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The gas-phase acidities of long chain alcohols

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Abstract

The gas-phase acidities of the C5–C9 normal alcohols, along with some more highly branched alcohols, have been measured by the equilibrium method in an ICR spectrometer. The acidities obtained for the 1-alkanols are consistently weaker than those obtained by the kinetic method, implying that some effect is altering the structure or dynamics of the transition state in the kinetic method. © 1998 Elsevier Science B.V. All rights reserved

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1. Introduction

The development of gas-phase ion-molecule chemistry was greatly influenced by the discovery by Brauman and Blair [1] of the reversal of the order of acidity of the simple aliphatic alcohols upon going from the gas-phase to solution. This revealed that there were important differences between solution and gas-phase reactivity, and provided the impetus for much more extensive measurements of acid/base chemistry in the gas phase. The acidities of more than 85 alcohols [2] have been quantitatively measured since that time, many by Prof. Taft and coworkers [3]. Two principal methods have been used by various groups: direct equilibration [4,5], and the kinetic method of Cooks and coworkers [6–11]. Although equilibration provides the correct answer, it requires mass spectrometric instrumentation designed to carry out such experiments, such as pulsed chemical ionization mass spectrometers or ion cyclotron resonance spectrometers [12]. The kinetic method, however, can be implemented on a wide variety of commercial instrumentation. As long as certain criteria regarding types of functional groups used are met, it is faster and easier than the equilibrium method in obtaining quantitative thermochemical values [6–8].

In the first study of alcohol acidities using the kinetic method, [9] MIKES spectra of metastable $\mathrm{ROH}\cdots{}^{-}\mathrm{OR}$ ions were obtained at 8 kV accelerating energy. The study covered a variety of branched- and straight-chain aliphatic alcohols. For the straight-chain 1-alkanols, a monotonic strengthening of acidity was observed as the chain lengthened. The incremental strengthening fell off with distance, but reached a near-constant value of ca. 0.5 kcal/mol for 1-hexanol and longer chains. It was noted that for some

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unspecified subset of these ions, the values obtained at 6 kV accelerating energy were identical within experimental error to those at 8 kV. The 'effective temperature' of the fragmenting complex derived from the calibration line, redetermined from the data as noted below in the Results section, was 198 K.

More recently, Harrison and coworkers [10] used both metastable ion decomposition in the collision quadrupole of a BEQQ instrument, (on a longer time frame than the earlier workers [9]) and low energy CID (50 eV) to determine alcohol acidities via the kinetic method. The 'effective temperatures' were 277 and 571 K, respectively. The acidities obtained from the two different energy regimes in their instruments agree to within 0.3 kcal/mol of each for branched alcohols, and to within the same value for the 13 branched alcohols in common with the earlier study [9].

However, Harrison and coworkers noted that as the effective temperature of the complex rose, the apparent acidity measured for the 1-alkanols longer than butanol became weaker, relative to the branched alkanols. As an extreme, this effect made the apparent acidity of 1-nonanol measured by the low energy CID method [10] 3.0 kcal/mol weaker than when measured by the metastable MIKES method [9].

To determine the true acidity of the long chain 1-alkanols, and to explore the reason for this energy-dependence of the kinetic method, we have measured the acidities of the 1-alkanols, pentanol through nonanol, by the equilibrium method. It is found that neither of the previous studies is correct: the trend in acidity with size is non-monotonic. In addition, the acidities of three branched alcohols, 2-methyl-3-pentanol, 2-methyl-2-hexanol and 3,3-dimethyl-1-butanol, were also determined. These were chosen as alcohols that were highly branched both proximal and distal to the functional group, and that had also been measured via the kinetic method.

2. Experimental

The alcohols were obtained commercially, and used as received with the exception of 1-pentanol and 1-hexanol, which needed to be distilled prior to use. The ICR mass spectra obtained for the alcohols verified their purity. The nitriles used as standard acids were distilled.

The ion cyclotron resonance spectrometer has been previously described [13–16], and the usual techniques for determining relative gas-phase acidities were followed [4]. Methyl nitrite prepared in situ [17] was used as a source of methoxide via dissociative attachment with near-thermal electrons. The methoxide then deprotonated the neutral alcohols and standard

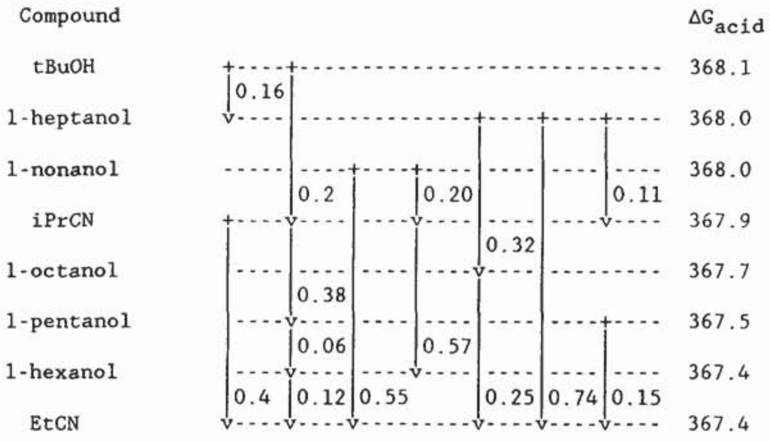

Fig. 1. Ladder of equilibrium measurements for long chain alcohol acidities (kcal/mol).

acids. Samples of the alcohols were admitted into the spectrometer at an instrument temperature of 30°C at the cell. Some of the measurements were repeated at 75°C to examine temperature effects. The ionization gauge neutral gas pressures were converted to true pressures using a calibration equation [18].

3. Results

Fig. 1 shows the measurements made, and Table 1 lists the free energies of acidity obtained for the alcohols from those measurements. The free energies were obtained from the measurements using a program designed to find the best fit to such ladders via least squares and multiplex methods [19]. They are anchored to the standard acidities reported in the literatures [2]. The alcohols were measured not only against the other alcohols, but against a series of nitriles. This was because a large alcohol and alkoxide have been known to cluster with stabilization via radiative emission in the ICR spectrometer [20]. Loss of alkoxide via such a mechanism might perturb the apparent equilibrium being measured. No such cluster ions were observed in the present study under the reaction conditions employed. Lacking direct measurement of ΔH and ΔS, we use statistical mechanics [4,5] to estimate the entropy of acidity, ΔS_{acid}, as that expected for a normal alcohol, +22.0 cal/mol K. This must be regarded as an approximation, because the question of the coiling of the tail in the alkoxide, and necessary restriction on motion, is central to the problem here.

It is evident that for the 1-alkanols there is a non-linear trend in the acidities with increasing chain length. 1-Pentanol is a stronger acid than expected, based on the falloff in acidity increments from methanol to 1-butanol. There is, then, a very small strengthening of acidity on proceding to 1-hexanol. A complete reversal of acidity occurs when proceeding to 1-heptanol, and only small changes from 1-octanol to 1-nonanol.

The measurements at 75°C show no change in the relative acidities of 1-pentanol through 1-octanol of more than 0.1 kcal/mol, compared with the 30°C values. All these values were 0.9 to 1.1 kcal/mol more acidic relative to the standard nitrile acids than at 30°C, however. If this change relative to the nitriles reflects a change in the entropy of acidity for these alcohols, it predicts, that ΔS_{acid} must be ca. 20–24 eu, comparable to that estimated via statistical mechanics [4,5] for a simple alcohol of 22.0 eu.

Owing to the adjustment of the gas-phase acidity scale in 1987 [21,22], the calibration equation used by Gaümann and coworkers [9] must be rederived based on the most recent equilibrium

Table 1
Comparisons of ΔG_{acid} values obtained by ICR spectrometry and the kinetic method[a]

Alcohol	ICR[b]	[9][c]	[10][d]	[10][e]
1-Pentanol	367.5	367.3	368.1	368.1
1-Hexanol	367.4	366.5	367.2	367.7
1-Heptanol	368.0	365.9	366.8	367.4
1-Octanol	367.7	365.2	366.4	367.2
1-Nonanol	368.0	364.6	365.9	367.0
2-Methyl-3-pentanol	364.8	364.9	364.8	365.0
3,3-Dimethyl-1-butanol	365.0	365.4	366.1	366.5
2-Methyl-2-hexanol	365.1	365.5	365.4	365.9

[a] All units are in kcal/mol.
[b] This work, relative values ± 0.2 kcal/mol.
[c] ± 0.3 kcal/mol, MIKES metastable dissociation.
[d] ± 0.2 kcal/mol, metastable dissociation in a quadrupole MS.
[e] ± 0.2 kcal/mol, CID, 50 eV.

acidity values. Using their $\ln(R'O^-/RO^-)$ values, we obtain:

$$\Delta G_{acid}(ROH) = -0.393\ln(RO^-/R'O^-) + 369.1,$$
$$T_{eff} = 198\ K \qquad (1)$$

compared with the original equation of $\Delta G_{acid}(ROH) = -0.321\ln(RO^-/R'O^-) + 368.1$. The 50 eV CID data of Hass and Harrison [10] yields the new calibration line of:

$$\Delta G_{acid}(ROH) = -1.135\ln(RO^-/R'O^-) + 368.9,$$
$$T_{eff} = 571\ K \qquad (2)$$

compared with the original of $\Delta G_{acid}(ROH) = -1.201\ln(RO^-/RO^-) + 369.0$. Likewise, the metastable decomposition calibration line [10] becomes:

$$\Delta G_{acid}(ROH) = -0.549\ln(RO^-/R'O^-) + 369.1,$$
$$T_{eff} = 278\ K \qquad (3)$$

compared with the original of $\Delta G_{acid}(ROH) = -0.513\ln(RO^-/R'O^-) + 369.1$. The re-derived acidities for the alcohols used here are given in Table 2.

The branched alcohols have equilibrium acidities that correspond more closely with the literature values from the kinetic method, than those of the 1-alkanols. The acidity of 2-methyl-3-pentanol agrees with those obtained by the three different kinetic measurements [9,10] within experimental error. The equilibrium value for 3,3-dimethyl-1-butanol is 0.4 kcal/mol stronger than by the MIKES method [9], and 1.5 kcal/mol stronger than by low energy CID [10]. 2-Methyl-2-hexanol is 0.8 kcal/mol stronger than the low energy CID value [10]. Although the data set is small, it appears that branched alcohols with lengthy tails have acidities that are given as slightly too weak by the kinetic method. This is in contrast to the 1-alkanols, where the kinetic method indicates that

Table 2
Enthalpy and entropy of acidity from the kinetic method[a]

Alcohol	ΔG^{b}_{acid}	ΔG^{c}_{acid}	ΔG^{d}_{acid}	ΔH^{e}_{acid}	$\delta\Delta S^{f}_{acid}$
*i*PrCH(Me)OH	366.4	365.9	366.1	373.1 ± 0.5	-1.1 ± 1.7
*t*BuOH	367.7	367.8	367.5	371.4 ± 0.1	-0.4 ± 0.5
*n*PrOH	369.5	369.7	369.3	376.2 ± 0.3	-0.2 ± 1.2
*i*BuOH	367.9	367.9	367.8	374.5 ± 0.0	-0.2 ± 0.2
2-BuOH	367.5	367.2	367.5	374.0 ± 0.3	-0.1 ± 1.3
Et_2CHOH	366.1	365.7	366.3	372.5 ± 0.6	0.3 ± 2.1
*i*PrCH(Et)OH	364.9	364.8	365.0	371.4 ± 0.1	0.4 ± 0.6
$EtC(Me)_2OH$	366.4	366.3	366.6	372.8 ± 0.1	0.5 ± 0.6
t$BuCH_2OH$	366.1	366.0	366.5	372.5 ± 0.2	1.1 ± 0.6
n$PrC(me)_2OH$	365.5	365.4	365.9	371.8 ± 0.2	1.1 ± 0.7
*n*BuOH	368.3	368.6	368.7	374.7 ± 0.2	1.1 ± 0.7
i$Pr(CH_2)_3OH$	366.5	366.9	367.3	372.6 ± 0.3	2.5 ± 1.1
i$PrCH_2CH_2OH$	366.8	367.3	367.7	373.0 ± 0.4	2.7 ± 1.4
*n*PmOH	367.3	368.1	368.1	373.5 ± 0.9	2.9 ± 3.2
*n*HxOH	366.5	367.2	367.7	372.5 ± 0.5	3.5 ± 1.9
*n*HpOH	365.9	366.8	367.4	371.7 ± 0.8	4.7 ± 3.1
*n*OcOH	365.2	366.4	367.2	370.8 ± 0.9	6.0 ± 3.5
*n*NoOH	364.6	365.9	367.0	370.1 ± 0.9	7.0 ± 3.5

[a] kcal/mol. ΔG_{acid} are recalculated as described in the text.
[b] [9], MIKES metastable decomposition,
[c] [10], metastable decomposition.
[d] [10], CID 50 eV.
[e] From Eq. (5).
[f] From Eq. (5), relative to the 'standard' alcohol entropy of acidity of ca. 22 eu.

they are stronger acids than they actually are. A highly branched compact alcohol gives the same acidities by both methods.

A rationalization of the 1-alkanol acidity trend can be presented, assuming that polarizability or some other through-space interaction of the alkoxide group with the hydrocarbon tail is the principal mode of stabilization of the ion. The fall-off in the incremental acidity on going from C-1 to C-4 is due to the increasing distance of the alkyl structure from the ionic site, even in the conformation of closest approach. At C-5, the distal end of the chain can now bend so as to approach the ionic site more closely. Polarizability as a stabilizing interaction falls off as r^{-4}, and thus it would be expected that there would be at some point an increase in this interaction as the chain lengthens. As the chain become longer, there is a chance of an increasing polarizability interaction and more stabilization. However, only so much of any length chain can get close enough to the ionic site to be effective, due to the short range nature of the polarizability interaction. The alkyl group's own bulk creates an excluded space near the ionic site after a certain point, and thus it is expected that the polarizability effect should reach some maximum value, and not continue increasing indefinitely.

Offsetting this polarizability effect is an increase in enthalpy due to gauche conformations being required for the chain end to approach the ionic site. Based on molecular mechanics [23–26], which has only minimal polarizability interactions built in,[2] the all-gauche, closest-approach conformation of 1-pentoxide is 2.8 kcal/mol higher in enthalpy than the all-anti lowest energy conformation. This is the opposite in trend to the polarizability interaction.

Finally, any polarizability interaction must result in some loss of free rotation of the alkyl chain, exacting an entropy price and destabilizing the anion. The balance of all three ot these interactions, one-stabilizing and two destabilizing of the anion, result in little net acid-strengthening effect after the chain becomes long enough to interact with the ionic functional group.

The non-linear, non-monotonic trend of the acidities of the 1-alkanols is in contrast to several studies that report a regular trend in ion/molecule reactivity for homologation. The 1-alkanamines have gas-phase basicities that become stronger in a monotonic fashion as the chain lengthens [27]. Some of the values for the longest amines are from the early days of the usage of ICR spectrometry to measure such quantities, and have not been published in the primary literature (D.H. Aue, personal communication). Nevertheless, it appears that for the C6 to C10 amines, basicity increases at a constant 0.15 kcal/mol per methylene [27]. The carboxylic acids, from C2 through C6, show a monotonic strengthening of acidity [28], though the increment from butanoic to pentanoic acid is much smaller (0.3 kcal/mol) than the propanoic to butanoic change (0.9 kcal/mol). As shown in Fig. 2, up to C5 there is a general parallel trend for the alcohol and

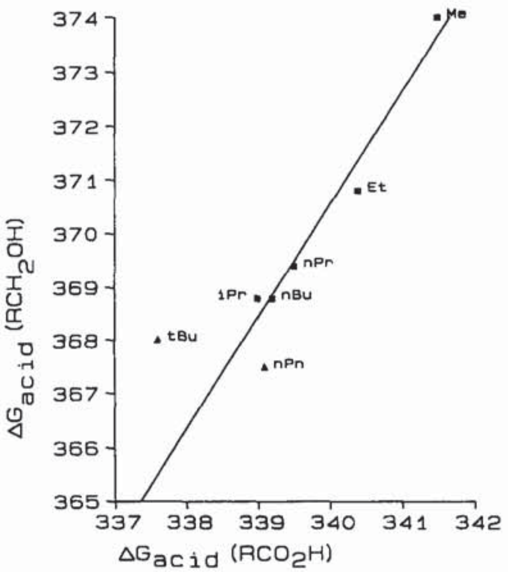

Fig. 2. Alcohol versus carboxylic gas-phase acidities. Values taken from [2] and this work (kcal/mol)

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[2] This version of molecular mechanics calculates an acidity order of MeOH < tBuOH < iPrOH, with tBuOH only 2.4 kcal/mol more acidic than MeOH.

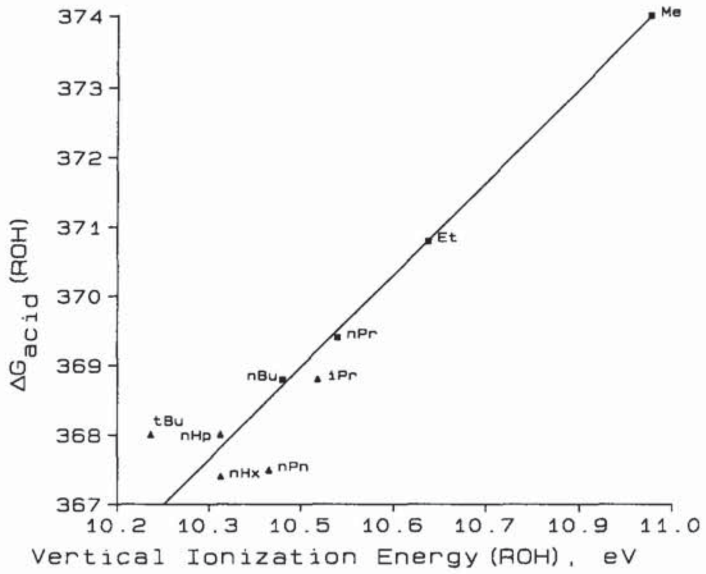

Fig. 3. Vertical ionization energies of alcohols in eV, versus alcohol acidities (kcal/mol). Data from [2,30,31], and this work.

carboxylic acid acidities, with $\Delta G_{acid}(RCH_2OH) = 2.09^* \Delta G_{acid}(RCO_2H) - 340.38530$, $r = 0.985$ for R = Me to *n*Bu. Pivalic acid is stronger in acidity than expected from the trend by ca. 1 kcal/mol. 1-Hexanoic acid is weaker by ca. 0.6 kcal/mol than this trend, or conversely 1-hexanol more strongly acidic by 1 kcal/mol. The slope of the line, $m = 2.09$, indicates that the alcohols are twice as sensitive to structural change as the carboxylic acids. Unfortunately, the acidities available for the carboxylic acids do not extend beyond the hexanoic acid case.

Catalan [29] has rationalized the difference between the constant increase in basicity of the alkylamines with chain length, and the apparent leveling off of the effect in the kinetic alcohol acidities [9], by attributing the former to a general polarization effect, and the latter to specific $O^- \cdots H\text{–}C$ hydrogen bonding, favoring the more acidic terminal primary carbon of the alkyl chain. This is supported by the parallel reactivity of the alkanamine basicities with the vertical ionization energies of the alkanamines [29]. The latter must reflect the neutral, less-coiled geometry, and thus imply that the ammonium ions are not highly cyclized [29]. In contrast, the kinetic acidities of the alcohols parallel their vertical ionization energies up to only C4; thereafter, the kinetic acidities of the alcohols are consistently stronger than expected from the vertical ionization energies. The equilibrium acidities obtained in this work, as shown in Fig. 3, also follow a linear correlation with the vertical IEs up to C4, with a fit of:

$$\Delta G_{acid}(ROH) = 0.432 \times IE(ROH) + 264.8\ \text{kcal/mol},\ r = 0.9994 \quad (4)$$

The C5 and C6 alcohols are more strongly acidic than expected from this fit by 0.4–1.0 kcal/mol, but C7 is back on the line[3] [30,31]. Thus, the present work is in general agreement with Catalan's reasoning, but indicates that the situation is considerably more complex than just cyclization.

Taft and coworkers [3], in correlating -OH gas-phase acidities with a master equation that considered polar, resonance, and polarizability effects, predicted that the long chain alcohols

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[3] The vertical ionization energies for 1-octanol and 1-nonanol were not measured but extrapolated from the smaller compounds' values, assuming a linear correlation.

Table 3
The 'straight chain anomaly'

Aqueous	p*K*as, RCO_2H	25°C[a] RNH_3^+
H-	3.75	9.24
Me-	4.75	10.64
Et-	4.88	10.67
*n*Pr-	4.82	10.57
*n*Bu-	4.84	10.63
*n*Pn-	4.87	10.64
*n*Hx-	4.89	10.64
*n*Hp-	4.90	

[a] [34,35].

should level off to a constant acidity at ca. 1-heptanol. To some extent this is seen in the present study, with only the inversion of acidities for the C6 to C7 case being different than predicted. The polarizability constants σ_α used for the master equation for the 1-pentyl and longer groups appear to have been estimated based on expected mathematical attenuation factors, and not measured, however [3]. Thus any non-monotonic trend would not be predicted by this method.

There is precedent for reactivity not varying in a monotonic fashion with homologation. Brown and co-workers [32] showed that in both the gas phase (alkanamine-trimethylborane complexation constants) and in solution (acidities of *n*-alkanoic acids and basicities of *n*-alkanamines) [33], there is a regular trend in enthalpies of reactivity, but a non-monotonic trend in entropies and therefore free energies. As shown in Table 3, butanoic acid is more strongly acidic than propanoic acid, even though the trend through all the other alkanoic acids is one of weakening acidity with increasing chain length. Called the 'straight-chain anomaly,' this was ascribed to a steric effect of excluded volume as the chain lengthened [32]. The discontinuity occurs at the point where the chain is long enough for the ends to just interact in one of the equilibrating forms, but not in the other. Chains both longer and shorter result in a net cancellation of any effect present between the two forms. Undoubtedly the presence of solvent affects both the effective length of the chain, as well as contributing to the entropy via solvent-ordering. The effect in solution, acid-strengthening at one point in the trend of acid-weakening with increasing chain length, is the opposite to that in the gas phase. The entropic effects in solution are primarily due to changes in solvent structure [36], but these establish a precedent for a non-monotonic effect in reactivity on homologation.

The kinetic method previously was used to examine the gas-phase acidities [37] and basicities [38] of α,ω-diols. Subsequently, it has been shown that the kinetic method seriously underestimates both the basicities and acidities [39,40] as too weak by up to 7 kcal/mol, though the kinetic results are in the correct order. Lund and Bojesen [41] have examined the nature of the dissociating complex in such cases by determining the kinetic energy release (KER) of the cationic proton-bound dimers of primary amines and α,ω-diamines. For homologous and isomeric series of the primary monoamines, the KER parallels the proton affinity (as determined by the equilibrium method) and the number of degrees of freedom in the complex. For the diamines and some dibasic amino acids, the KER is insensitive to the number of degrees of freedom and the basicity. This indicates that the nature of the potential energy surface on which the dissociation occurs is different for the monobasic and dibasic species.

Although the sum of these results do not allow one to derive a structure for the dissociating complex, it is clear that for difunctional compounds, the complex may have a very different structure in the transition state than the free ion does. The results from the kinetic method must thus be regarded as qualitative when dealing with difunctional compounds. The present work indicates that even for weak interactions of an ionic center with 'distant' alkyl groups, appreciable effects on energetics may not be reflected in the kinetic method, although the derived energetics are much closer (1–2 kcal/mol) to the equilibrium values than for difunctional compounds (4–7 kcal/mol) [39,40].

Wesdemiotis and coworkers have shown [42] that in some cases enthalpies and entropies can be extracted from free energies obtained from the kinetic method, via a van't Hoff plot of data obtained at several effective temperatures as in Eq. (5).

$$\Delta G_{\mathrm{acid}}/RT_{\mathrm{eff}} = \Delta H_{\mathrm{acid}}/RT_{\mathrm{eff}} - \Delta S_{\mathrm{acid}}/R \qquad (5)$$

Such an analysis of the kinetic data available for the branched and straight chain alcohol [9,10] is given in Table 2. The inversion of acidities evident in Table 1 is clearly not present here. There is an increasingly positive entropy of acidity as the straight chain alcohols become longer, while the entropies for all but one of the alcohols branched near the acidic site are within the error limits of zero change from the standard alcohol ΔS_{acid} of 22 eu. Because there is no evidence in this that the kinetic method shows the inversion of acidity at 1-heptanol, these values simply reflect the nature of the dissociative transition state, however, and not the actual equilibrium acidity process.

4. Conclusions

Acidities obtained by the kinetic method of dimer dissociation do not agree with values from the equilibrium method for 1-alkanols, although agreement is good for more rigid, branched alcohols. The kinetic results are not even in the correct order. A mixture of polarizability and gauche effects can explain the observed acidity order, where 1-heptanol is a weaker acid than 1-hexanol. Care must be taken when utilizing the kinetic method to determine the energetics of molecules where the distal end can interact with the ionic functionality.

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