Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

Acidity of silanethiols*

Silanols are stronger acids than carbinols, both as Bronsted acids and as proton donors in hydrogen bond formation[1]. The enhanced acidity has been explained in terms of dative π-bonding from oxygen to silicon in the silanols and especially in silanolate anions, such bonding not being possible for carbinols. This paper reports the results of similar studies to evaluate the protonic character of the analogous silicon–sulfur and carbon–sulfur compounds, using both infrared spectroscopy and potentiometric titration.

Infrared studies were used to evaluate the proton-donating power of a series of silanethiols and mercaptans, toward *N,N*-dimethylformamide and *N,N*-dimethylacetamide as reference bases. The shift ($\Delta\nu$) between S–H stretching frequency in the free and hydrogen-bonded compounds was taken as a measure of hydrogen bond strength, and thus of proton-donating character. The validity of the Badger–Bauer rule[2], which states that the enthalpy of the hydrogen bond is proportional to the frequency shift, is assumed. This assumption seems reasonable for this system, where both atoms interacting with hydrogen are always the same. That is, only Y in the system $Y{-}S{-}H\cdots B$ is varied. One would not, however, expect to use this correlation to compare relative hydrogen bond strengths of mercaptans and alcohols, for example. This point has been discussed at length in the literature[3-5].

The results of these measurements are given in Table 1. The order of Lewis acidity of the compounds investigated, as determined by their frequency shifts on hydrogen bonding, is:

$$Ph_3SiSH \gg PhSH > Me_3SiSH > Ph_3CSH > Me_3CSH$$

This order is essentially the same as that observed earlier for silanols and carbinols, using ether and mesitylene as reference bases[1]:

$$Ph_3SiOH > PhOH > Me_3SiOH > Ph_3COH > Me_3COH$$

TABLE 1

IR FREQUENCY SHIFTS (cm^{-1}) OF SH COMPOUNDS IN PRESENCE OF BASES

Compound	ν(S–H, free[a])	$\Delta\nu$(in DMA[b])	$\Delta\nu$(in DMF[c])
Ph_3SiSH	2580	105 ± 10	78 ± 18
PhSH	2588	72 ± 6	48 ± 4
Me_3SiSH	2584	60 ± 6	46 ± 6
Ph_3CSH	2577	52 ± 5	42 ± 7
Me_3CSH	2577	33 ± 5	21 ± 3

[a] "Free S–H" determined in CCl_4 solution; ± 2 cm^{-1}. [b] DMA = dimethylacetamide. [c] DMF = dimethylformamide.

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* Research supported by Air Force Office of Scientific Research, (SRC), O.A.R., U.S.A.F., Grant No. AF-AFOSR-62-244.

Relative Brønsted acidities were determined by a titrimetric method, using tetrabutylammonium hydroxide as a titrant in pyridine solution. The half-neutralization potential was taken as a measure of the equilibrium acid strength[6,7]. By this method, SH and OH compounds can be compared on the same scale. The results, including earlier data on triphenylsilanol and phenol[6], are reported in Table 2. The order of acidities determined in this manner is:

$$Ph_3SiSH > PhSH > Ph_3CSH > PhOH > Ph_3SiOH > Me_3SiSH,\ Me_3CSH$$

The orders of Brønsted and hydrogen bonding acid strengths for the sulfur compounds are in remarkably good agreement, considering the differences in the reactions studied. In both the Ph_3SiSH/Ph_3CSH and Me_3SiSH/Me_3CSH isostructural pairs, the silicon compound shows greater acidity than its carbon analog, by both measurement methods. The results are consistent with S–Si dative π-bonding in the free silanethiols, increasing the protonic character of the Si–S–H hydrogen, and so making silanethiols better hydrogen-bonding acids than mercaptans. The same effect would lead to easier dissociation and enhanced Brønsted acidity for silanethiols. However, a major factor leading to high Brønsted acidity for these molecules may be increased dative π-bonding in the silanethiolate anions over that in the parent silanethiols.

TABLE 2

HALF-NEUTRALIZATION POTENTIALS

Compound	$E_{\frac{1}{2}}$ (V)	
	Bu_4NOH/pyridine	NaOH/H_2O/dioxane
PhCOOH		0.10
CH_3COOH		0.09
Ph_3SiSH	−0.21	0.09
PhSH	−0.34	[a]
Ph_3CSH	−0.56	[a]
PhOH	−0.68	
Ph_3SiOH	−0.80	
Me_3SiSH	[a]	
Me_3CSH	[a]	

[a] Too weak an acid to titrate.

The acidity enhancement is at least as large for the Si–S–H compounds as for Si–O–H, comparing each with their carbon analogs. Thus Ph_3SiOH is a slightly weaker acid than phenol[6], whereas Ph_3SiSH is a slightly stronger acid than thiophenol. Simple overlap calculations[8] indicate that delocalization of sulfur lone pairs into π orbitals of silicon may be at least as effective as similar delocalization from oxygen to silicon, consistent with our results.

A few potentiometric measurements were carried out in 50% dioxane/water using sodium hydroxide as a base. The results (Table 2) show that triphenylsilanethiol is about as strong a Brønsted acid, in this system, as acetic acid. The other mercaptans and silanethiols proved too weak to be measured in this solvent system.

Experimental

Compounds. Triphenylsilanethiol was prepared by the method of Etienne[9] in 80% yield. M.p. 102–103°, lit. 103°. Trimethylsilanethiol was prepared by the method of Champetier[10] in 10% yield. B.p. 78–83°, lit.[10,11] 75–76°, 77–78°. Triphenylmethanethiol was prepared by the method of Kharasch and Williams[12]. M.p. 107–108°, lit. 106–107°. Other compounds were obtained commercially and purified as necessary.

Infrared spectroscopic studies. Measurements were made in the S–H fundamental region on a Perkin–Elmer 112 single beam recording spectrophotometer, using a LiF prism. Two spectra were obtained for each acid-reference base pair studied: (*a*) a CCl_4 solution of the acid in the presence of base and (*b*) a solution of reference base alone. The concentration of the base in (*a*) and (*b*), as well as cell dimension, were identical. Difference plots equivalent to log I_b/I_a *vs* frequency were constructed, giving a spectrum of the acid SH region as modified by the presence of base, but eliminating from the spectrum any absorption due to base or solvent.

Potentiometric titrations. Measurements in pyridine were made by the technique previously reported[6,7]. Because of an overall potential drift from one titration to another, a correction term equal to the difference between the plateau voltage after the titration end point and an arbitrary standard voltage (−0.885 V) was added to the measured half-neutralization potentials in order to obtain consistent, reproducible, half-neutralization values[13]. Reproducibility was ±0.01 V or better.

Titrations in 50% v/v dioxane/water were carried out with 0.012 *N* aqueous sodium hydroxide in the usual way, using a glass electrode. Because triphenylsilanethiol undergoes hydrolysis rapidly in these solvents, a special technique was necessary to obtain the half-neutralization potential. A weighed amount of Ph_3SiSH was quickly dissolved in dioxane/water and the calculated quantity of sodium hydroxide for half-neutralization was added. A plot of potential *vs.* time extrapolated to time of mixing provided the half-neutralization value. Reproducibility in several runs was ±0.01 V.

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Received August 11th, 1967

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