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Acidities of Stable Simple Enols and Bond Dissociation Enthalpies of Their H−O Bonds in DMSO

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The pK_{HA} values for eight stable enols and the oxidation potentials of their anions, $E_{ox}(A^-)$, were determined in DMSO, and the bond dissociation enthalpies (BDE) of their O−H bonds were estimated using the equation, $BDE_{HA} = 1.37pK_{HA} + 23.1E_{ox}(A^-) + 73.3$ kcal/mol (1). For $Mes_2C{=}C(OH)R$ enols the pK_{HA}'s increase with the bulk of R from 17.8 for R = H to 19.9 for R = *t*-Bu; the $E_{ox}(A^-)$ values become more negative, and the BDEs decrease from 82.2 kcal/mol for R = H to 78.3 for R = *t*-Bu. The pK_{HA} values roughly parallel the association constants of the enols with the DMSO solvent. These values are discussed in terms of steric and electronic effects.

Introduction

Enols are usually short-lived species. Nevertheless, the pK_{HA} values of many enols have been measured.[1] A number of stable enols have also been prepared, and a variety of their properties have been reported.[2] The pK_{HA} values of these water-insoluble enols are unknown, however. In the present paper, the acidities of eight of these enols **1** (**1a**−**h**) have been determined in DMSO,

$$\underset{\mathbf{1}}{R^2R^1C{=}C(OH)R} \qquad \underset{\mathbf{2}}{R^2R^1CHC({=}O)R}$$

and the oxidation potentials of their conjugate bases ($E_{ox}(A^-)$) have been measured. Combinations of the pK_{HA} and $E_{ox}(A^-)$ values according to eq 1 found in the abstract provide an estimate of the H−O bond dissociation enthalpies (BDEs).[3]

The pK_{HA}, $E_{ox}(A^-)$, and BDE_{HA} values for these enols are summarized in Table 1, together with a few literature pK_{HA} and $E_{ox}(A^-)$ values in MeCN[4] and association constants of these enols with a single DMSO molecule.[5]

Results and Discussion

The first six enols in Table 1 have $R^1 = R^2 = \beta$-mesityl (Mes) and differing α-R groups that cause progressive cathodic shifts of $E_{ox}(A^-)$ in the order (BDEs in kcal/mol estimated from eq 1 are given in parentheses): Mes (82.6) > Me_3Si (82.4) > H (82.2) > Ph (79.9) > *i*-Pr (78.6) > *t*-Bu (78.3). (Henceforth, kcal/mol will be abbreviated as kcal.)

The isolabilities and stabilities of these enols compared with less crowded enols are due to a blend of steric, resonance, conjugation, and hydrogen-bonding effects.[2]

Table 1. pK_{HA} and BDEs in DMSO of the H−O in Enols $R^1R^2C{=}C(OH)R$

no.	R^1	R^2	R	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE[d]	K_{assoc} DMSO
1a	Mes	Mes	H	17.8(32)[c]	−0.671 (−0.73)[c]	82.2	7.9;[e] 5.3[f]
1b	Mes	Mes	Mes	18.8(29)[c]	−0.713 (−0.75)[c]	82.6	1.81[f]
1c	Mes	Mes	Me_3Si	18.9	−0.729	82.4	0.52[f]
1d	Mes	Mes	Ph	18.1(30)[c]	−0.788 (−0.83)[c]	79.9	1.93[f]
1e	Mes	Mes	*i*-Pr	18.6	−0.873	78.6	0.70[g]
1f	Mes	Mes	*t*-Bu	19.9(33)[c]	−0.964 (−1.01)[c]	78.3	0.47[g]
1g	Mes[h]	Ph	Mes	18.4	−0.640	83.7	2.75[f]
1h	Me_5C_6	Me_5C_6	H	18.9	−0.731	82.3	
3	H	H	Me	18.0		83	

[a] Measured by titration against CNAH (4-chloro-2-nitroaniline). [b] Irreversible oxidation potentials measured as previously described using 1 mmol concentrations of anions. [c] Values in MeCN based on the ferrocenium ion/ferrocene couple from ref 4. [d] Calculated using eq 1. [e] Reference 5a. Value based on $K(\delta)$. [f] Reference 5c. [g] Reference 5b. [h] *Z* isomer.

The higher stability of these enols, where the two aryl groups are attached to sp^2 carbon atoms, allows a decrease in the steric interactions of the two aryl groups, relative to those present in the tautomeric keto form **2**.[6] This is borne out by X-ray data. The ArCAr bond angles are 117.3(4)°, 119.6(5)° [two forms] for **1b**, 116.0(6)° for ketone $Mes_2CHCOMes$,[7a] and 119.8(3)° and 120.4(4)° for the pair **1d** and $Mes_2CHCOPh$,[7b] respectively, i.e., identical within the experimental error for the enol and the ketone, but there is more strain in the keto form (sp^3C) than in the enol form (sp^2C). For the less crowded structures **1g** and MesCHPhCOMes the respective values (126.3(7)° and 114.4(4)°)[7a] are consistent with this explanation.

The pK_{HA} values for these enols average 18.7 ± 0.5, which is only 0.7 pK_{HA} unit greater than that for the O−H bond for phenol in DMSO (18.0).[8] The pK_{HA} values for the keto forms are expected to be lower because their ground-state energies are expected to be higher.[9] (Their pK_{HA} values could be estimated if the keto-enol equilibrium constants in DMSO were known.[10])

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The BDEs for the O–H bonds in these six enols average 80.7 ± 1.7. There is a progressive decrease in BDE along the series where R = Mes > Me_3Si > H > Ph > *i*-Pr > *t*-Bu. This order should reflect the operation of both steric and electronic effects. Indeed, it is not the exact order of increasing effective steric size of these groups, since the value for R = H differs little from those for the bulkier R = Me_3Si or R = Mes. Resonance and polar effects, which differ significantly for these R groups, also contribute. For the smaller subgroups, i.e., H > *i*-Pr > *t*-Bu or Mes > Ph, where the most significant effect is steric, the order follows the steric size. The progressive weakening of H–O bonds with increasing steric size of R accompanied by relatively little change in pK_{HA} values (except for R = *t*-Bu), conforms roughly with observations that we have made for the BDEs of three other series of weak acids: (1) progressively smaller BDEs with increasing size of alkyl groups R in $R_2C{=}NOH$ ketoximes,[12] (2) progressively smaller BDEs with increasing size of alkyl groups in 2,6-dialkylphenols,[13] and (3) progressively smaller BDEs with increasing size of alkyl groups in R_2-NOH, dialkylhydroxylamines.[14]

The position of the substituent R differs in **1** and **2** from those in the ketoximes or phenols, however. The R's are substituted on the central carbon of the heteroallylic C=COH or $C{=}CO^-$ systems and may not conjugate effectively with the oxygen of the OH or the O^- moieties. Conjugation exists with the β-substituents, but information on these is available only by comparison of compounds **1b**, **1g**, and **1h** of Table 1. Since the geometries of the aldehyde enols, **1**, R = H, $R^1 = R^2$ = Mes (**1a**) or C_6Me_5 (**1h**) are very similar,[15] the 1.1 pK_{HA} unit higher acidity of **1a** compared with **1h** reflects a higher destabilizing effect of the added *m*-Me group in the enolate ions compared with the enols.

The same applies for the higher pK_{HA} of trimesitylethenol (**1b**) (pK_{HA} 18.8) compared with (*Z*)-1,2-dimesityl-2-phenylethenol (**1g**) (pK_{HA} = 18.4). The individual twist angles ArC=C of the two aryl groups differ in the two compounds (**1a** = 52.5 (51.4), 54.6 (58.2); **1g** = 38.3, 74.4°),[7a] but their sums are only 3.1–5.6° higher for **1g** so that the effect is mainly due to the Me groups.

Our set of pK_{HA} and $E_{ox}(A^-)$ values can be compared with several values in MeCN and with other properties of the enols. Röck and Schmittel[4] have recently determined pK_{HA}'s and $E_{ox}(A^-)$ values in MeCN of several enols, including **1a**, **1b**, **1d**, and **1f**. The pK_{HA}'s in MeCN are 10–13 units higher than those in DMSO. Similar or greater differences were obtained for other acids in the two solvents. The BDE values were estimated from the oxidation potentials using a thermochemical cycle and are based on an AM1-calculated BDE value of 82 kcal/mol for the H–O bond. The pK_{HA} values will be lower by ca. 1 pK_{HA} unit if based on our average BDE value. The $E_{ox}(A^-)$ values are 0.04–0.06 V more negative in MeCN (based on the ferrocenium ion/ferrocene couple) than those in DMSO.

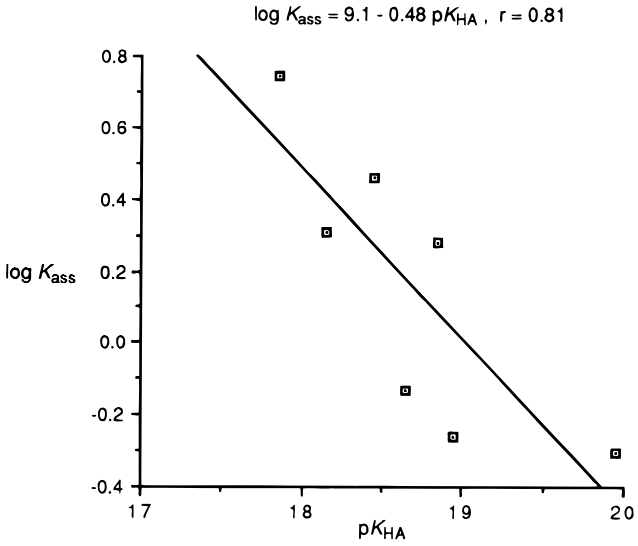

Figure 1. Plot of lo K_{assoc} vs pK_{HA} for $Mes_2C{=}C(OH)R$ in DMSO.

Comparison is also possible with the pK_{HA} values for several simpler enols **3** in water where the order for R(pK_{HA}) is: Me_3Si (11.54) > Me (10.94) > Mes (10.69) > H (10.50) > Ph (10.34).[1,16] This order differs somewhat from the pK_{HA} values for **1a**–**f**, i.e., for R = *t*-Bu > Me_3-Si > Mes > *i*-Pr > Ph > H. Whereas the pK_{HA} differences between R = H and R = Me_3Si are the same in both series, the Mes and Ph differences are smaller for series **3** and may indicate a contribution of the steric effect in the more crowded **1b** and **1d**.

$$H_2C{=}C(OH)R$$

3

Another comparison is with the keto–enol equilibrium constants (K_{enol}) in hexane. These values,[7b,17] except when R = Me_3Si,[18] decrease in parallel with the decrease[19] in the BDE values. The former are governed by both electronic and steric effects and apparently so are the BDE values (see above). The K_{enol} values reflect properties of both the ketones and the enols, however, and further comparison is not warranted. In contrast, comparison with the 1:1 association constants of the enols with one DMSO molecule (K_{assoc}),[5] which were obtained from studies of the $\delta(O^1H)$ chemical shifts (and in one case of the ^3J(HCOH) values)[5a] in CCl_4–DMSO mixtures, is of interest since the association occurs with the enolic O–H bond. These values are given in Table 1. As expected, there is a qualitative correlation between the two sets of parameters: the higher K_{assoc} is for the most acidic enol **1a** and the lowest K_{assoc} is for the least acidic enol **1f**. A linear relationship between K_{assoc} or log K_{assoc} with pK_{HA} was not obtained, however (Figure 1). A plot with the same trend and quality is obtained between the $^{13}C_\alpha$ chemical shifts[19] and the pK_{HA} values.

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(10) If the carbonyl/enol equilibrium constant in DMSO will be 650-fold higher than in hexane, as found for 2-tipyl-1-acenaphthyl enol,[6] then from the data in hexane and ref 11, all the enols will be thermodynamically more stable than the isomeric carbonyl compounds.

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The effect of the α-(trimethylsilyl) group, R_3Si, is calculated to increase the gas-phase acidity of an adjacent C−H group,[20] and experimentally in DMSO it increases the acidity of 9-H fluorene by 1.1 pK_a units (2.2 kcal), while a *t*-Bu group decreases it by 1.8 pK_a units (2.9 kcal). It was assumed that the latter effect is due to steric inhibition of solvation, which is considerably less for the Me_3Si group with the longer C−Si bond. In the enols, the Me_3Si group reduces the acidity by 1.1 kcal (see a similar value for **3** in water),[16] and the *t*-Bu group reduces it by 2.1 kcal. In this case, however, we believe that the steric effects of the *t*-Bu and the Me_3Si groups are similar as judged by (a) the almost identical ground-state structures,[21] (b) the similar rotation barrier of the mesityl groups in the two enols,[22] and (c) the almost identical δ(OH) values (7.30 and 7.32 ppm)[5c] in the ^{1}H NMR spectra. Indeed, in an analysis of these results, as well as calculations, Taft's E_s value of Me_3Si was deduced to be close to that of *t*-Bu.[21] The association constants of the two enols with a single DMSO molecule are almost the same (0.52 for R = Me_3Si and 0.47 for R = *t*-Bu).[5b,c] We tentatively ascribe the lower acidity of both enols compared with that with R = H to the steric effect described above. The lower effect of the Me_3Si group is due to a higher polarizability of the Me_3Si group, which operates in the opposite direction. The effect of the *i*-Pr group is in agreement with its lower electron donation. The different behavior than in the fluorene series is not surprising since the R and the C-H bond are geminal in this case.

The effects of *t*-Bu and Me_3Si also differ in the fluorene and the enol series. In the fluorene series *t*-Bu has practically no effect on the BDE while Me_3Si increases it by 3 kcal. For the enols Me_3Si has a small bond-strengthening effect of 0.2 kcal, but *t*-Bu weakens the H−O bond by 3.9 kcal. This behavior for *t*-Bu is in agreement with our frequent observation that an increase in the ground-state energy due to the presence of bulky groups decreases the BDE but is inconsistent with the lack of effect of Me_3Si.

A comparable interpretation is amenable to the effects of structural changes for the enols **1b**−**f**. The cathodic shift is much smaller here (0.251 V or 5.8 kcal), and the BDE weakening is 5.4 kcal, but the effects appear to be comparable.

Replacing a β-Mes by a β-Ph (**1b** compared with **1g**) causes an anodic shift of 73 mV (1.7 kcal) in $E_{ox}(A^-)$ and an increase in BDE of 1.1 kcal. Replacing the two Mes groups of **1a** by the Me_5C_6 groups of **1h** causes a 60 mV (1.4 kcal) anodic shift in $E_{ox}(A^-)$ and a negligible change in BDE.

The pK_{HA} of acetone in DMSO is 26.5.[8] The $\Delta G°$ for conversion of acetone to its enol **3** (R = Me) is 11 kcal, which indicates that the pK_{HA} of the enol is about 18 (i.e., 8.5 pK_{HA} units lower). The BDE of acetone in DMSO is about 94 kcal, which means that the BDE of the O−H bond in the enol is about 83, i.e., about 2 kcal higher than the average of the BDE of the O−H bonds in the six enols, $Mes_2C{=}C(OH)R$ or <1 kcal than for the two enols where R = H. A similar difference exists between the pK_{HA}'s of $CH_2{=}CHOH$ and $Ph_2C{=}CHOH$ in water (10.40[23a] and 9.40[23b]).

Experimental Section

Enols. The enols were available from previous work or were prepared by previously reported methods.

pK_{HA} Measurements. The enols were titrated with CNAH (4-chloro-2-nitroaniline) (pK_{HA} = 19.8) as the indicator. All titrations gave very small standard deviations (<5%). The choice for indicators was limited to CNAH because the conjugate bases of the enols have moderate absorptions at around 500 nm, and this will interfere with the titration if an indicator's titration wavelength is in the similar region. The conjugate base of CNAH has a rather long wavelength absorption (titrated at 607 nm), but other indicators with pK_{HA} close to 20 have much shorter titration wavelength absorptions.

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