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Preliminary communication

IONIZATION CONSTANTS OF HYDROXY COMPOUNDS OF CARBON, SILICON AND GERMANIUM. THE NOVEL ACIDITY OF THE COMPOUNDS, $Ph_3MM'Ph_2OH$

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Summary

The hydroxy compounds, $Ph_3MM'Ph_2OH$, (where M and M' = C, Si or Ge) are more acidic by 1.5 to 2.7 pK_a units than the compounds, Ph_3MOH, in dimethyl sulfoxide. This enhanced acidity which is not reflected in the hydrogen bonding studies is explained in terms of an $n_O \to LUMO_{MM'}$ interaction in the conjugate base form.

The ionization constants for a series of hydroxy compounds of carbon, silicon and germanium are reported for the first time (cf. Table 1).** Published data on th relative acidity of these types of compounds are based on PMR chemical shifts[2-5], half neutralization potentials[6] and hydrogen bonding studies.[4,7-9]

The acid dissociation constants were determined in dimethyl sulfoxide, DMSO, using a variation of the indicator method reported previously.[10] The order of acidity of the triphenylhydroxy derivatives of carbon, silicon and germanium is in

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[**] Recently, a pK_a value of 13.63 ± 0.07 has been determined for triethylsilanol in aqueous 1 M $NaClO_4$ using a solvent distribution method.[1]

Table 1. pK_a Values of Hydroxy Derivatives of Carbon, Silicon and Germanium in DMSO[a]

Compds.	No. Detns.	Indicator[b]	pK_a[c] (σ)[d]
Ph_3COH	6	I	16.97 (0.24)
Ph_3SiOH	21 8	II I	16.63 (0.07) 16.57 (0.11)
Ph_3GeOH	6	I	17.06 (0.17)
Ph_3SiCPh_2OH	5	II	14.33 (0.13)
Ph_3GeCPh_2OH	6	II	14.25 (0.05)
$Ph_3SiSiPh_2OH$	24 3	II I	13.87 (0.09) 13.99 (0.03)
Ph_3CGePh_2OH	6	I	15.50 (0.25)

[a] Base: tetramethylammonium hydroxide; temp: 25.0 ± 0.1°.
[b] Indicator I: 4-nitrodiphenylamine; pK_a, 14.3 ± 0.3.
Indicator II: 2,4-dintrodiphenylamine; pK_a, 12.4 ± 0.3. Ref. 11.
[c] Standard acid, p-$H_2NC_6H_4CO_2H$: found, pK_a, 12.83 (0.04), 17 detns; lit[11], pK_a, 12.7 ± 0.3. [d] Standard deviation.

accord with the "relative acidity" as determined from hydrogen bonding studies, Si > C $\simeq$ Ge.[8] A comparison of the pK_a values in DMSO and the pK values for hydrogen bond formation with THF in CCl_4 for the triphenylhydroxy derivatives,[*] reveals that the Si compound has a pK_a value of ~ 0.4 units lower than the C and Ge compounds while the pK value is ~ 0.7 units lower. One might expect some difference between the acidity order based on pK_a studies and the order based on hydrogen bonding studies, since in the former case, solvated ions are formed on dissociation, while in the latter case,

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[*] The pK values for hydrogen bond formation were calculated from the data reported in ref. 8: Ph_3COH, + 0.05; Ph_3SiOH, - 0.06; Ph_3GeOH, + 0.08.

the O-H bond is weakened by association with the Lewis base. The close corresponden between the pK_a values and the hydrogen bonding pK values suggests that solvent effe and degree of dissociation have little effect on the order of acidity in this series The above results are best rationalized in terms of inductive and pi bonding effects as proposed by West, *et al*.[8]

Surprisingly, the pentaphenylhydroxy compounds are more acidic than the triphen hydroxy compounds by 1.5 - 2.7 pK_a units, *cf*. Table 1. This enhanced acidity is not reflected in the hydrogen bonding studies. The i.r. hydroxyl spectral shifts on hydrogen bonding with DMSO, $\Delta\nu_{DMSO}$, are about the same for both series[*] and the pK determined for the hydrogen bonding of Ph_3GeCPh_2OH with THF, -0.06, differs little from the values calculated for Ph_3COH and Ph_3GeOH from the data in ref. 8. *The above results emphasize the dangers inherent in relating hydrogen bonding studies to acidity*.

The enhanced acidity of the pentaphenylhydroxy compounds over the triphenylhydroxy compounds is most easily explained in terms of an interaction between an oxygen nonbonding electron pair and the lowest energy unoccupied molecular orbital of the MM' system, $n_O \rightarrow LUMO_{MM'}$,[12,13] *i.e.*, the α-effect, in the pentaphenylhydroxy series. The nature of this $LUMO_{MM'}$ may be σ^*[14] and/or π^*[15]. The better energy matching between the $LUMO_{MM'}$ and the nonbonding pairs on oxygen in the anion form over the conjugate acid form leads to more extensive charge delocalization in the anion and, thus, enhanced acidity. The energy of the $LUMO_{MM'}$ may be further lowered in the phenyl derivatives as a consequence of mixing with the phenyl π^* systems.[16]

In order to substantiate the proposal that $n_O \rightarrow LUMO_{MM'}$ conjugation leads to the enhanced stability of the $Ph_3MM'Ph_2O^-$ ions, we have estimated the energy difference between the n_O levels and the $LUMO_{MM'}$. Based on spectral and thermodynamic data, th

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[*] $\Delta\nu_{DMSO}(cm^{-1})$: Ph_3COH, 251; Ph_3SiOH, 411; Ph_3GeOH, 270; Ph_3SiCPh_2OH, 242; Ph_3GePh_2OH, 254; $Ph_3SiSiPh_2OH$, 401; Ph_3CGePh_2OH, 262. The $\Delta\nu_{DMSO}$ values were determined on a Beckman IR-20 spectrophotometer using Pyrocell S22-350, 1 cm cells; solvent, CCl_4; R_3MOH, 0.008 M; DMSO, 0.10 M; accuracy ± 10 cm^{-1}.

LUMO$_{MM'}$ is calculated to be ~ 2 eV above the n_O levels of the DMSO solvated ion.*

The electronic spectra of the pentaphenylhydroxy compounds show an absorption band, 225-243 nm, which is absent from the spectra of the triphenylhydroxy derivatives This band which undoubtedly arises from a $\sigma \rightarrow$ LUMO$_{MM'}$ transition[14,15] is shifted to lower energy by substituent phenyl groups.[20]

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*The energy of the LUMO$_{MM'}$ was calculated from photoelectron spectroscopy data[16] and electronic spectral data[17] on $PhMe_2SiSiMe_3$. The energy of the n_O levels was estimated from data on alkoxide ions, using affinity energy data,[18] solvation energy data[19] and assuming that the solvation energy of ROH > RO· in DMSO.

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