J. Am. Chem. Soc. **1992**, 114, 2354-2359

It is possible that even though the gauche transition state (**5**) does not involve intramolecular hydrogen bonding, it may preferentially lead to the solvate ($CH_3CH_2O^-\cdot H_2O$); however, the experimental studies indicate that the ethoxide–water complex is the major product,[7c,8] whereas the theoretical studies predict that the gauche elimination should have a significantly larger barrier (5.2 kcal/mol) than the antiperiplanar elimination. Additional evidence against competing pathways is found in the calculated vibrational frequencies. On the basis of zero-point energy differences, the calculations predict that the barriers for both the antiperiplanar and gauche eliminations of $CD_3CD_2OCH_3$ are about 1.1 kcal/mol above those of $CH_3CH_2OCH_3$, and therefore both pathways should give similar kinetic isotope effects.[32,33] Our calculated differences in transition state barriers are in good accord with Bierbaum and Bowers' earlier estimate.[7c] Using their statistical rate model and the observed kinetic isotope effects, they predicted that the barrier in $CD_3CD_2OCD_2CD_3$ is 1.1 kcal/mol greater than that in $CH_3CH_2OCH_2CH_3$. Given the present theoretical results, it seems unlikely that a cyclic transition state is involved in the gas-phase reactions of HO^- with ethers, and therefore another explanation must be found for the different isotope effects observed in the two product channels. Although it is not completely consistent with the energy dependence that de Koning and Nibbering reported,[8] a rational explanation is that the reaction involves only an antiperiplanar pathway[34] and that a second isotope effect is active in the partitioning between solvated and unsolvated products.

Conclusions

For β-elimination reactions with a high degree of $E1_{cb}$-like character, the preference for periplanarity is greatly reduced. Because the carbon-leaving group bond is hardly broken in the transition state, there is little advantage to hyperconjugation and partial π-bond formation. As a result, steric effects can become important in determining the preferred conformation. Synperiplanar transition states are only possible when the advantage of conjugation outweighs the steric disadvantages of an eclipsed conformation. In $E1_{cb}$-like reactions, this is not necessarily true and gauche transition states are possible. These effects are almost perfectly balanced in the reaction of HO^- with $CH_3CH_2OCH_3$ where a gauche transition state is slightly more stable than a synperiplanar transition state. This highlights the fact that in $E1_{cb}$-like syn eliminations, the transition state barrier is relatively insensitive to the torsional angle (H_β–C_β–C_α–X). However, antiperiplanar transition states generally are preferred for gas-phase β-eliminations because they allow for conjugation within a staggered conformation. Further studies on the effect of substitution in E2 transition states have been completed and will be published subsequently.[35]

Acknowledgment. We thank the Chemical Instrumentation Program of the National Science Foundation (CHE-8822716) for providing the funds to purchase the Multi-Flow-Trace14 computer used for these calculations.

Registry No. Hydroxide, 14280-30-9; ethyl methyl ether, 540-67-0.

Supplementary Material Available: Listing of Z-matrix elements, energies, frequencies, and reaction coordinates (10 pages). Ordering information is given on any current masthead page.

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(31) In all previous theoretical studies of E2 eliminations, nearly linear proton transfer geometries (base–H_β–C_β) have been observed (see ref 2, 3, 6).

(32) The zero-point-energy differences predict a smaller isotope effect for the antiperiplanar and gauche eliminations of the (HO^-–$DCH_2CH_2OCH_3$) system (a transition state barrier difference of about 0.8 kcal/mol compared to the all hydrogen substrate). Therefore, both primary and secondary isotope effects are important in these reactions. Experimentally, de Koning and Nibbering have noted this result; see ref 8.

(33) Attempts to analyze the theoretical results with a simple RRKM dynamics approach (see ref 27a) led to unrealistically low rates and exceptionally large k_H/k_D values. Undoubtedly these errors result from treating low-frequency vibrations as harmonic oscillators rather than as hindered rotors (the differences cannot be explained solely on the basis of errors in the calculated barrier). Although beyond the scope of the present study, a more sophisticated dynamics treatment is appropriate for a system that is characterized by many low-frequency vibrations and the possibility of tunnelling (see ref 27c–e).

(34) Although entropy may slightly favor the gauche elimination (the small torsional barrier and the presence of two gauche pathways should increase the entropy), the large difference in activation energy (5.2 kcal/mol) should ensure that antiperiplanar eliminations dominate.

(35) Syn–gauche transition states have been observed in other systems, and the borderline between synperiplanar and syn–gauche transition states has been investigated: Gronert, S. Manuscript in preparation.

Ab Initio Calculations on Silicon Analogues of the Allyl Radical

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Abstract: Calculations at the CI-SD/6-31G* level of theory have been performed in order to determine the effect on the A–H bond dissociation energy (BDE) in X–AH_3 (A = C and A = Si) of replacing X = H_3C– by X = $H_2C{=}CH$– and $H_2Si{=}CH$– and of replacing X = H_3Si– by X = $H_2C{=}SiH$– and $H_2Si{=}SiH$–. The conjugative stabilization energies (CSEs) of the resulting allylic radicals have been obtained from the energies calculated to be required to twist a terminal $AH_2^\bullet$ group out of conjugation. Except for X = $H_2C{=}CH$– and $H_2Si{=}CH$– in X–$CH_2^\bullet$, these two definitions of allylic resonance energy give nearly identical values. The reason for the calculated difference between $-\Delta$BDE and CSE in $H_2C{=}CH{-}CH_2^\bullet$ and in $H_2Si{=}CH{-}CH_2^\bullet$ is discussed. It is also found that, with the exception of $H_2Si{=}CH{-}SiH_2^\bullet$, the calculated allylic resonance energies are generally those expected from the π BDEs in $H_2C{=}CH_2$, $H_2C{=}SiH_2$, and $H_2Si{=}SiH_2$. It is shown that pyramidalization at silicon lowers the resonance energy of $H_2Si{=}CH{-}SiH_2^\bullet$ from that expected, based on the strength of the C–Si π bond in $H_2C{=}SiH_2$.

The results of ab initio calculations show that substituents, X, affect the A–H bond dissociation energy (BDE) of X–AH_3 differently, depending on whether A is carbon or silicon.[1] For A = C, as well as for A = Si, X groups that can delocalize the unpaired electron in the X–$AH_2^\bullet$ radical tend to lower the A–H BDE. However, since carbon forms stronger π bonds than silicon,[2] conjugative stabilization of the radical formed by breaking the A–H bond is generally found to be more important for A = C than for A = Si.

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(2) Review: Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

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Table I. CI-SD/6-31G* Energies Calculated at (U)HF/6-31G* Geometries

	$X{-}AH_3$		$X{-}AH_2^{\bullet a}$		$X{-}AH_2^{\bullet b}$	
X	A = C	A = Si	A = C	A = Si	A = C	A = Si
CH_3	−79.5040	−330.5020	−78.8490	−329.8678		
$H_2C{=}CH$	−117.4470	−368.4434	−116.8142	−367.8098	−116.7898	−367.8095
$H_2Si{=}CH$	−368.4122	−619.4223		−618.7896	−367.7596	−618.7884
SiH_3	−330.5020	−581.4909	−329.8491	−580.8624		
$H_2C{=}SiH$	−368.4255	−619.4191	−367.7862	−618.7920	−367.7731	−618.7914
$H_2Si{=}SiH$	−619.4222	−870.4226		−869.8036	−618.7703	−869.7947

[a] $AH_2^{\bullet}$ group conjugated with the π bond in unsaturated X groups. [b] $AH_2^{\bullet}$ group rotated out of conjugation with the π bond in X.

Table II. Calculated (CI-SD/6-31G*) Decreases in A–H Bond Dissociation Energies (−ΔBDEs) Caused by Unsaturated Substituents, X, in $X{-}AH_3$ and Calculated (CI-SD/6-31G*) Conjugative Stabilization Energies (CSEs) in $X{-}AH_2^{\bullet}$ (kcal/mol)

	$-\Delta BDE\ (X{-}AH_3)^a$		$CSE\ (X{-}AH_2^{\bullet})$	
X	A = C	A = Si	A = C	A = Si
CH_3	0	0		
$H_2C{=}CH$	13.9^b	0.4^b	15.3	0.2
$H_2Si{=}CH$	33.0^b	0.9^b	31.5	0.8
SiH_3	0	0		
$H_2C{=}SiH$	8.5^c	0.9^c	8.2	0.4
$H_2Si{=}SiH$	14.2^c	6.0^c	13.6	5.6

[a] A positive value indicates a lowering of the A–H BDE. [b] BDE relative to X = CH_3. [c] BDE relative to X = SiH_3.

Our calculations revealed an important effect of substituent electronegativity on the A–H BDE in $X{-}AH_3$. For both A = C and A = Si, the A–H BDE was found to increase with the electronegativity of X. Substituent electronegativity affects the A–H BDEs in this way because the amount of s orbital character in the A–H bond of $X{-}AH_3$ increases with the electronegativity of X.[3] Since, especially for π electron donating substituent groups, conjugative stabilization of $X{-}SiH_2^{\bullet}$ is of relatively minor importance, compared to conjugative stabilization of $X{-}CH_2^{\bullet}$, substituent electronegativity has a very strong effect on the strengths of Si–H bonds.[1]

Our previous study was confined to substituents that were either π electron donor groups (e.g., NH_2) or π electron acceptor groups (e.g., BH_2) but that did not themselves contain π bonds. Although it is well known experimentally that the π bonds that are present in vinyl and phenyl substituents result in the BDEs of allylic and benzylic C–H bonds being 12–14 kcal/mol lower than the C–H BDEs in saturated molecules,[4] the Si–H BDE is apparently unaffected by the presence of an adjacent phenyl group.[5] Moreover, the EPR spectra of both 1-silaallylic[6] and 1-silabenzylic[7] radicals show the unpaired spin density to be largely, though not completely, localized on silicon.

The present computational study was motivated by the desire to understand in detail the effect of an adjacent π bond on C–H and Si–H BDEs. We also wanted to compare the computed barriers to rotation and spin densities in the resulting allylic and silaallylic radicals. For completeness, our study included, in addition to vinyl, both possible silavinyl substituents and also disilavinyl. Herein we report the results of our calculations.

Computational Methodology

Geometries were optimized[8] with RHF calculations for closed-shell molecules and with UHF calculations for radicals, using the 6-31G* basis set.[9] For allylic and other radicals in which delocalized wave functions are a possibility, UHF calculations are preferred to ROHF calculations for geometry optimizations.[10] In order to obtain energies that contain the effects of electron correlation, CI-SD calculations were performed at the RHF and UHF optimized geometries.

CI-SD calculations, which give pure doublet wave functions for radicals, are preferable to UMP calculations, which do not. The latter are based on the application of Møller–Plesset perturbation theory[11] to UHF wave functions, and UMP calculations tend to give correlated wave functions which still contain the higher spin states that contaminate UHF wave functions.[12] Spin contamination is especially severe in the UHF wave functions for allylic radicals. In the UHF wave functions for the radicals studied by us, S^2 ranges from 0.97 for allyl to 1.31 for trisilaallyl. For a pure doublet wave function S^2 is 0.75.

Geometries were optimized and energies were calculated with the Gaussian 86 package of ab initio programs.[13] Spin population analyses on the CI-SD wave functions were obtained with MELDF,[14] which projects populations computed with a split-valence basis set onto an equivalent minimal basis set,[15] thus facilitating analysis. Because of the large number of configurations involved in the CI-SD calculations, perturbation theory was used to select the most important configurations for the MELDF population analyses. The CI-SD wave functions were truncated so that less than 5% of the correlation energy was lost.

Results and Discussion

Table I gives the energies computed at the CI-SD level with the 6-31G* basis set. From the CI-SD energies the calculated amount by which various substituents, X, reduce the A–H BDE in $X{-}AH_3$ were obtained for A = C and A = Si. The reductions in BDEs are given in Table II, relative to X = $H_3C{-}$ and X = $H_3Si{-}$. We have discussed previously the effect on the BDE's of methane and silane of replacing a hydrogen with a methyl or a silyl group.[1,16]

The −ΔBDEs in Table II are actually the energies for the reactions

$$X{-}AH_2^{\bullet} + H_3C{-}AH_3 \rightarrow X{-}AH_3 + H_3C{-}AH_2^{\bullet} \qquad (1)$$

and

$$X{-}AH_2^{\bullet} + H_3Si{-}AH_3 \rightarrow X{-}AH_3 + H_3Si{-}AH_2^{\bullet} \qquad (2)$$

depending on whether substituent X has carbon or silicon attached to atom A. Since the reactions in eqs 1 and 2 are isodesmic,

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cancellation of errors makes the relative BDEs in Table II more accurate than the absolute A–H BDEs computed at the CI-SD/6-31G* level.[17]

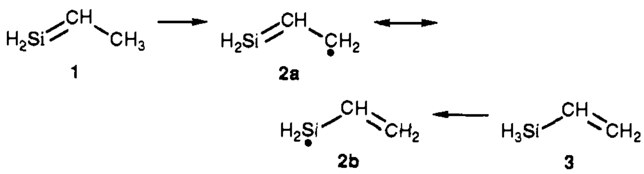
One way to attempt to disentangle possible electronegativity effects of substituents on BDEs from radical stabilizing conjugative effects is to calculate the energetic cost of twisting the substituent out of conjugation.[1] The conjugative stabilization energies (CSE) given in Table II are defined as the energies required to twist the unsaturated group, X, in the X–$AH_2^\bullet$ radicals out of conjugation with the $AH_2^\bullet$ radical center. With the exception of $H_2C{=}CH{-}CH_2^\bullet$ and $H_2Si{=}CH{-}CH_2^\bullet$ (vide infra), the CSEs in Table II are within 1 kcal/mol of the relative BDEs. This agreement demonstrates that the major way the unsaturated substituents in Table II affect A–H BDEs is by providing conjugative stabilization for the radicals formed.

The –ΔBDEs in Table II show that unsaturated substituents have a much greater effect on lowering C–H, compared to Si–H, BDEs. Moreover, the CSEs in Table II demonstrate that this difference is due to the fact that unsaturated groups, X, provide much more conjugative stabilization for X–$CH_2^\bullet$ radicals than for X–$SiH_2^\bullet$ radicals. These results indicate that, for each substituent group, π bonding to a carbon-centered radical provides more stabilization than does π bonding to a silicon-centered radical.

This conclusion is wholly consistent with the relative strengths of π bonds to carbon and to silicon. The BDEs of π bonds involving carbon and silicon are: π-C=C ≈ 65 kcal/mol,[18-21] π-C=Si ≈ 35 kcal/mol,[20,21] and π-Si=Si ≈ 23 kcal/mol.[21,22] Based on these π BDEs, one would anticipate that the stabilization provided by π bonding to the carbon radical center in X–$CH_2^\bullet$ would, for all four unsaturated X groups in Table II, exceed that furnished by π bonding to the silicon radical center in X–$SiH_2^\bullet$.

Allylic Radicals with Different Terminal Groups

1-Silaallyl (2). The significantly greater strength of a C=C π bond, compared to a C=Si π bond, is responsible for the finding that, of the substituents in Table II, the X = $H_2Si{=}CH{-}$ group is computed to provide the greatest lowering of the C–H BDE in X–CH_3. Cleavage of a C–H bond in **1** generates allylic radical



2, which can be represented by two resonance structures, **2a** and **2b**. The fact that the latter contains a C=C π bond, instead of the C=Si π bond in the former, suggests that **2b** makes a much larger contribution to the structure of the radical than **2a**. Thus, upon cleavage of a C–H bond in **1**, an allyl radical is formed in which the C=Si π bond in **1** is replaced by a stronger π bond that is largely localized between two carbon atoms.

Several pieces of additional data are in accord with this explanation of why X = $H_2Si{=}CH{-}$ lowers the C–H BDE more than any of the other substituents in Table II. For example, if **2b** contributes more than **2a** to the structure of **2**, the $H_2C{=}CH{-}$ group in **3** should have little effect on lowering the Si–H BDE in X–SiH_3. In fact, as shown in Table II, X = $H_2C{=}CH{-}$ decreases the Si–H BDE by only 0.4 kcal/mol, compared to X = $CH_3{-}$. The very small effect of vinyl on the calculated BDE of an adjacent Si–H bond is totally consistent with the experimental finding that phenyl has a negligible effect on the BDE of an adjacent Si–H bond.[5]

The energy required to twist the $H_2C{=}CH{-}$ group out of conjugation with the $SiH_2^\bullet$ radical center in **2** is minimal, amounting to only 0.2 kcal/mol.[23] In contrast, the energy required to twist the $H_2Si{=}CH{-}$ group out of conjugation with the $CH_2^\bullet$ radical center is large, amounting to 31.5 kcal/mol. The difference of 31.3 kcal/mol between the energies required to rotate about the C–C bond and the Si–C bond in **2** is about the same as the difference of 32.6 kcal/mol between the –ΔBDEs in forming **2** from, respectively, **3** and **1**. Not surprisingly, both differences are approximately the same as the difference of about 30 kcal/mol between the strengths of C=C and C=Si π bonds.

From the foregoing discussion, it is easy to understand why in allylic radical **2** the UHF optimized C–C and C–Si bond lengths (1.353 Å and 1.849 Å) are very similar to those (1.325 Å and 1.878 Å) in the same radical with the $H_2C{=}CH{-}$ group rotated out of conjugation with the $SiH_2^\bullet$ radical center. Loss of conjugation also has little effect on the degree of pyramidalization of the SiH_2 group. The SiH_2 pyramidalization angle, ϕ (the angle between the H–Si–H bisector and the extension of the C–Si bond) increases by only 2.7°, from $\phi = 48.0°$ in **2** to $\phi = 50.7°$, when the $H_2C{=}CH{-}$ group is rotated out of conjugation.

In contrast, there are, as expected, substantial differences between the C–C and C–Si bond lengths of **2** and those (1.477 Å and 1.700 Å) of the much higher energy radical with the $H_2Si{=}CH{-}$ group twisted out of conjugation with the $CH_2^\bullet$ center. In the latter geometry the existence of a full Si–C π bond also results in complete planarization of the SiH_2 group, while the $CH_2^\bullet$ center is slightly pyramidalized ($\phi = 13.0°$).

Despite the fact that both energetics and the geometry of **2** indicate that **2b** contributes much more to its structure than **2a**, the calculated unpaired electron densities in **2** suggest some delocalization of unpaired spin from the $SiH_2^\bullet$ center into the $H_2C{=}CH{-}$ group. At the CI-SD level the computed unpaired electron densities at the heavy atoms are 0.94 at silicon, –0.04 at the central carbon, and 0.09 at the carbon of the terminal methylene group. This finding, that the unpaired spin in **2** resides mainly on the SiH_2 group but that positive unpaired spin also appears at the doubly-bonded carbon which is β to it, is in qualitative accord with the experimental results for 1-silaallylic[6] and 1-silabenzylic[7] radicals.

In good agreement with the experimental finding that the Si–H hyperfine coupling constant in **2**[6] is essentially the same as that in $CH_3SiH_2^\bullet$,[24] we calculate the CI-SD unpaired spin density of 0.94 at Si in **2** to be almost the same as the 0.97 that we compute in the methylsilyl radical. However, the size of the C–H hyperfine coupling constant reported for the β carbon in **2**[6] is indicative of a spin density at this carbon that is roughly three times larger than the value of 0.09 that we calculate at the CI-SD level of theory.[25]

1,2-Disilaallyl (5). The relative strengths of C=Si and Si=Si π bonds account for the substantial effect of the X = $H_2Si{=}SiH$ group on the C–H BDE of X–CH_3 (**4**), the very much smaller effect of X = $H_2C{=}SiH$ on the Si–H BDE of X–SiH_3 (**6**), and

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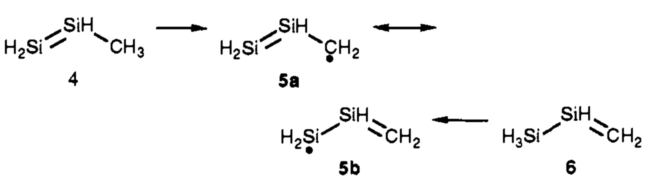

the barriers to rotation in the radical (**5**) that results from homolytic A–H bond cleavage in both these $X-AH_3$ molecules. The differences of 13.3 kcal/mol in the $-\Delta$BDEs between **4** and **6** and 13.2 kcal/mol in the barriers to rotating about the C–Si and Si–Si bonds in **5** are both close to the difference of about 12 kcal/mol between the estimated strengths of C=Si and Si=Si π bonds.

Despite the fact that **5** is expected to resemble **5b** more than **5a**, the geometry of **5** is calculated to be intermediate between those of the radicals formed by rotating the $H_2C=SiH-$ and the $H_2Si=SiH-$ groups out of conjugation. The optimized C–Si and Si–Si bond lengths in **5**, respectively, 1.796 Å and 2.281 Å, may be compared with the corresponding bond lengths of 1.701 Å and 2.329 Å in the nonconjugated radical formed by rotating the $H_2C=SiH-$ group[23] and of 1.854 Å and 2.126 Å in the nonconjugated radical formed by rotating the $H_2Si=SiH-$ group.[26] The Si–Si bond in **5** is shorter only by 0.048 Å than in the nonconjugated radical that results from rotation of the $H_2C=SiH-$ group, but the C–Si bond in **5** is 0.095 Å longer than in the nonconjugated radical formed by rotation of the $H_2Si=SiH-$ group.

The unexpectedly long C–Si bond in **5** is almost certainly a consequence of the pyramidalization at both these atoms in **5**. The pyramidalization angles are $\phi = 8.0°$ at C and $\phi = 32.0°$ at the central Si. Pyramidalization at the central Si is in the opposite direction from that at C and also from that at the terminal $SiH_2^{\bullet}$ center, for which $\phi = 45.0°$. Presumably, anti-pyramidalization[27] occurs at the central Si, in order to maintain as much bonding as possible with the highly pyramidalized, terminal $SiH_2^{\bullet}$ center in **5**, for, when the latter group is rotated out of conjugation, the central Si becomes planar.

Maximum bonding with the central Si in **5** is presumably the origin of the pyramidalization found at the terminal CH_2 group. On twisting the terminal SiH_2 group out of conjugation, planarization of the CH_2 group accompanies planarization of the central Si. The pyramidalization angle at the terminal $SiH_2^{\bullet}$ center is little affected by twisting it out of conjugation with the C–Si π bond; ϕ is calculated to increase by only 2.1°.

As in the case of **2**, the unpaired spin density in **5** resides largely on the terminal silicon. At the CI-SD level the calculated unpaired electron densities at the heavy atoms in **5** are 0.95 at the terminal Si, −0.06 at the central Si, and 0.13 at C. Somewhat greater interaction between the $SiH_2^{\bullet}$ center and $X = CH_2=SiH-$ in **5**, compared to $X = CH_2=CH-$ in **2**, is indicated by comparison of the calculated spin densities in the two radicals. This finding is consistent with the greater change in bond lengths in **5** than in **2**, on going from a conjugated geometry to one with the $SiH_2^{\bullet}$ center rotated out of conjugation.

Allylic Radicals with Identical Terminal Groups

For unsymmetrical allylic radicals, the results described in the previous section show that the greatest amount of stabilization in $X-AH_2^{\bullet}$ is provided when the π bond formed between A and the atom in X that is adjacent to A is much stronger than the π bond in X. For symmetrical allylic radicals, i.e., allylic radicals with identical terminal groups, the strength of the partial π bond that is made between A and X should be proportional to the strength of the full π bond in the unconjugated X group.[28] Therefore, the expected order of increasing CSEs would be $H_2Si=SiH-SiH_2^{\bullet} < H_2Si=CH-SiH_2^{\bullet} \approx H_2C=SiH-CH_2^{\bullet} < H_2C=CH-CH_2^{\bullet}$. Moreover, based on the Si=Si, Si=C, and C=C π bond strengths,[18-22] the CSEs in the symmetrical allylic radicals would be expected to increase in the ratios of about 1:1.5:1.5:3.

The actual ratios, computed from the data in Table II, are 1:0.1:1.5:2.7. Thus, except for $H_2Si=CH-SiH_2^{\bullet}$, which appears to have an anomalously small CSE, the CSEs increase in the expected order, and their ratios are also about what might be expected from the ratios of the strengths of the Si=Si, Si=C, and C=C π bonds.

2-Sila- and 1,3-Disilaallyl Radicals. The reason why $H_2Si=CH-SiH_2^{\bullet}$ is computed to have a much lower CSE than $H_2C=SiH-CH_2^{\bullet}$, when both contain C–Si π bonds, is revealed by a comparison of the optimized geometries for these two allylic radicals. The terminal SiH_2 groups in the former radical are both highly pyramidalized, with $\phi = 41.0°$. The central carbon is also pyramidalized with $\phi = 15.0°$. The direction of its pyramidalization, anti to the two terminal SiH_2 groups, presumably maximizes bonding to these two highly pyramidalized centers.

In contrast to $H_2Si=CH-SiH_2^{\bullet}$, the equilibrium geometry of $H_2C=SiH-CH_2^{\bullet}$ is calculated to be planar.[42] Since there is only one Si center in the latter radical, and it is bonded to two carbons, any possible stabilization due to silicon pyramidalization in this radical is apparently overcome by the decrease in π bonding that would result. As a consequence of the planar geometry of $H_2C=SiH-CH_2^{\bullet}$, the C–Si bond lengths of 1.778 Å are significantly shorter than the 1.813 Å bond lengths in $H_2Si=CH-SiH_2^{\bullet}$.

The contrast between the highly pyramidalized geometry of $H_2Si=CH-SiH_2^{\bullet}$ and the planar geometry of $H_2C=SiH-CH_2^{\bullet}$ provides an attractive explanation of the finding that $H_2Si=CH-SiH_2^{\bullet}$ is computed to have a much lower CSE than $H_2C=SiH-CH_2^{\bullet}$. This explanation was tested computationally by constraining the SiH_2 groups in $H_2Si=CH-SiH_2^{\bullet}$ to be planar, both in the conjugated structure and in the structure with one SiH_2 group rotated out of conjugation. CI-SD calculations at the UHF geometries optimized with this constraint led to a computed CSE for $H_2Si=CH-SiH_2^{\bullet}$ of 7.4 kcal/mol. This value is quite close to the CSE of 8.2 kcal/mol computed for $H_2C=SiH-CH_2^{\bullet}$.

1,2,3-Trisilaallyl Radical. In the UHF optimized geometry for $H_2Si=SiH-SiH_2^{\bullet}$, the terminal SiH_2 groups are highly pyramidalized, with $\phi = 44.0°$, and the central Si group too is highly pyramidalized, in an anti fashion, with $\phi = 42.0°$. It should be noted that for $H_2Si=SiH_2$, which contains a full Si–Si double bond, anti-pyramidalized geometries are calculated at comparable levels of theory.[21,22,27] Since, even with planar Si centers in $H_2Si=SiH-SiH_2^{\bullet}$, the two terminal SiH_2 groups can form only partial double bonds to the central silicon, the large amount of anti-pyramidalization found for the more weakly π bonded silicon centers in $H_2Si=SiH-SiH_2^{\bullet}$ is not surprising.[29]

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[26] Vibrational analysis at the C_s geometry of the twisted radical finds two imaginary frequencies, one of which corresponds to anti-pyramidalization of the doubly bonded silicons.[27] Therefore, the transition state for rotating about the C–Si bond in **5a** has lower symmetry and slightly lower energy than the C_s geometry that we optimized.

[27] For reviews and discussions of anti-pyramidalization see: Malrieu, J.-P.; Trinquier, G. *J. Am. Chem. Soc.* **1989**, *111*, 5916. Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095.

[28] This follows from simple Hückel theory. Ignoring possible effects of the difference between the electronegativities of the central and terminal atoms in a symmetrical allyl radical, in Hückel theory the CSE is $(2\sqrt{2} - 2)\beta \approx 0.8\beta$, and 2β is the strength of a full π bond between the central and terminal atoms. For a discussion of the effect of electronegativity differences on reducing the CSEs in symmetrical allylic radicals see: Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513.

[29] In order to assess the effect of the substantial spin contamination ($\langle S^2 \rangle = 1.31$) in the UHF wave function for 1,2,3-trisilaallyl on its optimized geometry, we reoptimized the geometry at the ROHF level, so that a pure doublet wave function was obtained. Symmetry-breaking in the ROHF wave function[10] was avoided by imposing C_s symmetry on it. At the ROHF optimized geometry the silicons were slightly less pyramidalized ($\phi = 33.0°$ at the terminal silicons and $\phi = 31.6°$ at the central silicon) than at the UHF optimized geometry, and the ROHF energy was 2.0 kcal/mol lower at the former geometry. However, the CI-SD energies at the two geometries were essentially the same, suggesting that the geometry optimized at the CI-SD level would probably be found to be intermediate between those obtained at the UHF and ROHF levels and to have a CI-SD energy very close to that obtained at both of these two geometries. In 1,2,3-trisilaallyl radical, as in $H_2Si=SiH_2$,[21,22,27] the energy appears to be relatively insensitive to the amount of pyramidalization at silicon, so that the amount of pyramidalization found is highly dependent on the type of wave function used to optimize the geometry.

What is somewhat surprising is that, when the silicon centers in $H_2Si{=}SiH{-}SiH_2^{\bullet}$ are constrained to be planar, the CSE actually decreases, from 5.6 kcal/mol to 5.0 kcal/mol. This contrasts with the finding for $H_2Si{=}CH{-}SiH_2^{\bullet}$ and for numerous other molecules studied by us,[30] where constraining π bonded atoms to planarity increases the CSE, often substantially. In contrast, constraining the silicons in $H_2Si{=}SiH{-}SiH_2^{\bullet}$ to planarity raises the energy of the fully conjugated geometry slightly more than the energy of the geometry with one center twisted out of conjugation.

The reason why $H_2Si{=}SiH{-}SiH_2^{\bullet}$ is exceptional can be traced to the highly pyramidalized geometries at all three silicon centers in the fully conjugated geometry. Despite the increase in π bonding when all three silicons are planarized, planarization of these three centers increases the calculated CI-SD energy by 4.0 kcal/mol. In contrast, in the UHF geometry with one SiH_2 group rotated out of conjugation, only this SiH_2 group is nonplanar.[31] Planarization of this SiH_2 group, which is calculated to require 3.4 kcal/mol, is energetically more costly than planarization of any of the individual Si centers in the fully conjugated geometry, but 0.6 kcal/mol less costly than simultaneously planarizing all three.

Allyl Radical. With the exception of allyl, for each of the other radicals in Table II, $-\Delta BDE$ for forming $X{-}AH_2^{\bullet}$ from $X{-}AH_3$ is the same or slightly larger than the CSE of $X{-}AH_2^{\bullet}$. Experimentally, the CSE of allyl has been measured to be 15.7 ± 1 kcal/mol,[32] which is in excellent agreement with the calculated value of 15.3 kcal/mol in Table II. The experimental value for the CSE of allyl is about 2 kcal/mol greater than the difference between primary C–H BDEs in alkanes[33] and that measured in propene.[4] The existence of a difference of about this size between the CSE of allyl and $-\Delta BDE$ for forming allyl is supported by our calculations, which find that the CSE of allyl radical exceeds by 1.4 kcal/mol the reduction of the C–H BDE in $X{-}CH_3$ on replacing $X = H_3C{-}$ with $X = CH_2{=}CH{-}$.

Either the CSE or the $-\Delta BDE$ can be taken as a measure of the resonance stabilization of the allyl radical, and it can be shown that the values should, in fact, differ.[34] The difference between them is equal to the energy change for eq 1, when $X = CH_2{=}CH{-}$ is constrained to a geometry in which it cannot conjugate with the unpaired electron. Specifically, the difference of 1.4 kcal/mol in Table II between the CSE for $CH_2{=}CH{-}CH_2^{\bullet}$ and the $-\Delta BDE$ for $CH_2{=}CH{-}CH_3$ means that our calculations find an unconjugated vinyl substituent, X, increases the C–H BDE in $X{-}CH_3$ by 1.4 kcal/mol, relative to $X = H_3C{-}$.[35]

The reason for this increase could be due to the operation of one or both of two effects. First, the nominally sp^2 hybridized carbon in a vinyl group is more electron withdrawing than the sp^3 carbon in a methyl group; and this increase in substituent electronegativity would be expected to increase the C–H BDE.[1] Second, the stronger bonds formed by an sp^2 hybridized carbon[37] should hyperconjugate less well with an adjacent radical center than do the bonds formed by an sp^3 hybridized carbon and, thus, provide less stabilization for the radical center.

Evidence for the importance of hyperconjugation is found in the results for $H_2Si{=}CH{-}CH_2^{\bullet}$ in Table II. For $X = H_2Si{=}CH{-}$ in $X{-}CH_3$ comparison of $-\Delta BDE$ with the CSE shows that, when the π bond in the vinylic group is prohibited from conjugating with the radical center, $X = H_2Si{=}CH{-}$ is computed to *decrease* the C–H BDE in $X{-}CH_3$ by 1.5 kcal/mol, relative to $X = CH_3{-}$. This contrasts with the finding for nonconjugated $X = H_2C{=}CH{-}$, which, as discussed above, is calculated to *increase* the C–H BDE in $X{-}CH_3$ by 1.4 kcal/mol, relative to $X = H_3C{-}$.

It is conceivable that the difference in electronegativity between $X = H_2Si{=}CH{-}$ and $X = H_2C{=}CH{-}$ accounts for part of the 2.9 kcal/mol difference between their effects at nonconjugated geometries on the C–H BDE in $X{-}CH_3$. However, it seems more likely that the bulk of this difference is due to the greater hyperconjugative stabilization of $X{-}CH_2^{\bullet}$ that is provided by the C–Si σ bond in $X = H_2Si{=}CH{-}$, relative to the C–C σ bond in $X = H_2C{=}CH{-}$.

Support for hyperconjugation, rather than electronegativity, as the major factor in the 2.9 kcal/mol difference between nonconjugating $X = H_2C{=}CH{-}$ and $X = H_2Si{=}CH{-}$ groups on the C–H BDE in $X{-}CH_3$ comes from calculations of the effect on the C–H BDE in $X{-}CH_3$ of the substituent group $X = H_3Si{-}CH_2{-}$. This saturated group decreases the C–H BDE by 2.8 kcal/mol, relative to $X = CH_3$. Hyperconjugation, rather than electronegativity, is indicated to be the major source of this reduction, since, when the C–Si bond is oriented orthogonal to the singly occupied orbital on carbon in $H_3Si{-}CH_2{-}CH_2^{\bullet}$, the energy of the radical increases by 2.2 kcal/mol.[39]

Hyperconjugation involves the formation of a partial π bond between a radical center and a non-hydrogen atom bonded to it. Due to the much greater strength of C–C, compared to C–Si, π bonds, hyperconjugation is considerably more important in stabilizing $X{-}CH_2^{\bullet}$ when the atom in X that is bonded to the $CH_2^{\bullet}$ center is C, rather than Si. The relative unimportance of hyperconjugative stabilization of $X{-}CH_2^{\bullet}$, when the α atom in the substituent group, X, is Si, explains why replacing $X = H_3Si{-}$ by twisted $X = H_2Si{=}SiH{-}$ has less than half the effect on lowering the C–H BDE in $X{-}CH_3$ as replacing $X = H_3C{-}$ with twisted $X = H_2Si{=}CH{-}$.

The importance of hyperconjugation, when it leads to formation of partial C–C π bonds, is what gives twisted $X = H_2Si{=}CH{-}$ and $X = H_2C{=}CH{-}$ groups their unique effects on C–H BDEs. The ability of twisted $X = H_2Si{=}CH{-}$ to hyperconjugate more strongly than any other twisted X group with the radical center in $X{-}CH_2^{\bullet}$ is responsible for the $-\Delta BDE$ for this group exceeding its CSE by more than that of any other group. Similarly, we attribute the fact that the $-\Delta BDE$ for formation of allyl radical is actually smaller than its CSE to the poorer ability of twisted $X = H_2C{=}CH{-}$, compared to $X = H_3C{-}$, to hyperconjugate with the radical center in $X{-}CH_2^{\bullet}$.

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Supplementary Material Available: Tables of the RHF optimized geometries and energies of the closed shell molecules and the UHF geometries and energies of the radicals that appear in Table I (3 pages). Ordering information is given on any current masthead page.

An ab Initio MO Study on Ethylene and Propylene Insertion into the Ti–CH_3 Bond in $CH_3TiCl_2^+$ as a Model of Homogeneous Olefin Polymerization

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Abstract: As a model of olefin polymerization by a homogeneous Ziegler–Natta catalyst, the mechanism of the insertion reaction of ethylene and propylene into $CH_3TiCl_2^+$ has been studied by the ab initio MO method. The structures of the reactant, the intermediate, the transition state, and the product have been optimized with the RHF/3-21G (Ti:MIDI4) method. The transition state is four-centered and is slightly nonplanar to avoid C–H bond eclipsing. In the product strong C^{β}–C^{γ} and C–H agostic interactions take place to donate electrons to Ti vacant d orbitals. The energetics calculated at the unrestricted second-order Møller–Plesset perturbation level with double spin projection (DPUMP2) shows that the reaction proceeds via an ethylene complex with a binding energy of 45 kcal/mol and through the transition state with an activation energy from the ethylene complex of about 4 kcal/mol. In propylene polymerization, the barrier is higher than in ethylene insertion, and the primary insertion is easier than the secondary insertion, both consistent with experiments. The energy decomposition analysis indicates that these chemo- and regioselectivities are controlled by electrostatic and exchange (steric) interactions. The nonplanarity of the transition state makes one of two stereospecific primary insertion pathways substantially more favorable than the other; this tendency of a nonplanar transition state may have significance in determining stereospecificity in olefin polymerizations.

I. Introduction

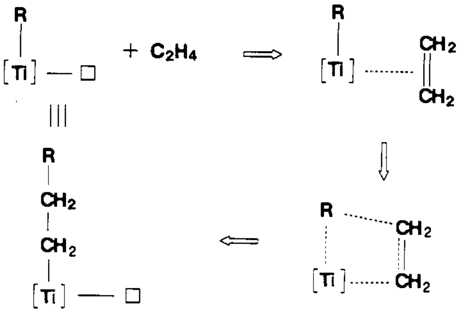
The discovery of Ziegler–Natta polymerization in 1953 is one of the most important achievements in the field of synthetic polymer chemistry during the past half-century. For this olefin polymerization, a heterogeneous as well as homogeneous catalyst has been adopted. Heterogeneous catalysts are usually transition metal halides with cocatalysts such as aluminum alkyl compounds and electron donors; an example of such a combination studied experimentally very extensively is $TiCl_3 + (C_2H_5)_2AlCl$ + aromatic ester.[1-5] Homogeneous catalysts, on the other hand, are metallocenes,[6-9] transition metal dihalide dialkoxides[10] (e.g., $(RO)_2TiCl_2$), and metal tetraalkyls,[11,12] which are soluble in hydrocarbon solvent.

The mechanism proposed by Cossee[13] has been accepted widely as the most plausible, though it is very generic and qualitative. This mechanism is illustrated for Ti in Scheme I. The first step is olefin coordination to a vacant site of Ti. In the second step olefin inserts into the Ti–C bond through a four-membered cyclic transition state. This newly grown alkyl Ti species reinitiates olefin coordination and thus the propagation step.

Based on this mechanism, many MO theoretical studies have been carried out for this catalytic system.[14-24] In the earliest ab initio MO study, Novaro, Clementi, and co-workers[20] calculated the energy profile and analyzed briefly the electronic structure for each step of this mechanism with assumed geometries. Fujimoto and co-workers used a model cationic reaction (eq 1) with

$$\underset{\mathbf{1}}{CH_3TiX_2^+} + CH_2{=}CHR \rightarrow \underset{\mathbf{2}}{CH_3TiX_2(CH_2{=}CHR)^+} \rightarrow \underset{\mathbf{3}}{[\text{transition state}]} \rightarrow \underset{\mathbf{4}}{C_3H_6RTiX_2^+} \quad (1)$$

Scheme I



X = Cl for ethylene insertion (R = H) and optimized the transition structure with the ab initio restricted Hartree–Fock (RHF) method

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