS for [1,3] H-shift in the acetone enolate showing the optimized parameters.

triplet gap is 369.6 kJ/mol. For [1,3]-carbon shifts, the belief in near-degeneracy is well founded.¹³ This is probably because carbon is less able to bond in two directions at once in concerted reactions.⁷ This results in a greater diradical character in carbon shift TSs than in hydrogen shift TSs. Our calculations clearly do not support a near-degeneracy for the [1,3]-H shifts. For the propene and acetone enolate TSs, the similarity of the geometries found by CAS, B3LYP, and QCISD geometries suggests that the latter two methods do not find stationary points for these [1,3]-H shifts for which no counterparts exists with MC-SCF methods. Since CASSCF frequently overestimates the activation energies for

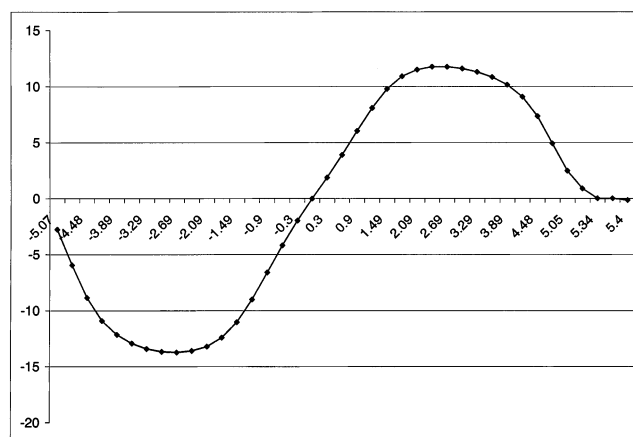


FIGURE 2. H₁C₁C₂C₃ dihedral angle as a function of reaction coordinate in the [1,3]-H shift of the acetone enolate.

Woodward–Hoffmann processes,¹⁴ we prefer to rely on the more balanced correlation treatment of the B3LYP and QCISD methods.

Except for the TS with the CO⁺ substituent, the TSs encountered in this work are all fairly similar to each other. The following remarks apply to the substituents other than CO⁺. The process with the CO⁺ substituent is sufficiently different that it is discussed in a separate section.

The TSs with symmetrical substituents (H, O⁻, and ethynyl) have C₂ symmetry, as expected for antarafacial processes. Thus, most [1,3]-H shifts are probably antarafacial, and the assumption by S&B,¹⁰ and probably many other chemists as well, of a necessarily suprafacial process is contradicted by our calculations.

The only process we characterized that is quantitatively comparable to experiment is the energy of H loss from propene. Table 1 shows that all of our energies are too low for this process by 2–7 kJ/mol, but the best agreement with experiment is obtained with the highest level calculations. The dissociation energies vary less with method than the TS energies do. This gives us reason to believe that the restricted ability to perform

(14) Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 67–75.

TABLE 2. HC1C2C3 Dihedral Angles and C–H_t Bond Lengths in Transition States for [1,3]-H Shifts^a

substituent	dihedral 1 ^b	dihedral 2 ^c	C–H _t bond length
H	146.1	–68.1	1.506
O [–]	–150.0	83.0	1.450
ethynyl	144.0	–71.5	1.480
vinyl ^d	142.4, 145.0	–72.4, –70.5	1.467, 1.482
NH ₂	146.8	–73.7	1.474
CO ⁺ d,e			1.188, 1.521

^a As optimized at the B3LYP/6-311+G** level. ^b For the atom less twisted out of the CCC plane. ^c For the atom more twisted out of the CCC plane. ^d Asymmetrical molecule having two different values for the parameters. ^e C2 and its substituents are not coplanar (see text).

TABLE 3. C–C Bond Lengths in Ground and Transition States for [1,3]-H Shifts^a

substituent	C1–C2 ground	C2–C3 ground	TS
H	1.331	1.500	1.410
O [–]	1.386	1.547	1.492
ethynyl	1.341	1.512	1.425
vinyl	1.342	1.508	1.425, 1.427
amino	1.341	1.505	1.429
CO ⁺	1.354	1.517	1.430, 1.506

^a As optimized at the B3LYP/6-311+G** level.

high-level calculations on the radicals did not strongly influence the results.

The geometries of the TSs provide strong evidence of a reduction in π -bonding between C1 and C2, which are doubly bonded in the ground states. C2 remains planar with the atoms bonded to it in the TSs. We assessed this by summing the bond angles about C2. Any pyramidalization about C2 would manifest itself with a bond angle sum less than 360°. All of the TSs have bond angle sums about C2 of 360.0°. However, C1 (and C3) of the TSs are pyramidalized and the hydrogens on those atoms are rotated out of planarity with the substituents on C2. The hydrocarbon TSs have bond angle sums about C1 (excluding the partial bond to H_t) of 350.8–351.7°. The TSs with electron-donating substituents are more highly pyramidalized at C1; the angle sum is 347.4° in the amine and 337.9° in the acetone enolate. More will be said later about the exceptional nature of the acetone enolate TS. Table 2 gives the HC1C2C3 dihedral angles that the hydrogen atoms at C1 make in the TSs. In each case, one hydrogen is substantially more twisted out of the plane (0 or $\pm 180^\circ$) than the other. For the hydrogen less twisted out of the plane, the range is 30.0–37.6°. For the more highly twisted hydrogen, the range of angles is 68.1–83.0°. The bond lengths in the ground state and the TS also support the idea that the π -bonding is substantially reduced between C1 and C2 in the TS. Table 3 shows that, for the hydrocarbons, the C1–C2 bond length in the TS is very close to the average of the C1–C2 and C2–C3 (where C3 is the methyl) bond lengths in the ground state. This suggests that the π -bond is about half broken in the TS. In the acetone enolate, the C–C bonds in the TS are somewhat longer than the average of their lengths in the ground state. This is probably because the O[–] substituent is a better conjugating group than the ethynyl or vinyl groups insofar as this reaction is concerned (see the discussion of bond lengths to H_t below). By the same argument, the C1–C2 π -bond is more than half broken in the acetone enolate TS.

TABLE 4. Bond Lengths to the Substituent in Substituted Alkenes, [1,3]-H Shift TSs, and Allyl Radicals^a

substituent	bond length alkene	bond length TS	bond length allyl radical
H	1.089	1.090	1.088
O [–]	1.272	1.244	1.276
ethynyl	1.431	1.412	1.439
vinyl	1.467	1.450	1.483
amino	1.400	1.356	1.406
CO ⁺	1.402	1.312	1.412

^a As optimized at the B3LYP/6-311+G** level.

Table 1 shows that every substituent lowers the energy of the rearrangement and raises the energy of dissociation. Both of these phenomena are easy to understand. To undergo an antarafacial [1,3]-H shift, the substituents on C1 are strongly twisted out of the plane of the substituents on C2, substantially reducing the strength of the π -bond between them. A conjugating substituent on C2 will interact favorably with the p orbital on C2 that can therefore no longer overlap as effectively with an orbital on C1, lowering the energy required to twist the C1–C2 bond. To understand the effect of a C2 substituent in raising the energy of dissociation by H atom loss, consider the cases of propene and isoprene. According to simple Hückel theory,¹⁵ in which the unit of energy is the resonance integral on adjacent atoms (β), the loss of a hydrogen atom from the methyl group of propene results in a ΔE_π of $\alpha + 0.828\beta$. The loss of a hydrogen atom from the methyl group of isoprene results in a ΔE_π of $\alpha + 0.684\beta$. Our interpretation is that a conjugating substituent at C2 stabilizes propene more than it stabilizes the allyl radical. This is not surprising, because a substituent at the 2-position does not interact with the active positions of the allyl radical. These effects are reflected in the bond lengths to the substituent. Table 4 shows that the bond lengths to conjugating substituents computed with optimization at the B3LYP/6-311+G** level decrease at the rearrangement TS and increase in the H loss products. The small changes in the C2–H bond length from propene to the [1,3]-H shift TS to the allyl radical are in the opposite direction from the bond length changes to the conjugating substituents. Since previous calculations suggested that H loss is marginally lower in energy than the [1,3] shift in propene, and since substituents lower the energy of the shift and raise the energy of dissociation, our computations suggest that there is a reasonable chance of detecting [1,3] sigmatropic shifts in conjugated alkenes.

Since the four-membered rings in the TSs are planar, our explanation requires that the vinyl group in the isoprene TS be coplanar with the ring, or nearly so. As expected, the dihedral angle between the ring and the vinyl group is 8.4° at the B3LYP/6-311+G** level and 10.5° at the QCISD/6-311G** level. These deviations from planarity are probably due to steric interactions between the cis hydrogen of the vinyl group with C1 and its hydrogens.

Table 2 shows that the bond lengths to H_t in the TSs are shorter when a conjugating substituent is present.

(15) Isaacs, N. S. *Physical Organic Chemistry*; Wiley & Sons: New York, 1987.

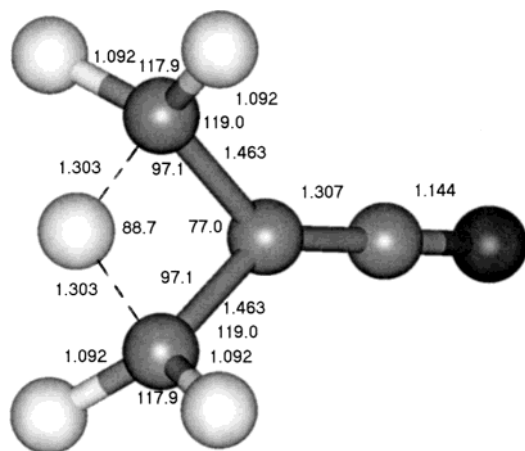


FIGURE 3. Intermediate in the [1,3]-H shift of the 1-methylacryloyl cation as optimized at the QCISD/6-311G** level.

In the C_3H_6 TS, C1 and C3 effect the best compromise they can between bonding to H_t and maintaining π -overlap with the p orbital on C2. As the substituent takes over more of the bonding to C2, C1 and C3 devote more bonding to H_t and less to C₂ (Table 3).

CO⁺ Substituent. We wanted to assess the effect of a strong electron-withdrawing group on the energetics of the [1,3]-H shift. We chose CO⁺ because it is an excellent representative of this class of substituents and it is the least computationally demanding. B3LYP and QCISD calculations agree that the symmetrical species with equal C1 and C3– H_t bond lengths exists in a shallow minimum, but the two methods do not agree completely as to its nature. At the B3LYP level, this intermediate has C_{2v} symmetry, while at the QCISD level it has a plane of symmetry (C_s symmetry) containing the substituent and perpendicular to the C1C2C3 plane. The QCISD structure has C2 slightly pyramidalized with a bond angle sum about C2 of 354.6°. In addition, the ring is not quite planar (C4C2H_tC3 dihedral angle of 1.2°) and the substituent is not quite linear (CCO bond angle of 176.5°). Figure 3 shows the QCISD/6-311G** structure of this species. It is well-known that organic structures with three-center bonds such as this intermediate play a much greater role in the chemistry of cations than in neutrals or anions.¹⁶ Consequently, it is only mildly surprising that a stable structure with three-center bonding occurs with the CO⁺ substituent and no surprise at all that the other substituents examined here do not have this type of symmetrical species as a stable structure.

The real TS for the [1,3]-H shift in $CH_2=C(CH_3)CO^+$ is for its conversion to the symmetrical intermediate. The energy difference between this TS and the symmetrical intermediate is given at several levels of theory in Table 5. The barrier between the precursor and the intermediate and the energy of H atom loss from the methyl are given in Table 1. The TS for the [1,3]-H shift with the CO⁺ substituent has no symmetry at all, unlike the symmetric or near-symmetric TSs discussed so far. Some

TABLE 5. Energy Difference between the Symmetrical $C_4H_5O^+$ Structure and the [1,3]-H Shift TS

method	ΔE (kJ/mol)
B3LYP/6-311+G**//B3LYP/6-311+G** (A//A)	0.3
QCISD/6-311G**//QCISD/6-311G** (B//B)	2.1
QCISD(T)/6-311G**//QCISD/6-311G** (C//B)	0.5

of the differences are as follows: at the B3LYP/6-311+G** level, C1 and C3– H_t bond lengths are markedly unequal (1.521 and 1.188 Å, respectively). C2 is pyramidalized: the sum of the bond angles is 354.5°. Both the inequality in bond lengths to H_t and the pyramidalization are more marked with QCISD/6-311G** optimization, with bond lengths of 1.554 and 1.176 Å and a bond angle sum of 342.8°. The pyramidalization at C2 means that there is no longer a pure p orbital at C2 for the substituent to overlap with. Nevertheless, the CO⁺ substituent lowers the energy of the rearrangement markedly compared to that of propene (Table 1). The dissociation energy for H atom loss from $CH_2=C(CH_3)CO^+$ is greater than that for propene. Both the reduction in activation energy for the rearrangement and the increase in H loss dissociation energy are in the same direction as those for the other conjugating substituents. The bond length from C2 to the CO⁺ is shortened more in going from the precursor to the TS than for any other substituent (Table 4). The bond length to the substituent increases in going from the precursor to the allyl radical, as it does for all of the conjugating substituents.

Comment on Previous Treatment of the Acetone Enolate. In 1995, S&B concluded on the basis of their experimental observations of the occurrence of [1,3] shifts in enolates and from an orbital correlation diagram that a [1,3] suprafacial shift is allowed in the acetone enolate.¹⁰ The correlation diagram is hard to use for analyzing the degree to which sigmatropic shifts are allowed because the reactant, TS, and product have no common element of symmetry for classifying their MOs. Thus, in the absence of detailed calculation, there is nothing to prevent one from connecting the lowest relevant orbital of the reactant to the lowest relevant orbital of the TS. The second lowest orbital can be connected to the second lowest, and so on, as S&B's correlation diagram does. This leads to the conclusion that all suprafacial shifts are allowed. Sigmatropic shifts are better analyzed by the method given by W&H in 1965.^{1c} One detaches the migrating group from the rest of the molecule and examines the phase of the SOMOs to determine which lobes of the reaction termini can bond simultaneously to the migrating group. This method is somewhat tricky for the analysis of the [1,3]-H shift in the acetone enolate. Detachment of the migrating group gives a hydrogen atom and the 2-oxo-1,3-propanediyl anion radical [$CH_2(C=O)CH_2^{\cdot-}$]. The symmetries and energies of the occupied orbitals show that this radical is unusual in that the HOMO and SOMO are not the same orbital. Thus, in the 2-oxo-1,3-propanediyl anion radical, it is important to use the a_2 SOMO rather than the b_1 HOMO. This is because, in this case, the HOMO is already doubly occupied, it cannot accommodate an extra electron from the migrating H in the TS without a major disruption. However, the SOMO can interact with the migrating H favorably.

(16) (a) Kosower, E. M. *Physical Organic Chemistry*; Wiley & Sons: New York, 1968. (b) Baer, T. *J. Am. Chem. Soc.* **1980**, *102*, 2482–83. (c) Bohme, D. K.; Mackay, G. I. *J. Am. Chem. Soc.* **1981**, *103*, 2173–75. (d) Perera, S. A.; Bartlett, R. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 8476–77.

Summary

The [1,3]-H shift in the acetone enolate is antarafacial in character near the TS. Conjugating substituents at the 2-position of alkenes reduce the energy of [1,3]-H shift TSs and raise the dissociation energy of H atom loss. Strongly electron-donating (O^-) and electron-withdrawing (CO^+) groups lower the energy of the rearrangement much more than the neutral substituents vinyl and ethynyl. This explains why such [1,3]-H shifts are readily observed in enolate anions. A moderately electron-donating group (NH_2) has an effect on the rearrangement TS energy that is intermediate between that of the strongly electron-donating and neutral substituents. The electron-withdrawing and electron-donating groups also have a larger effect on the structure of the TS than the neutral

substituents do. Our best calculations predict that the [1,3]-H shift is lower in energy than dissociation by 120.8 kJ/mol in the 1-methylacryloyl cation, 114.5 kJ/mol in the acetone enolate, 58.9 kJ/mol in 2-aminopropene, 36.8 kJ/mol in isoprene, and 27.8 kJ/mol in 2-methyl-1-butene-3-yne. There is therefore some chance of observing [1,3]-H shifts in conjugated alkenes such as isoprene.

Supporting Information Available: Z-Matrices or Cartesian coordinates of optimized structures, energies in hartrees, zero-point energies, the number of imaginary frequencies, a description of the CASSCF methods, and an explanation of gaps in Table 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO020624I