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A Theoretical Study of the Allene Effect in [1,*n*] Sigmatropic Hydrogen Shifts

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Abstract: The [1,*n*] hydrogen shift reactions ($n = 3, 5, 7, 9$, and 11) in $CH_3-(CH{=}CH)_{(n-3)/2}-CH{=}CH_2$ have been investigated by ab initio calculations, and the results are compared with the corresponding reaction in systems where the terminal double bond is substituted by an allene unit. Activation energies at the MP2/6-31G*//HF/3-21G level reproduce experimental results for the [1,5] and [1,7] reactions quite accurately. For the [1,3] and [1,5] reactions the introduction of an allene moiety lowers the activation energy by 10−12 kcal/mol, while the effect for the [1,7] and [1,9] reactions is only 1−2 kcal/mol. By considering the transition structures as two interacting radical fragments it is possible to rationalize both the variation in activation energy for the parent systems and the difference in activation energy between the parent and allene systems. The calculations indicate only a very weak dependence of primary kinetic isotope effects on transition state geometries (linearity and symmetry of the hydrogen transfer), and the calculated values are much smaller than experimental data, suggesting that tunneling is important.

Introduction

Sigmatropic hydrogen shift reactions exemplify the Woodward−Hoffmann (W−H) symmetry rules.[1] The [1,3] and [1,7] migrations are predicted to occur in an antarafacial manner, while [1,5] migrations should occur suprafacially. Both [1,5] and [1,7] hydrogen shifts have rather low activation energies and are commonly observed reactions.[2] The theoretically predicted supra- and antarafacial migrations of the hydrogen for these reactions have been confirmed by experiments.[3,4] [1,3] hydrogen shifts in carbon systems have not been observed experimentally,[5] which is understandable since theoretical calculations suggest that the activation energy for a concerted unimolecular reaction (i.e. not a dissociation−recombination mechanism, two consecutive [1,2] shifts or an intermolecular reaction) is very high, around 90 kcal/mol.[6] Hydrogen migrations in larger systems, for example [1,9] or [1,11] shifts, have not been observed experimentally, nor have they been studied theoretically.

Okamura et al. have studied [1,5] and [1,7] hydrogen migrations in systems where the terminal double bond of a polyene is replaced by an allene unit.[4,7] Here the hydrogen migrates to the central sp-hybridized carbon rather than to the terminal sp^2-hybridized carbon. For the [1,5] case they observe that the activation energy is $\cong$10−12 kcal/mol lower than for other typical [1,5] migrations, while the effect for the [1,7] system is close to zero. Meier and Schmitt have observed a [1,3] hydrogen shift in an allene system under flash vacuum pyrolysis conditions where the activation energy can be estimated to be $\cong$50 kcal/mol.[8] If this process is concerted, it corresponds to a decrease in activation energy of $\cong$40 kcal/mol relative to the parent system.

We were intrigued by this allene effect indicated by the experiments and wish here to report calculations on [1,*n*] hydrogen shifts ($n = 3, 5, 7, 9, 11$) in the parent polyene and the corresponding allene systems.

Background

[1,5] hydrogen shifts are well-known, and examples from simple acyclic systems are shown in Table 1. For the parent (*Z*)-1,3-pentadiene $\Delta H^{\ddagger} = 35.2$ kcal/mol and $\Delta S^{\ddagger} = -9.5$ eu.[9] The corresponding allene system, (*Z*)-1,2,4-hexatriene, has not been studied experimentally, but 5-methyl-1,2,4-hexatriene has $\Delta H^{\ddagger} = 23.8$ kcal/mol and $\Delta S^{\ddagger} = -13.7$ eu.[10] The presence of the 5-methyl substituent has a very small effect, as indicated by the data for 2-methyl-1,3-pentadiene.[11] The systems studied by Okamura et al. are somewhat more complex, but similar activation parameters are observed.[7a,d] The [1,7] hydrogen shift in the parent system, (*Z,Z*)-1,3,5-heptatriene has not been studied, but (*Z,Z*)-1,3,5-octatriene gives $\Delta H^{\ddagger} = 19.5-20.6$ kcal/mol (*Z* and *E* products)

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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[2] Spangler, C. W. *Chem. Rev.* **1976**, *76*, 187.

[3] Roth, C. W.; König, J.; Stein, K. *Chem. Ber.* **1970**, *103*, 426.

[4] (a) Hoeger, C. A.; Okamura, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 268. (b) Hoeger, C. A.; Johnston, A. D.; Okamura, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 4690.

[5] Experimental evidence for an activation energy in excess of 60 kcal/mol for a [1,3] hydrogen migration can be found in: Lewis, D. R.; Cochran, J. C.; Hossenloop, J. M.; Niller, D. M.; Sweeny, T. E. *J. Phys. Chem.* **1981**, *85*, 1787.

[6] (a) Bouma, W. J.; Vicent, M. A.; Radom, L. *Int. J. Quantum Chem.* **1978**, *14*, 767. (b) Rodwell, W. R.; Radom, L. *Int. J. Quantum Chem.* **1980**, *18*, 107. (c) Poirier, R. A.; Majlessi, D.; Zielinski, T. J. *J. Comp. Chem.* **1986**, *7*, 464. (d) Bernardi, F.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1984**, *106*, 1198.

[7] (a) Shen, G.-Y.; Tapai, K.; Okamura, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 7499. (b) Barrack, S. A.; Okamura, W. H. *J. Org. Chem.* **1986**, *51*, 3201. (c) Elnagar, H. Y.; Okamura, W. H. *J. Org. Chem.* **1988**, *53*, 3060. (d) Palenzuale, J. A.; Elnagar, H. Y.; Okamura, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 1770. (e) Okamura, W. H. *Acc. Chem. Res.* **1983**, *16*, 81. (f) Curtin, M. L.; Okamura, W. H. *J. Am. Chem. Soc.* **1991**, *113*, 6958. (g) Okamura, W. H.; Elnagar, H. Y.; Ruther, M.; Dobreff, S. *J. Org. Chem.* **1993**, *58*, 600.

[8] Meier, H.; Schmitt, M. *Tetrahedron Lett.* **1989**, 5873. Experimentally the reaction occurs under flash vacuum pyrolysis at 540 °C. Assuming a contact time of 1 s and a $\Delta S^{\ddagger}$ of -0.2 au (calculated at the HF/3-21G level) a $\Delta H^{\ddagger}$ value of $\cong$50 kcal/mol can be estimated.

[9] Roth, W. R.; König, J. *Ann. Chem.* **1966**, *699*, 24. Note that the reported activation parameters in this reference for the hydrogen migration are not consistent with the kinetic data. According to the kinetic data the equation for the hydrogen migration rate should read $k_H = (2.2 \times 10^{11})\, e^{-36.1/RT}$, corresponding to $\Delta H^{\ddagger} = 35.2$ kcal/mol and $\Delta S^{\ddagger} = -9.5$ eu. The k_D expression is correct. The corrected expression for the KIE is $k_H/k_D = 0.941e^{1.563/RT}$.

[10] Skattebol, L. *Tetrahedron* **1969**, *25*, 4933.

[11] Frey, H. M.; Ellis, R. J. *J. Chem. Soc.* **1965**, 4770.

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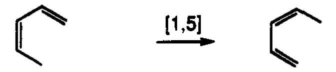
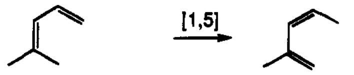
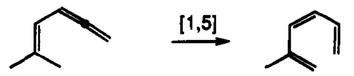
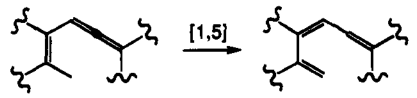
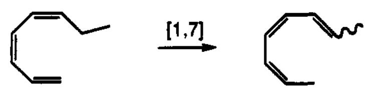
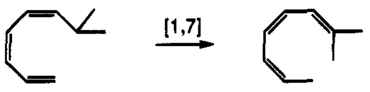
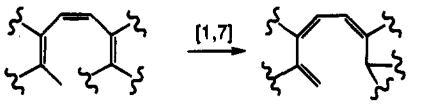
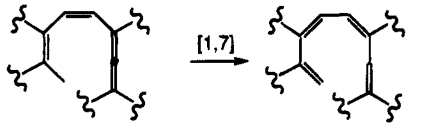
Table 1. Experimental Data

	$\Delta H^{\ddagger,a}$	$\Delta S^{\ddagger,a}$	KIE^b	Ref.
	≈50			8
	35.2	−9.5	5.0^c (7.8)^d	9
	35.2	−7.9		11
	23.8	−13.7		10
	18.7 - 24.2	−7.6 - −19.7	5.3 - 7.6	7
	19.5 - 20.6	−19.3	6.6	12
	20.8	−16.1	5.2	13
	21.0 - 23.5	−16.1 - −19.9	2.6 - 7.5	4,7
	20.2	−22.8	4.4	7*d*

[a] $\Delta H^\ddagger$ in kcal/mol, $\Delta S^\ddagger$ in eu. [b] KIE at 100 °C. [c] At 200 °C. [d] Extrapolated to 100 °C,

and $\Delta S^\ddagger = -19.3$ eu.[12] The 7-methyl analogue has $\Delta H^\ddagger = 20.8$ kcal/mol and $\Delta S^\ddagger = -16.1$ eu.[13] Very similar values have been observed in more complex systems.[2,4,7] For an allenic system Okamura et al. obtained $\Delta H^\ddagger = 20.2$ kcal/mol and $\Delta S^\ddagger = -22.8$ eu.[7d] Thus for [1,5] migrations, the introduction of an allene unit lowers $\Delta H^\ddagger$ by ≅11 kcal/mol while the stabilization for [1,7] shifts is small, ≅1−2 kcal/mol.

The [1,3] hydrogen shift in propene has been studied theoretically by several groups.[6,14] At sufficiently high theoretical levels only the W−H allowed antarafacial migration has a true transition structure (TS).[6d] The activation energy calculated by various methods is around 90 kcal/mol, indicating that a C−H bond breakage probably is a lower energy pathway. The [1,5] hydrogen migration in (*Z*)-1,3-pentadiene has also been studied several times, and again only the W−H allowed suprafacial migration has a genuine TS.[14−16] High-level calculations reproduce the activation energy to within experimental accuracy, and even MP2/6-31G* calculations give an acceptable value of 37.6 kcal/mol.[16] The TS for the [1,7] migration in (*Z*,*Z*)-1,3,5-heptatriene has been optimized at the HF/3-21G level by Hess, Schaad, and Pancir, assuming that the TS has the expected C_2 symmetry.[14] The activation energy calculated at this level was 44.1 kcal/mol, while a more reasonable value of 22.1 kcal/mol is obtained at the MP2/6-31G* level, as shown below.

Bond has reported calculations on conformations of vinylallenes relevant for [1,5] migrations.[17] He speculated that the lower activation energy for the allene analogue is due to the exothermicity of the reaction compared to the thermoneutral parent reaction, or to the fact that the migration takes place to a sp-hybridized carbon. A conformational effect was ruled out by his calculations. As shown below, neither of these speculations can explain why there is a large allene effect for the [1,5] but not for the [1,7] systems. We note in passing that Carpenter's theory[18] for calculating substituent effects based on simple Hückel theory predicts that a conjugating group at C_1, as the allenes studied here, should slow the reaction, in contrast to experimental and ab initio results.

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(12) Baldwin, J. E.; Reddy, V. P. *J. Am. Chem. Soc.* **1987**, *109*, 8051.

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(14) Hess, B. A.; Schaad, L. J.; Pancir, J. *J. Am. Chem. Soc.* **1985**, *107*, 149.

(15) (a) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7185. (b) Rondan, N. G.; Houk, K. N. *Tetrahedron Lett.* **1984**, 2519. (c) Kahn, S. D.; Hehre, W. J.; Rondon, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 8291. (d) Dormans, G. J. M.; Buck, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 3235. (e) Dormans, G. J. M.; Buck, H. M. *J. Mol. Struct.* **1986**, *136*, 121. (f) Chantranupong, L.; Wildman, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 4151.

(16) Jensen, F.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3139.

(17) Bond, D. *J. Org. Chem.* **1990**, *55*, 661.

(18) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877.

Computational Details

All geometries have been fully optimized at the RHF/3-21G level. The authenticity of transition structures has been confirmed by frequency calculations. Better estimates of activation energies have been obtained at the MP2/6-31G* level, using the HF/3-21G geometries.[19,20] This level has been shown to reproduce activation parameters for the [1,5] parent system.[16] Calculations have been performed on the parent polyenes $CH_2{=}CH{-}(CH{=}CH)_n{-}CH_3$, the corresponding allenes $CH_2{=}C{=}CH{-}(CH{=}CH)_n{-}CH_3$, and the allene rearrangement products $CH_2{=}CH{-}(CH{=}CH)_n{-}CH{=}CH_2$, with $n = 0-4$. Only the [1,*n*] hydrogen transfer reactions occurring in a single step between the terminal carbons have been studied. The calculated activation energies for some of these reactions are so high that other processes are much more likely to occur; however, for establishing the theoretical model such alternative processes are irrelevant. Kinetic isotope effects and activation entropies have been calculated from HF/3-21G vibrational frequencies scaled by a factor of 0.9. All optimized geometries and frequencies are available upon request.

Results

The geometries of reactants and products are unremarkable and will not be discussed. The optimized TS geometries are shown in Figure 1, and geometrical data are given in Tables 2−4. The TS for hydrogen migrations larger than [1,7] have not been described previously. The W−H rules require that the [1,9] reaction should occur suprafacially, thus the TS for (*Z,Z,Z*)-1,3,5,7-nonatetraene should have C_s symmetry. Similarly the [1,11] reaction should be antarafacial, with the TS for (*Z,Z,Z,Z*)-1,3,5,7,9-undecapentaene having C_2 symmetry. Both of these predictions are born out, and frequency calculations confirm that the geometries shown in Figure 1 are indeed TS's with a single negative Hessian eigenvalue. The TS's for the allene systems are in general very close to those of the parent compounds, except for the [1,11] reaction which is discussed below. The allene reactions are all exothermic by ≅12 kcal/mol (Table 5), and the Hammond postulate[21] would predict that the breaking C−H bond should be shorter than the forming C−H bond. The [1,3] and [1,11] TS's are at variance with this rule, while the other systems obey it. The CHC angle around the transferring hydrogen increases until the [1,9] reaction and decreases slightly for the [1,11] TS.

Contrary to the other reactions, the [1,11] allene TS is very different from that of the parent compound. Location of the allene TS's was typically done by starting the optimization from the optimized geometries of the parent TS's. When applying this procedure to the [1,11] reaction, the optimization initially reduces the gradient norm to 0.0003 au. The geometry of this structure is very similar to the TS of the parent reaction. However, upon further attempts to reduce the gradient, the geometry collapses to that shown in Figure 1. Table 2 shows that the [1,11] allene TS has strongly alternating bonds in the backbone, while all other TS's have bond lengths close to 1.40 Å. In the [1,11] allene TS a Peierls distortion has thus occurred with the structure transforming from a delocalized to a localized geometry. The energy difference between these two forms is 12 kcal/mol at the HF/3-21G level, but −1 kcal/mol at the MP2/6-31G* level. This suggests that the localized form may return to a delocalized TS if optimized at a correlated level. For these reasons the [1,11] allene reaction has been omitted in the analysis below.

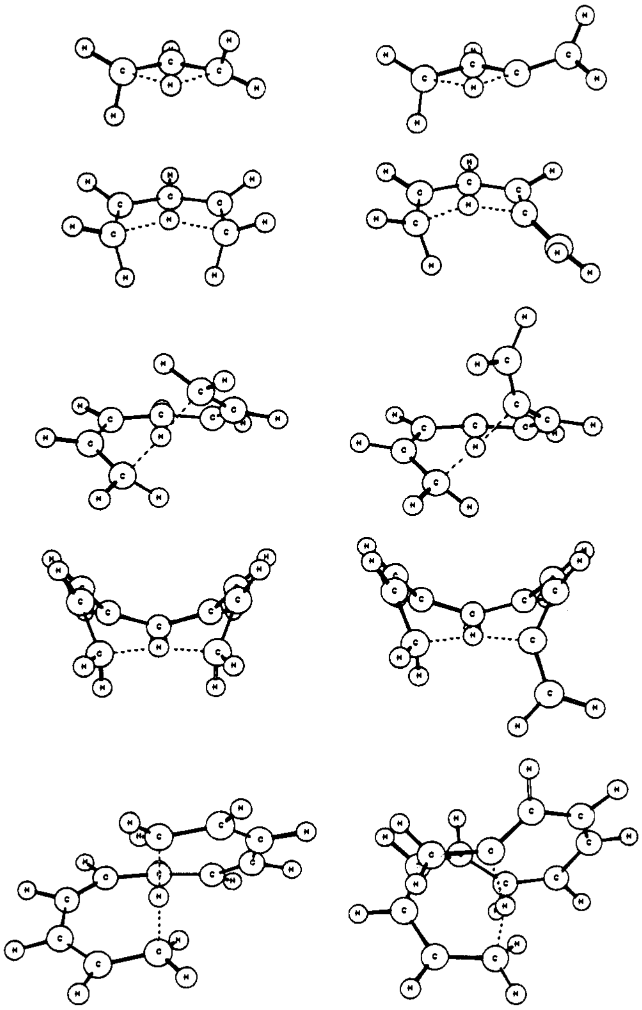

Figure 1. HF/3-21G transition structures for the [1,3], [1,5], [1,7], [1,9], and [1,11] hydrogen shift reactions in the parent and allene systems.

The calculated activation energies are shown in Table 5. These values are differences in electronic energies. The activation energy correction due to zero point energies and finite temperature effects is an essential constant −3 kcal/mol for all reactions. Relative activation energies are changed by less than 0.1 kcal/mol by inclusion of these corrections. For the [1,5] and [1,7] reactions the MP2/6-31G* level gives activation energies slightly higher than the experimental values by 1−2 kcal/mol; inclusion of zero point energies would give values slightly lower than the experimental data. The calculated activation energy for the [1,9] migration is 45 kcal/mol; however, such a reaction will be difficult to observe experimentally as both [1,5] and [1,7] migrations occur much easier. The [1,11] migration has a substantially higher activation energy, 63 kcal/mol. The change in activation energy from the parent to the allenic system is calculated to be −12.8, −9.4, −1.8, and −2.5 kcal/mol for the [1,3], [1,5], [1,7], and [1,9] systems, respectively. The values for the [1,5] and [1,7] systems are in satisfactory agreement with the experimental data discussed in the Background section. Calculations on the products of the migration in the allene systems show that all these reactions are exothermic by ≅12 kcal/mol, i.e. the exothermicity cannot explain why the allene effect is significantly different for the [1,5] and [1,7] migrations.

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

(20) (a) *Gaussian 92*, Revision A, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomberts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1992. (b) *GAMESS*, Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(21) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

Table 2. HF/3-21G Transition Structure Bond Lengths (Å)[a]

	$\|CH\|_b$	$\|CC\|$	$\|CC\|$	$\|CC\|$	$\|CC\|$	$\|CC\|$	$\|CC\|$	$\|CC\|$	$\|CC\|$	$\|CC\|$	$\|CC\|$	$\|CH\|_f$
$[1,3]_p$	1.538	1.404									1.404	1.538
$[1,3]_a$	1.538	1.426									1.361	1.469
$[1,5]_p$	1.448	1.405	1.386							1.386	1.405	1.448
$[1,5]_a$	1.404	1.410	1.376							1.394	1.377	1.419
$[1,7]_p$	1.376	1.397	1.383	1.391					1.391	1.383	1.397	1.376
$[1,7]_a$	1.331	1.405	1.375	1.394					1.389	1.387	1.374	1.376
$[1,9]_p$	1.338	1.399	1.376	1.392	1.397			1.397	1.392	1.376	1.399	1.338
$[1,9]_a$	1.312	1.407	1.369	1.401	1.388			1.403	1.387	1.380	1.378	1.339
$[1,11]_p$	1.378	1.395	1.372	1.398	1.397	1.405	1.405	1.397	1.398	1.372	1.395	1.378
$[1,11]_a$	1.401	1.401	1.374	1.477	1.326	1.478	1.325	1.473	1.332	1.470	1.320	1.377

[a] Subscripts p and a denote parent and allene systems, respectively. $|CH|_b$ and $|CH|_f$ are the breaking and forming C–H bond lengths, and $|CC|$ are the C–C bond lengths in the backbone from the breaking to the forming C–H bond.

Table 3. HF/3-21G Transition Structure Bond Angles (deg)[a]

	CCH_b	CCC	CCC	CCC	CCC	CCC	CCC	CCC	CCC	CCC	CCH_f
$[1,3]_p$	78.0	108.5								108.5	78.0
$[1,3]_a$	78.4	104.4								104.4	82.9
$[1,5]_p$	98.1	123.2	120.4						120.4	123.2	98.1
$[1,5]_a$	99.2	120.7	120.5						120.5	123.1	101.2
$[1,7]_p$	104.4	125.8	130.2	132.2				132.2	130.2	125.8	104.4
$[1,7]_a$	105.5	125.0	129.5	132.6				132.6	131.9	126.8	106.4
$[1,9]_p$	106.7	125.5	131.0	135.9	135.0		135.0	135.9	131.0	125.5	106.7
$[1,9]_a$	106.5	125.4	130.7	135.9	135.8		135.8	137.0	132.5	125.4	109.7
$[1,11]_p$	100.7	126.0	133.3	141.8	145.0	148.5	145.0	141.8	133.3	126.0	100.7
$[1,11]_a$	96.2	125.0	132.5	134.9	130.7	129.2	133.4	135.9	134.6	130.3	115.1

[a] Subscripts p and a denote parent and allene systems, respectively. CCH_b and CCH_f are the angles to the breaking and forming C–H bonds, and CCC are the C–C–C bond angles in the backbone from the breaking to the forming C–H bond.

Table 4. Selected Geometrical Features of Transition Structures[a]

reaction	$\|CC\|^a$	$\|CC\|^b$	α_{CHC}	β_1	β_2
$[1,3]_p$	2.279		95.6	90.0	
$[1,3]_a$	2.204	1.314	94.2		5.4
$[1,5]_p$	2.624		129.9	52.8	
$[1,5]_a$	2.540	1.313	128.2		31.9
$[1,7]_p$	2.654		149.3	21.7	
$[1,7]_a$	2.629	1.308	152.6		65.5
$[1,9]_p$	2.651		164.0	6.3	
$[1,9]_a$	2.621	1.308	162.8		81.4
$[1,11]_p$	2.711		158.8	16.9	
$[1,11]_a$	2.715	1.358	155.4		20.4

[a] HF/3-21G values, distances in Å, angles in deg. Subscripts p and a denote parent and allene systems, respectively. $|CC|^a$ is the distance between the two carbons where the migration takes place, $|CC|^b$ is the C_1-C_2 bond in the vinyl group, and α_{CHC} is the angle around the migrating hydrogen. β_1 is the torsional angle between the breaking C–H bond and the p-orbital on C_2; β_2 is the torsional angle between the p-orbitals on C_2 and C_3.

Table 5. Calculated Activation and Reaction Parameters[a]

reaction	$\Delta E^{\ddagger}$	$\Delta S^{\ddagger}$	ΔE_0	KIE
$[1,3]_p$	90.5	−4.3		3.01
$[1,3]_a$	77.7 (−12.8)	−3.7	−11.8	3.16
$[1,5]_p$	37.6	−8.2		2.93
$[1,5]_a$	28.2 (−9.4)	−9.1	−12.2	2.97
$[1,7]_p$	22.1	−13.9		2.88
$[1,7]_a$	20.3 (−1.8)	−12.5	−12.4	2.93
$[1,9]_p$	44.7	−13.8		2.63
$[1,9]_a$	42.2 (−2.5)	−13.8	−12.4	2.74
$[1,11]_p$	62.6	−16.6		2.80

[a] Energies in kcal/mol from MP2/6-31G*//HF/3-21G calculations, entropies and KIE (T = 100 °C) from HF/3-21G data. Values in parentheses are relative to the corresponding parent reaction.

While the calculated stabilization of the [1,3] reaction by an vinyl unit is substantial, it is not even close to the ≃40 kcal/mol required by the experimental data if the reaction is concerted.[8] The calculated activation energy for the actual experimental system, ethenylidenecyclopentane, is only 0.3 kcal/mol higher than for the 1,2-butadiene model, thus the discrepancy is not due to differences between the model and actual experimental compound. It is thus likely that the rearrangement of ethenylidenecyclopentane proceeds via an intermolecular or multistep mechanism.

It has previously been shown for the [1,5] hydrogen migration in 1,3-pentadiene that the activation entropy calculated using HF/3-21G frequencies is in good agreement with the experimental value (at 200 °C the calculated $\Delta S^{\ddagger}$ is −9.3 eu, the experimental value is −9.5 eu).[16] For the [1,7] migration in heptatriene, the calculated activation entropy is −13.9 eu, in fair agreement with the experimental value of −19.2 eu found in octatriene.[12] As seen in Table 5, there is a clear trend that $\Delta S^{\ddagger}$ become more negative as the carbon chain gets longer, which is consistent with the loss of more low-frequency torsional modes upon formation of the TS for the larger systems. The difference in the calculated $\Delta S^{\ddagger}$ between the parent and allene systems is small, as could be expected from the close similarity of the TS geometries.

Model studies of primary kinetic isotope effects (KIE) indicate that the largest isotope effect should be observed for a symmetrical TS and for linear hydrogen transfer.[22] These conclusions are based on classical transition state theory and do not include tunneling. In general it is assumed that tunneling will contribute most when the KIE is large, i.e. the correlation between TS geometry and KIE is independent of the inclusion of tunneling.[23] The present data offer a possibility for testing the predicted dependence of KIE on TS geometry. The parent systems have equal breaking and forming C–H bonds, and the KIE is thus expected to correlate with the hydrogen transfer angle. These angles are 96°, 130°, 149°, 164°, and 159° for n = 3, 5, 7, 9, and 11, respectively (Table 4). Model calculations

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suggest that the KIE should increase from 1.7 to 6.2 when the transfer angle is increased from 90° to 150°.[22a] The KIE's calculated at 100 °C from HF/3-21G frequencies scaled[24] by 0.9 are 3.0, 2.9, 2.9, 2.6, and 2.8 (Table 5). It appears that the KIE is essentially independent of the transfer angle. If the small variation is significant, it is actually opposite to model calculations; and the KIE appears to have a minimum for a linear transfer angle. Furthermore, the KIE's are in all cases slightly larger for the unsymmetric allene systems than for the symmetric parent system, which again is at variance with conclusions based on model calculations.

The experimental KIE values for the [1,5] and [1,7] systems are much larger than the calculated values, indicating that tunneling is important (Table 1). The variation in the experimental KIE's between different systems is so large that it is not possible to determine whether [1,5] or [1,7] shifts have the larger KIE. Calculations by Liu et al. have shown that the KIE for the [1,5] shift can be reproduced quite accurately when tunneling is included in the small curvature approximation.[25] No attempt has been made to include such effects in the present work. We merely note that the postulated correlation between KIE and TS geometry is not supported by the present calculations.[26,27] This is significant as the model calculations and the present ab initio calculations rest on the same basic assumption, transition state theory.

Analysis and Discussion

The above results establish that MP2/6-31G* calculations are able to reproduce experimental activation parameters. The close similarity of the parent and allene TS geometries suggests that the vinyl moiety can be considered as a substituent on the parent structure. However, the calculated activation energies themselves do not provide any understanding of why there is a substantial decrease in activation energy for the [1,3] and [1,5] systems, but only a small effect for the [1,7] and [1,9] systems.

The allene effect is a differential (de)stabilization of the reactant compared to the TS by the vinyl group. These effects may be separated by considering isodesmic reactions[19] of the type (illustrated for the propene/butadiene system):

$$H_2C{=}C{=}CH{-}CH_3 + CH_4 \rightarrow H_2C{=}CH{-}CH_3 + H_2C{=}CH_2 \quad (1)$$

$$[1,3]\text{-}TS_{but} + CH_4 \rightarrow [1,3]\text{-}TS_{pro} + H_2C{=}CH_2 \quad (2)$$

Reaction 1 measures how much the reactant is (de)stabilized by the change $=CH_2 \rightarrow =C=CH_2$ relative to the change from methane to ethylene, while (2) measures the same effect for the TS. The MP2/6-31G* calculated values given in Table 6 indicate that the reactant is destabilized by a near constant 2.5 kcal/mol for all the members in the series. It is evident from Table 6 that the allene effect is a specific stabilization of the TS's for the [1,3] and [1,5] systems.

Table 6. MP2/6-31G*//HF/3-21G Calculated Stabilization Energies[a] by Introduction of a Vinyl Unit

reaction	reactant	TS
[1,3]	−2.6[b]	10.2
[1,5]	−2.4	7.0
[1,7]	−2.3	−0.5
[1,9]	−2.3	0.2

[a] In kcal/mol, calculated by means of isodesmic reactions of types (1) and (2), see text. Positive values correspond to a stabilization. [b] Experimental value is −3.0 kcal/mol, ref 28.

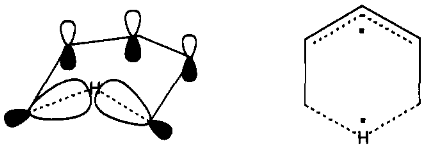

Figure 2. Illustration of the biradical character of the transition state for hydrogen migrations.

We will now show that the variation of the activation energy in the parent systems, and the different effect of introducing a vinyl group, may be qualitatively understood by considering the TS as consisting of two interacting radical fragments, as illustrated in Figure 2. One electron is delocalized in the breaking/forming C−H bonds, and the other is delocalized in the backbone π-system. The interaction between these two subsystems is determined by the orbital overlap between the breaking/forming C−H bonds and the p-orbital on C_2;[29] this torsional angle will be denoted β_1 and calculated values are given in Table 4.

The p-orbitals of the backbone π-system will try to maximize the overlap between neighboring p-orbitals, favoring roughly planar or helical geometries. At the TS, the ends of the carbon chain must be ≅2.6 Å apart in order for the hydrogen transfer to take place. The [1,5] and [1,7] systems can easily adapt such conformations: the [1,5] TS resembles a flattened cyclohexane ring and the accommodation of 7 carbons in the helical TS for the [1,7] migration poses no problem. For the larger [1,9] and [1,11] systems, the TS's involve a considerable widening of the in-plane angles and/or twisting around the C−C bonds, as can be seen in Figure 1 and Table 3. Consequently, there is a significant amount of strain involved in acquiring the appropriate TS geometries. The [1,3] shift suffers from severe angle strain due to the acute hydrogen transfer angle. A semiqualitative measure of the amount of strain in the TS's can be obtained from force field calculations. Using the MM3 parameters[30] and the HF/3-21G optimized geometry, the relative TS strain energies[31] are calculated to be 55, 9, 0, 30, and 63 kcal/mol, i.e. the [1,7] TS is the least strained followed by the [1,5] and the [1,9], while both the [1,3] and [1,11] TS's are significantly more strained.

The energy cost for attaining the TS geometry is one of the factors that influence the activation energy; the other is a stabilization due to interaction between the C−H−C moiety and the backbone π-system. The latter is measured by the β_1 angle, i.e. a small β_1 value indicates a good orbital overlap. This stabilization is zero for the [1,3] system, small for the [1,5] system, but large for the [1,7], [1,9], and [1,11] systems (Table 4). Both the [1,5] and [1,7] TS geometries have little strain,

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and the better overlap between the two radical fragments results in a lower activation energy for the [1,7] migration. The [1,9] and [1,11] TS's also have a large orbital stabilization, but the higher strain energies make the activation energies significantly higher than for the [1,7] migration. The [1,3] TS also has a high strain energy, and there is no stabilizing interaction between the two fragments due to the 90° β_1 angle, thus it has the highest activation energy of all. The stabilization by interaction between the two fragments also serves to explain why the [1,5] hydrogen migration in cyclopentadiene has a lower activation energy (experimental value is 23.6 kcal/mol[32]) than the corresponding reaction in 1,3-pentadiene. The cyclopentadiene TS has a β_1 angle of 31° compared to the 53° for the acyclic case.[15b] As neither of the two TS's has much strain, the cyclic system should experience the larger stabilization and thus have the lower activation energy, as observed.

A small value for the β_1 angle indicates that there is significant interaction between the two radical fragments. This is equivalent to saying that TS's with large β_1 values have much biradical character, and TS's with small β_1 angles have wave functions with a more closed-shell nature. Indeed there is a good correlation between the β_1 values and the length of the breaking/forming C−H bond (Tables 2 and 4).

The introduction of a vinyl group transforms the receiving carbon atom at the TS from sp^3-like to sp^2-like hybridization. This opens the possibility that the backbone π-radical can extend the conjugation into the vinyl moiety and thereby stabilizes the TS. The magnitude of this stabilization depends on two factors: (i) how well the p-orbital on C_1-C_2 is aligned with the backbone π-system, and (ii) the maximum stabilization for extending the conjugation by an additional vinyl unit. The torsional angle between the p-orbitals on C_2 and C_3 is denoted β_2 and given in Table 4. As the angle between the p-orbital on C_2 and the forming C−H angle is close to 90°, β_2 varies approximately as $90° - \beta_1$.

The [1,3] TS has a β_1 angle of 90° and is thus expected to display biradical character. The β_2 orbital overlap is large, and the backbone radical is essentially changed from being localized on a single carbon to an allyl radical. Experimental data indicate that the allyl radical is $\cong$13 kcal/mol more stable than a localized radical.[33] Allowing for the small β_2 orbital misalignment, this value compares favorably with the calculated TS stabilization of 10 kcal/mol (Table 6). The [1,5] TS also has significant biradical character, as indicated by the β_1 angle of 53°. The p-orbitals on C_2 and C_3 form an angle of 32°, and the backbone change is from an allyl to a pentyl radical. Experimental estimates of the latter stabilization are $\cong$4 kcal/mol while the theoretical value is slightly higher, $\cong$6 kcal/mol.[33] The calculated TS stabilization of 7 kcal/mol is slightly higher than these values.

The larger [1,7] and [1,9] systems should have less biradical character than the [1,3] and [1,5] TS's, and the β_2 values indicate that the C_2-C_3 orbital overlap is small. Furthermore, for these systems the maximum stabilization by extending the conjugation decreases, e.g. for the [1,7] case the change is from a pentyl to a heptyl radical. Experimentally this stabilization is estimated to be $\cong$2 kcal/mol.[33] The allene effect for the larger system should thus be close to zero, as is both calculated and observed experimentally. We note that the C_1-C_2 bond length at the TS supports this analysis. The more the backbone π-system is delocalized into the vinyl moiety, the longer is the C_1-C_2 bond (Table 4). The allene effect can thus be decomposed into a constant reactant destabilization of $\cong$2.5 kcal/mol and a differential stabilization of TS. The latter is governed by two factors: (i) the maximum effect is given by the stabilization from extending the conjugation of the backbone radical by an additional vinyl unit, and (ii) this maximum effect is attenuated by how well the p-orbitals on C_2 and C_3 are aligned.

The analysis shows that structural and energetical features of both the parent and allene TS's may be understood by considering the electronic structure of the TS's as having significant biradical character. This model also allows some predictions to be made regarding substituent effects on the activation energy of sigmatropic hydrogen shift reactions. A radical stabilizing substituent should thus have a large effect on [1,5] migrations when located at the C_2/C_4 positions of a pentadiene system, but only a small effect at the C_3 position. Similarly, the effect for [1,7] migrations should be largest at the C_2/C_6 and C_4 positions of a heptatriene. Given that the biradical character for the [1,7] TS is less than for the [1,5] TS, the substituent effect is expected to be smaller for [1,7] migrations. The [1,3] reaction is predicted to display the largest effect of a radical stabilizing substituent, but the inherent high activation energy makes it difficult to study such reactions experimentally.

It may also be possible to lower the activation energy by adding radical stabilizing substituents at the carbons between which the migration takes place. If there is no steric hindrance, such substituents may interact with the radical nature of the C−H−C moiety. Again such effects are expected to decrease along the series [1,3], [1,5], [1,7], and [1,9].

Conclusion

By considering the electronic structure of the TS for [1,*n*] hydrogen shift reactions as two interacting radical fragments, it is shown that both the variation in the activation energy of the parent systems and the effect of introducing a vinyl groups can be rationalized. The activation energy in the parent reaction is interpretated as a combination of steric strain involved in acquiring the proper TS geometry and a stabilization between the two radical fragments. The latter is determined by the orbital overlap between the breaking/forming C−H bonds and the backbone π-system. The allene effect is a stabilization of the TS by further conjugation of the backbone π-radical. For the [1,3] and [1,5] reactions, the TS geometry is such that there is a good orbital overlap for this extension of conjugation, and consequently there is a large allene effect. For the larger systems, the orbital overlap is poor, and the allene effect is small.

Calculated primary KIE for the parent and allene systems do not show the expected variation with respect to the linearity and symmetry of the hydrogen transfer. It appears that primary KIE's depend only weakly on the TS geometries, and the small variation observed is actually opposite to that expected from simple model calculations.

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