Vinyl Hydrogen Acidities of Two Stereoisomers

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Received: October 8, 2006; In Final Form: November 22, 2006

The gas-phase acidities of the vinyl hydrogens of *cis*- and *trans*-2-butene were measured by the silane kinetic method in a Fourier-transform ion cyclotron resonance spectrometer. The acidities of ethene and the secondary vinyl hydrogen of propene were measured by the same method. The method was calibrated using the known acidities of methane and benzene. The vinyl hydrogens of *trans*-2-butene are more acidic than the vinyl hydrogens of *cis*-2-butene by 4.5 kcal/mol; the acidities of ethene and the secondary vinyl hydrogen of propene are between those of the two butenes. The acidity of *cis*-2-butene is 409 ± 2 kcal/mol, and the acidity of *trans*-2-butene is 405 ± 2 kcal/mol. Density functional theory calculations are in good agreement with the experiments. The results are discussed in terms of steric interactions, polarizabilities, dipole−dipole interactions, and charge−dipole interactions.

Introduction

Structural changes can lead to very large energetic and reactivity differences. For example, substitution of one atom for another to give different functional groups, such as substitution of a sulfur for an oxygen in an alcohol to give a thiol, or a phosphorus for a nitrogen in an amine to give a phosphine. This can have an enormous effect on the energetics and reactivities of the molecules.

Structural isomers exhibit more subtle differences than functional group changes. These effects can be large: methylphenols are significantly more acidic than benzyl alcohol in the gas phase,[1−3] or modest *ortho*-, *meta*-, and *para*-methylphenols have different macroscopic properties, such as boiling points and melting points, as well as different gas-phase acidities.[1−3] Another example of structural changes affecting acidity is the acidity of the isomers 3-methyl-2-butanone and 3-pentanone. Cumming and Kebarle showed that 3-methyl-2-butanone is more acidic than 3-pentanone.[4] Squires and coworkers showed that the primary hydrogen in 3-methyl-2-butanone is significantly more acidic than the tertiary hydrogen.[5]

Stereoisomerism provides an even more subtle structural difference than structural isomerism. One class of stereoisomers is cis and trans isomers of a disubstituted ring, for example, *cis*- and *trans*-1,4-cyclohexanediols.[6] Because the anion of *cis*-1,4-cyclohexanediol can form an internal hydrogen bond, its acidity is greatly increased, compared to the trans isomer, whose anion cannot form an intramolecular hydrogen bond. Even *cis*-1,4-methylcyclohexanol has been shown to be slightly more acidic than *trans*-1,4-methylcyclohexanol.[7] In that case, there is no internal hydrogen bond, but the cis compound has an axial alcohol, whereas, in the trans isomer, the alcohol is equatorial.

Cis versus trans across a double bond is another class of stereoisomers that has been studied. In this case, the electronics are very nearly the same, and only the positions in space have changed. There have been several studies on the effects of cis versus trans across a double bond on energetics and reactivity. Ho and Squires examined the hydrosilation reaction of a hexylsilane with alkyl-substituted cyclohexanones and determined the relative ratios of the stereoisomeric products using collision-induced dissociation.[8] Efforts have also been made to determine the relative acidities of the allyl hydrogens of *cis* and *trans*-2-butene.[9]

A simpler set of cis and trans compounds studied is the enolate anions and radicals of propionaldehyde. Römer and Brauman determined the electron affinities of the radicals corresponding to the (*E*) and (*Z*)-propionaldehyde enolate anions by measuring the two spectra individually.[10] In addition, the (*E*)-propionaldehyde enolate anion had observable dipole bound states, whereas the (*Z*) isomer did not. Williams, Harding, Stanton, and Weisshaar used laser-induced fluorescence to examine a mixture of *cis*- and *trans*-2-propionaldehyde enolate radicals.[11] These interconvert during their experiments, and calculations of the two radicals helped them to assign the spectrum. Alconcel, Deyerl, and Continetti measured the photoelectron spectrum of a mixture of *cis*- and *trans*-propionaldehyde enolate anions.[12] The spectrum was assigned using simulated spectra of the individual species.

An extremely simple pair of isomers, *cis*- and *trans*-1-propenyl anions, has also been studied. Chou and Kass used (*E*) and (*Z*)-1-(trimethylsilyl)-propene to generate the two anions individually in the gas phase.[13] The two species had different product distributions when allowed to react with N_2O, and there was no evidence of interconversion of the two species.

In this paper, we report the relative acidities of the vinyl hydrogens of one of the simplest pair of stereoisomers possible: *cis*- and *trans*-2-butene. Using a kinetic method, we obtained the acidities of the vinyl hydrogens of *cis*- and *trans*-2-butene. In addition, we obtained the acidities of ethene and the secondary vinyl hydrogen of propene. We also calculated the acidities for these four species, and we found good agreement between experiment and theory.

Experimental Section

Instruments. All experiments were conducted in a Fourier-transform ion cyclotron resonance (FT−ICR) mass spectrometer. The instrument consists of an inlet system, a vacuum system,

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10.1021/jp0666075 CCC: $37.00

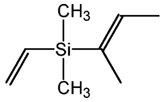

Figure 1. Dimethyl-((*E*)-1-methyl-propenyl)-vinyl-silane.

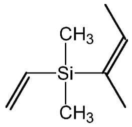

Figure 2. Dimethyl-((*Z*)-1-methyl-propenyl)-vinyl-silane.

and 5.08 cm cubic analyzer cell placed between the poles of an electromagnet operated at 0.60 T. IonSpec software and electronics were used to control the duty cycle and data collection. Unwanted ions were ejected by exciting them at the their natural ICR frequency. Impulse excitation was used to excite all of the ions simultaneously for detection. Rough pressures were measured with a Duniway T-100K vacuum ion gauge. The typical background pressure was 2×10^{-9} Torr. During the experiments, the total pressure was $\sim 3 \times 10^{-6}$ Torr. Details of the Fourier transform instrumentation can be found elsewhere.[14,15]

Reagents. Dimethylphenylvinylsilane (98%), 2-bromopropene (99%), chlorodimethylvinylsilane (97%), chlorodimethylsilane (98%), 1.0 M vinyl magnesium bromide in tetrahydrofuran (THF), and 2-butyne (99%) were purchased from Aldrich. The dimethylphenylvinylsilane was subjected to multiple freeze−pump−thaw cycles before introduction into the spectrometer. Chlorodimethylvinylsilane and chlorodimethylsilane were distilled from CaH_2 prior to use. The other chemicals were used without purification. Chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, 99.9% purity), was purchased from Strem, and Cp*-$(MeCN)_3RuPF_6$ was synthesized in B. M. Trost's group.[16] Nitrous oxide (N_2O) was purchased from Matheson.

Isopropenyl dimethylvinylsilane was synthesized by a Grignard reaction from 2-bromopropene and chlorodimethylvinylsilane. Magnesium (1.75 g) was activated by stirring for 72 h. Fifty milliliters of dry ether and 3.6 mL of 2-bromopropene were added and refluxed for 4 h. The solution then was cooled to room temperature. Chlorodimethylvinylsilane (6.9 mL) freshly distilled from CaH_2 was added dropwise over a period of 20 min. The solution was stirred for 8 h, then diluted with 100 mL of ether and washed with 100 mL of $NH_4Cl(aq)$, 100 mL of $NaHCO_3(aq)$, and 100 mL of brine. It was dried over $MgSO_4$ and filtered. Most of the solvent was removed by distillation, and the silane was purified by preparatory gas chromatography (prep-GC).

Dimethyl-((*E*)-1-methyl-propenyl)-vinyl-silane (Figure 1) was synthesized using a literature procedure similar to that described by Ryan and Speier.[17] Two milliliters of chlorodimethylsilane was distilled from CaH_2 and placed in a pressure tube with 1.5 mL of 2-butyne. Ten milligrams of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was added, and the solution was heated overnight. The solution was cooled to room temperature and added to 25 mL of a 1.0 M vinyl magnesium bromide solution in THF. The solution was refluxed for several hours, diluted with 100 mL of ether, and quenched with 100 mL of $NH_4Cl(aq)$. The organic layer was washed three times with water and once with brine, and then the material was dried over $MgSO_4$. Most of the solvent was removed by distillation, and the compound was purified using prep-GC.

Dimethyl-((*Z*)-1-methyl-propenyl)-vinyl-silane (Figure 2) was synthesized from dimethyl-((*Z*)-1-methyl-propenyl)-chloro-silane, which was synthesized following the procedure of Trost and Ball.[18] Chlorodimethylsilane (1.7 mL) that was distilled from CaH_2, and 1.0 mL of 2-butyne were added to 26 mL of methylene chloride at 0 °C. Cp*$(MeCN)_3RuPF_6$ (31.8 mg) was added, and the solution was warmed to room temperature and stirred for 1 h. The product of this reaction was ((*Z*)-1-methyl-propenyl)-chloro-silane. The methylene chloride was distilled off and 20 mL of 1.0 M vinyl magnesium bromide in THF was added. The resulting mixture was stirred overnight, diluted with ether, and washed with $NH_4Cl(aq)$, three times with water; the material then was dried over $MgSO_4$. The suspension was filtered, and the majority of the solvent was removed by distillation. The compound was further purified using prep-GC.

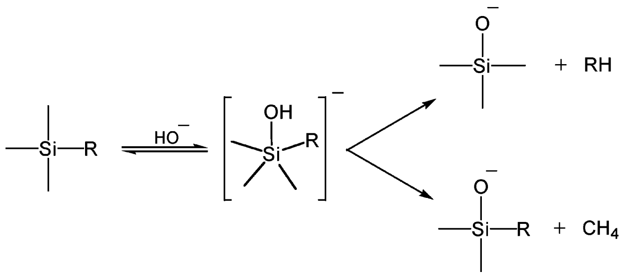

Figure 3. Reaction of hydroxide to form RH and CH_4.

All silane compounds were analyzed using nuclear magnetic resonance (NMR) and were determined to be >99% pure. They were also degassed using multiple freeze−pump−thaw cycles before introduction into the spectrometer.

Kinetic Method. The kinetic method has been discussed extensively by Cooks and co-workers.[19,20] In the conventional kinetic method, a proton-bound dimer, for example, is excited by collisional activation to provide the energy for decomposition to either of two different products. The relative ratio of the final products is related to the relative energies of the products. This kinetic method has been applied to a wide range of species.[21]

Another approach, which involves chemical activation and uses a pentacoordinate silane as the intermediate, has been developed by Depuy and co-workers.[22,23] They determined that, when an alkyltrimethylsilane reacts with a hydroxide anion, two actions are observed: a loss of methane and loss of the alkane. Empirically, they determined that there was a linear free-energy relationship between the acidity difference of methane and the alkane, and the logarithm of the ratio of the products formed. This forms the basis for the silane kinetic method: the pentacoordinated silane can decompose to several products, and the ratios of the products are related to the relative energies of products. Although the mechanism of decomposition for the silane kinetic method is more complex than the mechanism of decomposition in the proton-bound dimer kinetic method, the silane kinetic method can be a more appropriate choice when looking at the acidity of hydrogens that are not the most acidic hydrogens on the molecule. For example, Wenthold and Squires used the silane kinetic method to determine the gas-phase acidities of various hydrogens of some halogenated aromatic compounds.[24]

This kinetic method requires the gas-phase generation of hydroxide anions as the first step. To generate the hydroxide anion, we use dissociative electron capture by N_2O (eq 1):

$$N_2O + e^- \rightarrow O^{-\bullet} + NO^{\bullet} \qquad (1)$$

The anion radical generated removes a hydrogen from any acidic source (eq 2), which is probably another silane in this experiment.

$$O^{-\bullet} + RH \rightarrow HO^- + R^{\bullet} \qquad (2)$$

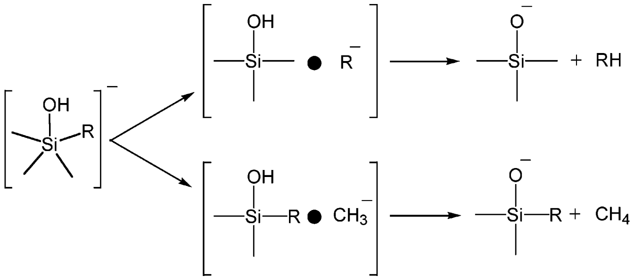

Figure 4. Proposed stepwise mechanism.

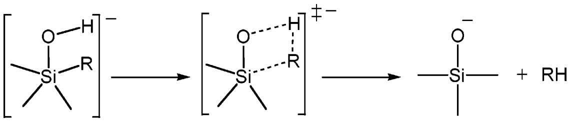

Figure 5. Concerted mechanism. For the sake of simplicity, only one pathway is shown.

The hydroxide anion then reacts with another silane to form a chemically activated pentacoordinate intermediate. The formation of the Si−O bond is extremely exothermic, and the compound will decompose (Figure 3). It can lose CH_4 or RH, or lose HO^- and return to the starting materials. To use this kinetic method, one must prepare a series of alkyltrimethylsilanes. The relative acidities of the different species can be determined using eq 3:

$$\ln\left(\frac{[\text{loss of } R_1H]}{[\text{loss of } R_2H]}\right) = -\beta[\Delta H^0_{\text{acid}}(R_1H) - \Delta H^0_{\text{acid}}(R_2H)] \quad (3)$$

To use this equation, we need a compound with two groups of known acidity. (Usually, methyl and phenyl are the two groups chosen.) The parent compound, phenyltrimethylsilane, is used to set the value of β in eq 3.

The mechanism for this reaction was originally postulated to be stepwise. It was hypothesized that the leaving group formed an ion−dipole intermediate with the resulting silanol (Figure 4). The ion−dipole interaction stabilizes the complex by 10−15 kcal/mol. Later calculations on the reaction of tetramethylsilane with the hydroxide ion indicate that the cleavage reaction is concerted, but that the methyl group has significant negative charge at the transition state, and the Si−C bond is very long.[25,26] Finally, experimental work has shown that the reaction is concerted, with the R−H bond forming while the Si−R bond is breaking (Figure 5).[27]

This kinetic method relies on the existence of a linear free-energy relationship between the logarithm of the siloxide ratios and the acidities of the alkanes. This requires the difference between the R−Si bond energy and the R−H bond energy to be a constant value for different species of R. To validate this kinetic method, DePuy and co-workers examined the ratio of methane loss to ethane loss for the reaction of the hydroxide anion with a series of silanes, $Me_nEt_{4-n}Si$ (where $n = 1, 2, 3$).[22,23] After statistical correction, the ratios they observed were within the experimental error bars. In addition, they examined the loss of H_2 versus the loss of ethane from diethylsilane, and the loss of H_2 versus the loss of methane in trimethylsilane. The relative values of the two ratios matched the ratio of methane loss to ethane loss, within their error limits. As a further validation of the method, their value for the acidity of ethene agrees, within 2 kcal/mol, with the value determined by a later experiment by measuring the forward and backward rate constants.[28] Finally, Brauman and co-workers compared the results from kinetic method experiments using silanes and chemical activation to the results from kinetic method experiments that used alkoxides and collisional activation.[27] For all but a few alkyl species, the two systems agreed well.

TABLE 1: Branching Ratios for the Reaction of $R(CH_2{=}CH)(CH_3)_2Si$ with HO^-

RH	[loss of RH]/[loss of ethene][a]
cis-2-butene[b]	0.91 ± 0.08
propene	1.2 ± 0.1
trans-2-butene[c]	1.7 ± 0.2
benzene	2.7 ± 0.2

[a] The ratio is determined by measuring the relative amounts of the corresponding siloxide anions. [b] Obtained from dimethyl-((*E*)-1-methyl-propenyl)-vinyl-silane. See text for details. [c] Obtained from dimethyl-((*Z*)-1-methyl-propenyl)-vinyl-silane. See text for details.

Equation 3 is an an approximation. In cases where the compounds of interest are structurally dissimilar to the reference compound, the corrected equation is given by eq 4.[21,29,30]

$$\ln\left(\frac{[\text{loss of } R_1H]}{[\text{loss of } R_2H]}\right) = -\beta[\Delta H^0_{\text{acid}}(R_1H) - \Delta H^0_{\text{acid}}(R_2H) - T_{\text{eff}}\Delta\Delta S^0_{\text{acid}}] \quad (4)$$

The additional $T_{\text{eff}}\Delta\Delta S$ term affects the apparent value of the acidity for the measured compound. However, if the compounds of interest are structurally similar, they will have similar entropy terms. The measured acidities will be similarly affected, so the relative acidities between the compounds of interest will be almost unaffected, because the $T_{\text{eff}}\Delta\Delta S$ terms will cancel.[31]

In this work, we used alkyl dimethylvinylsilanes instead of using alkyl trimethylsilanes. There were several reasons for this choice. The value of β obtained by DePuy was 0.22. This would make the loss of methane very small, compared to the loss of 2-butene. A small amount of noise would result in error bars that could be larger than the intrinsic differences between *cis*- and *trans*-2-butene. By including a species with an acidity similar to the acidities of the butenes, we can see smaller differences in acidity by comparing the loss of butene to the loss of ethene. In addition, this immediately gives the order of acidities of the butenes compared to ethene. Finally, the structural differences between ethene and butene are smaller than those between methane and butene, which lowers the uncertainty of the relative acidities.

Sources of Error. There are several experimental sources of error. The ratios were dependent on various instrumental parameters, such as the trapping potentials and pressures. This caused variations in the ratios up to 10%. When using constant instrumental parameters, the ratios varied up to 5%, because of random fluctuations. Averaging additional spectra helped to reduce this error. When similar instrumental parameters were used on different days, the ratios varied by as much as 10%. The ratios in Table 1 are an average of several days worth of experiments. In addition, the uncertainties in the acidities of the anchor points, methane and benzene, will contribute slightly to the uncertainties in the acidity measurements. Methane has an uncertainty of ±0.7 kcal/mol, and benzene has an uncertainty of ±0.5 kcal/mol.

There are also structural differences between the compounds which contribute some uncertainty to the final acidity. However, the structural differences between the two butenes should be very small, so the relative acidities for the cis and trans species will be almost unaffected. The structural differences between

TABLE 2: Acidities Derived from the Branching Ratios

	Acidity (kcal/mol)			
	Experimental		Calculated	
compound	absolute, (ΔH^0_{acid})[a]	relative to ethene, ($\Delta\Delta H^0_{acid}$)[a,b]	absolute, (ΔH^0_{acid})[a]	relative to ethene, ($\Delta\Delta H^0_{acid}$)[a]
trans-2-butene	405 ± 2	−3.5 ± 0.8	403.2	−3.7
propene[c]	407 ± 2	−1.0 ± 0.4	404.0	−2.9
ethane	408 ± 2	0	406.9	0
cis-2-butene	409 ± 2	0.5 ± 0.3	408.7	1.8

[a] The acidity of the vinyl hydrogen. [b] The uncertainty increases as the acidity relative to ethene increases. See text for details. [c] The secondary vinyl hydrogen.

the butenes and the other compounds (ethene and propene) are larger than the structural differences between the two butenes. However, we feel that the relative differences should still be small.

The absolute experimental error can be determined using error propagation calculations. The 10% difference between ratios on different days produces an ~0.6 kcal/mol difference in the acidities, as does the 10% difference between ratios from different instrumental parameters. Because several days worth of experiments are averaged, this contributes another ±0.3 kcal/mol. The uncertainty in the anchors' acidities also contributes approximately ±0.5 kcal/mol. However, the largest source of error is the uncertainty in β. We assigned β a value of 0.15, and, based on the ratios obtained from dimethylphenylvinylsilane, and we are confident that the true value of β lies somewhere between 0.13 and 0.17. This contributes ±1.5 kcal/mol to the uncertainty. The uncertainty in the ratios from different instrumental parameters contributes an additional 0.6 kcal/mol. Assuming that these errors are all normal distributions and independent, we estimate the absolute experimental error to be ~1.8 kcal/mol.

The relative errors are significantly smaller than the absolute errors, and are all <1 kcal/mol. The major source of error in this case is the 10% difference in ratios, which contributes 0.6 kcal/mol. Shifting of the anchor values would not have a major effect on the relative acidities. It could, in fact, be viewed as affecting the uncertainty in β. However, this effect would be much smaller than the uncertainty in β that has already been discussed. Finally, the uncertainty in β makes only a small contribution to the uncertainty in the acidities relative to ethene. Most affected by the uncertainty in β is *trans*-2-butene, because it has the largest loss of the [loss of RH]/[loss of ethene] ratio. Finally, we believe that the compounds of interest, structurally, are sufficiently similar to each other so that the magnitude of the $T\Delta\Delta S$ does not contribute significantly to the uncertainty.

Results

In Table 1, we report the results for the cleavage reactions for the four silanes with the hydroxide ion in our FT−ICR analysis. Note that, when dimethyl-((*E*)-1-methyl-propenyl)-vinyl-silane (Figure 1) reacts with the hydroxide and decomposes, the product is *cis*-2-butene. Analogously, the cleavage product from dimethyl-((*Z*)-1-methyl-propenyl)-vinyl-silane is *trans*-2-butene.

Because each silane had three alkyl groups, we could calculate the acidities using the [loss of RH]/[loss of CH_4] ratio or the [loss of RH]/[loss of ethene] ratio. During the experiments, the [loss of CH_4] was the smallest peak, and had the most uncertainty associated with it. Consequently, there is a larger uncertainty in the [loss of RH]/[loss of CH_4] ratios, compared to the [loss of RH]/[loss of ethene] ratios. Thus, we choose to use the [loss of RH]/[loss of ethene] ratios to determine the acidities.

To obtain the acidities from the ratios listed in Table 1, the value of β must be calculated in eq 3 for a compound with R_1H and R_2H of known acidities. Ideally, the R_1H and R_2H will have a large difference in acidities, and they will have acidities that are known accurately. In addition, both the loss of R_1H and the loss of R_2H should have a large signal-to-noise ratio. These criteria will give the most reliable value for β. From dimethylvinylphenylsilane, for which R_1H and R_2H are methane and benzene, we obtain a value of $\beta = 0.15$.

Physically, β is related to the amount of excess energy in the system, the critical energies for the cleavage reactions, and the sum of states at the transition states. Because most of the excess energy in the chemically activated intermediate comes from the Si−O bond that is formed, β is expected to be relatively independent of the instrument used; however, it should be somewhat dependent on the compound series used, because each set has a different density of states.[32] DePuy et al. obtained a value of $\beta = 0.22$ using alkyl trimethylsilanes, which we can reproduce.[27] Our choice of alkyl vinyldimethylsilanes gives $\beta = 0.15$ and results in acidities for ethene and propene that are consistent with the acidities reported by DePuy et al.[23] At low pressures, the value of β varied slightly with the pressure. This is probably because the hydroxide ion that is formed is hot and cools more quickly with higher pressure. Therefore, we chose a pressure region where the value of β was constant.

Using $\beta = 0.15$ gives the values listed in Table 2. The acidity ordering of the compounds, from most acidic to least acidic vinyl hydrogens, is as follows:

trans-2-butene > propene > ethene > *cis*-2-butene

Calculations

All calculations were performed using Gaussian 98.[33] Optimized geometries, energies, and zero-point energies were calculated at the B3LYP/6-311++G** level of theory. Vibrational calculations were performed for each geometry to ensure that they were true minima, and to obtain zero-point energies and thermal corrections. The vibrational frequencies were used unscaled. The results of the calculations are given in Table 2.

The calculations fall within the experimental ranges for all of the species except for propene. The largest absolute error was 3 kcal/mol, and the largest relative error was 2 kcal/mol; both were observed for propene. Smaller basis sets and different levels of theory gave similar relative numbers, but worse absolute numbers. In addition, calculations correctly predict that the ordering of the compounds by acidity, from most acidic to least acidic vinyl hydrogens, is as follows:

trans-2-butene > propene > ethene > *cis*-2-butene

Discussion

Polarizabilities, dipole−dipole interactions, and charge−dipole interactions are the main factors that determine the acidities of these molecules. It is known that polarizability can have a major role in determining the acidities in the gas phase. For example, the acidity order of alcohols in the gas phase is reversed, compared to the order in solution, because of polarizability effects.[34] Charge−polarizability interactions always stabilize anions. The polarizabilities of *cis*- and *trans*-2-butene, propene, and ethene can be estimated from group additivity.[35] From these estimates, propene should be more acidic than ethene, because the anion of propene is more stabilized than the anion of ethene. Similarly, the vinyl hydrogens of butenes should be more acidic than those of propene.

The distance between the charge and the polarizable groups is important in regard to determining the magnitude of the charge−dipole interaction. Because the charge is not a point charge on the carbon, but is, instead, a diffuse charge located off the carbon, the distance between the charge and the methyl group in the two vinyl butene anions is different. The distance between the charge and the methyl group is larger for the vinyl anion of *cis*-2-butene than for the vinyl anion of *trans*-2-butene. Therefore, we expect that the vinyl hydrogen of *trans*-2-butene is more acidic than the vinyl hydrogen of *cis*-2-butene. The overall order predicted by polarizabilities is

trans-2-butene > *cis*-2-butene > propene > ethene

This accounts for the order of *trans*-2-butene, propene, and ethene, but it significantly overestimates the acidity of the vinyl hydrogen of *cis*-2-butene. Therefore, there must be other factors that affect the acidity of these species.

To examine the acidity difference between *cis*-2-butene and *trans*-2-butene, we must examine both the anion and neutral species of the two butenes. The acidity is a reflection of the relative stability of the anion and the neutral species. The difference between two acidities can be analyzed in terms of the relative stabilities of the two neutrals and the relative stabilities of the two anions.

The *trans*-2-butene neutral species is more stable than the *cis*-2-butene neutral species by ~1.0 kcal/mol.[36−42] Calculations on these two species agree fairly well with the experimental value, and give a difference of 1.5 kcal/mol. The bond angles and distances of the two species are similar, except for the dihedral angle of the carbon skeleton. The C−C−C bond angle in the cis isomer is ~3° larger than the angle in the trans isomer. This is consistent with the well-established notion that the energy difference between the two species is a result of the steric strain. This strain energy constitutes most of the energy difference between the two neutral species.

The calculations for the vinyl anions of *cis*-2-butene and *trans*-2-butene show that the trans isomer is more stable, by 6.5 kcal/mol. The bond angles and distances are similar for the two species, although they are different from the neutral species. The major difference is observed in the C−C−C bond angles. The angles of the cis isomer are ~3°−5° larger than those of the trans isomer. The slightly larger difference in angles between the anions, compared to the neutral species, indicates an increase in the strain energy difference between the two sets.

Although the strain energy can account for some of the 6.5 kcal/mol energy difference between the cis and trans anions, it cannot account for all of it. We believe that the remainder lies in electrostatic factors. The difference can be analyzed in terms of local dipoles and dipole−dipole repulsions (Figure 6). Unlike charge−polarizability interactions, charge−dipole and dipole−dipole interactions can be either stabilizing or destabilizing. It is known that methyl groups are electron-donating to unsaturated carbons, and, therefore, the local dipole will point toward the C=C bond, as shown in Figure 6.[43] For both anions, the interaction between the negative charge and the negative end of the local dipole is approximately the same. Therefore, it can be ignored when comparing the stabilities of the two anions. In the vinyl anion of *trans*-2-butene, the negative charge is syn to the positively charged methyl group. This is a very stabilizing interaction. In contrast, the anion of *cis*-2-butene has the negative charge anti to the positively charged methyl group. Because the energy of a charge−dipole interaction energy falls off as $1/r^2$, the increased distance in the anion of *cis*-2-butene, compared to the anion of *trans*-2-butene, makes the interaction significantly less important. Thus, the anion of *trans*-2-butene is more stabilized than the anion of *cis*-2-butene.

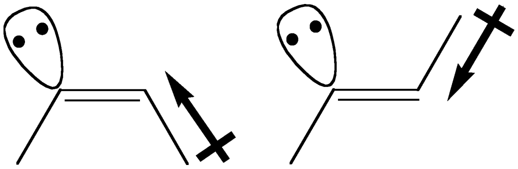

Figure 6. Anions of *cis*- and *trans*-2-butene, and their local dipoles.

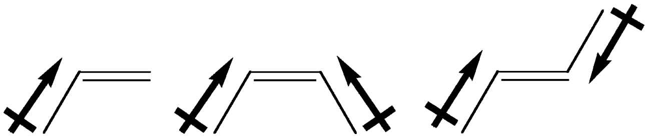

Figure 7. Local dipoles for neutral propene and *cis*- and *trans*-2-butene.

These local dipoles are also present in the neutral isomers. Propene has a dipole moment of 0.37 D.[44] If we assume that this is all in the local dipole of the methyl group, and that the local dipole of *cis*- and *trans*-2-butene are the same magnitude as the local dipole of propene (Figure 7), we can calculate the dipole−dipole interaction energy. This calculation reveals dipole−dipole interactions account for only ~5% of the energy difference in the neutral species. In contrast, a charge−dipole interaction calculation on the anions shows that this interaction accounts for ~2 kcal/mol of the difference between the two species.

This analysis allows us to compare the vinyl hydrogen acidities of *cis*- and *trans*-2-butene by comparing the stabilities of the neutral species and their anions. In both cases, the trans isomer is more stable, but the difference in stability is much larger for the anions than for the neutral species. Therefore, the dipole−dipole interactions and charge−dipole interactions indicate that *trans*-2-butene is more acidic than *cis*-2-butene, which is consistent with the experimental results.

The experimental results show that the vinyl hydrogen of *cis*-2-butene is less acidic than propene and ethene. A charge-polarizability analysis predicts that *cis*-2-butene should be more acidic. However, the charge−dipole interaction in the anion of *cis*-2-butene shows that the anion is destabilized, which reduces the acidity of the *cis*-2-butene. To be consistent with the experiments, the dipole−dipole interactions and charge−dipole interactions must be more important than the polarizability effects in regard to determining the acidity of *cis*-2-butene.

Summary

We have explored the subtle effects of structure on the energetics by examining the acidities of the vinyl hydrogens of *cis*-2-butene, *trans*-2-butene, ethene, and the secondary vinyl hydrogen of propene. The acidities were measured in a Fourier-transform ion cyclotron resonance spectrometer, using the silane kinetic method. The acidity order, from most acidic to least

acidic, was determined to be

trans-2-butene > propene > ethene > *cis*-2-butene

The results were explained by a combination of steric interactions and polarizabilities, as well as dipole−dipole and charge−dipole interactions. Calculations done at the B3LYP/6-311++G** level were consistent with the relative and absolute experimental values.

Acknowledgment. We are grateful to the National Science Foundation for support of this research. D. W. thanks Atofina for a graduate fellowship.

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