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BASICITY OF SILOXANES, ALKOXYSILANES AND ETHERS TOWARD HYDROGEN BONDING *

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Summary

Thermodynamic constants have been determined for hydrogen bonding of phenol to several siloxanes and alkoxysilanes, as well as to $Me_3SiSCMe_3$ and $Me_3SiSSiMe_3$. Alkoxysilanes are slightly weaker bases toward phenol than the isostructural ethers. Unstrained siloxanes have low values of $-\Delta H$ for hydrogen bonding of 3.5—3.9 kcal/mol and are therefore distinctly weaker bases than either alkoxysilanes or ethers. Siloxanes with small SiOSi bond angles show increased basicity. $Me_3SiSCMe_3$ ($-\Delta H$ 1.9 kcal/mol) and $Me_3SiSSiMe_3$ ($-\Delta H$ 0.8 kcal/mol) are markedly less basic than dialkyl sulfides. The results are discussed using a molecular orbital model.

Twenty years ago we published studies of the hydrogen bonding of phenol to some oxygen compounds of carbon and silicon [1,2]. The frequency shift of the phenol O—H infrared stretching absorption was taken as a measure of the relative basicity of the electron donor molecule. On this basis we concluded that the basicity of ethers, alkoxysilanes and siloxanes declines in the order $R_3COCR_3 > R_3COSiR_3 >> R_3SiOSiR_3$. This work has been replicated in other laboratories [3—8] often using other proton donors and/or base molecules, but always with the same general results. There is also qualitative evidence that siloxanes are weaker bases than ethers; for example work by Sternbach and MacDiarmid shows that H_3SiOCH_3 and $H_3SiOSiH_3$ are weaker bases than H_3COCH_3 toward diborane [9].

However, all of these studies are at best semiquantitative. The hydrogen-bonding results depend on the Badger—Bauer relationship [10] between frequency shift and hydrogen bond strength, and although this holds rather well for similar classes of compounds [11] it is less valid for different classes [12, 13]. In this paper we present thermodynamic studies of the hydrogen bonding

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* Dedicated to Professor E.G. Rochow on the occasion of his 70th birthday.

of phenol to six siloxanes, two alkoxysilanes, a mercaptosilane and a disilthiane, and compare the measured $-\Delta H$ values for association with those determined earlier for ethers and dialkyl sulfides [14]. The results allow a quantitative comparison of basicities and, together with other information which has become available since our earlier studies, will be used to illumine a discussion of the nature of silicon—oxygen and silicon—sulfur bonding.

Experimental

Procedure. All spectra were determined in tetrachloromethane solution on a Cary Model 14M spectrometer, using a path length of 10 cm and a slit width of 0.27 mm. Two or three solutions were studied for each base, at seven different temperatures spaced between −5° and +45° C. Base and phenol concentrations were chosen so that the free phenol concentration after complex formation was 0.01—0.02 *M*. Base concentrations were typically between 0.2—0.6 *M*. The free phenol concentration was determined as explained in earlier papers [14,15] from the intensity of the first overtone of the free O—H infrared absorption band and used to determine the equilibrium constant K = [phenol-base]/[free phenol] · [free base]. A least squares fit was computed to give the best straight line of ln K vs. $1/T$, from which the enthalpy values were determined.

Materials. Mallinckrodt tetrachloromethane from freshly opened bottles was distilled from P_2O_5 into carefully dried receivers immediately before the solutions were prepared. The phenol was Merck reagent grade, twice fractionally crystallized and then distilled under N_2 in vacuo, then stored over P_2O_5. t-Butylthiotrimethylsilane was prepared from trimethylchlorosilane and the lithium salt of t-butylmercaptan; the purified product showed physical constants in agreement with those previously reported [16]. 2,2,5,5-Tetramethyl-1-oxacyclopentane was a purified sample kindly provided by Dr. William Piccoli. Synthesis and purification of the other compounds used in this study was described in our earlier publications [2,14].

Results and discussion

Thermodynamic constants for hydrogen bond formation between phenol and the various electron donor molecules are summarized in Table 1. As we have found earlier [14], hydrogen bonding is remarkably insensitive to steric effects, as shown by the fact that the highly hindered molecules di-t-butyl ether * is the strongest base toward phenol of any of the molecules listed.

In general the results confirm those of earlier, more qualitative studies. For isostructural compounds basicities, measured by $-\Delta H$ for hydrogen bonding, decline in the order $R_3COCR_3 > R_3COSiR_3 > R_3CSCR_3 > R_3SiOSiR_3 >> R_3SiSSiR_3$. However structural effects also influence the basicities markedly. Basicity decreases with decreasing alkyl chain branching among the ethers; the same effect is noted for the alkoxysilanes, i.e., $Me_3SiOCMe_3$ is a stronger base than Me_3SiOEt. The alkoxysilanes and ethers are so similar in base strength that the basicities for these classes overlap, decreasing in the order $Me_3COCMe_3 > Me_3$-

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* Di-t-butyl ether is nonbasic toward moderately hindered Lewis acids such as N_2O_4 [17].

TABLE 1

THERMODYNAMIC CONSTANTS FOR HYDROGEN BONDING OF PHENOL TO SILICON AND CARBON COMPOUNDS

Compound	—ΔH (kcal/mol)	$P_{\Delta H}$[a] (kcal/mol)	—ΔG, 28° (kcal/mol)	—ΔS (cal/° mol)	Ref.
Me_3COCMe_3	7.31	0.11	0.745	22.0	14
$Me_3SiOCMe_3$	6.89	0.24	0.148	22.6	this work
$Me_3COCH_2CH_3$	6.52	0.05	1.400	17.2	14
$Me_3SiOCH_2CH_3$	5.76	0.04	0.876	16.4	this work
n-Bu_2O	5.71	0.09	1.086	15.5	14
$Me_2SiOSiMe_2$	5.47	0.07	0.776	15.7	this work
$(Me_2SiO)_3$	4.48	0.17	—0.001	15.0	this work
$Me_3SiOSiMe_2OSiMe_3$	3.85	0.11	—0.632	15.0	this work
$Me_3SiOSiMe_3$	3.82	0.15	—0.849	15.7	this work
$(Me_2SiO)_4$	3.65	0.10	—0.399	13.6	this work
$(Me_2SiO)_5$	3.52	0.17	—0.341	13.0	this work
Me_3CSCMe_3	4.87	0.20	0.423	14.9	14
n-Bu_2S	4.19	0.33	0.167	13.5	14
$Me_3SiSCMe_3$	1.93	0.22	0.821	3.7	this work
$Me_3SiSSiMe_3$	0.82	0.20	1.472	—2.2	this work

[a] 90% confidence limits on precision calculated as in ref. 15. The value given is either the statistical or theoretical (calculated) limit, whichever is larger.

$SiOCMe_3 > Me_3COEt > Me_3SiOEt$, n-$Bu_2O$ *. Siloxanes however are generally far weaker bases toward phenol. The unstrained siloxanes show —ΔH values of 3.5 to 3.9 kcal/mole compared with 5.7 to 7.3 for the alkoxysilanes and ethers.

As has often been pointed out, the electropositive silicon should release electrons much more effectively than carbon [2,18]. If inductive effects alone were important the silicon compounds would therefore be expected to be more basic than the ethers. The decreased basicity of alkoxysilanes, and especially of siloxanes, can be explained if the inductive electron release is more than compensated by an electron-attracting effect. Earlier we and others [2,18] have proposed that dative π-bonding from oxygen lone pairs to silicon is responsible for the electron-withdrawing effect. This explanation still seems the most plausible, although some have argued that electron withdrawal by silicon takes place through hyperconjugation involving σ^* orbitals of appropriate symmetry associated with the Si—C bonding system [19]. For the compounds in question there seems to be no good experimental test of these two models at present **.

The equilibrium Si—O—Si bond angle in unstrained methylsiloxanes has very large values which lie in the range from 145 to 150° [21,22]. Two particularly interesting compounds in the table are cyclic siloxanes in which the Si—O—Si

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* This order is somewhat different from that obtained earlier from shifts of the phenol O—H stretching frequency upon hydrogen bonding to the same bases, which was $Me_3COCMe_3 > Me_3COEt >$ n-$Bu_2O > Me_3SiOEt > Me_3SiOCMe_3$ [2]. Thus alkoxysilanes and ethers, taken together, constitute a class of substances for which the Badger—Bauer [10] relationship between $\Delta\nu$(OH) and —ΔH fails [12,13].

** Recent NMR data on silicon substituents attached to aromatic rings appears to favor electron withdrawal by dative π-bonding rather than by hyperconjugation [20].

bond angle is constrained to smaller angles. These compounds are hexamethylcyclotrisiloxane (D_3) in which the bond angle is 131.6° [22], and 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane (TDO) in which the Si—O—Si angle is probably less than 120° [23]. In these compounds with strongly bent siloxane bonds, the basicity is increased over that of unstrained siloxanes. For TDO the enthalpy of hydrogen bonding rises almost to equal that of alkoxysilanes and ethers.

The increased basicity of siloxanes as the Si—O—Si bond angle is compressed can be rationalized in terms of the molecular orbital model of Bock and coworkers, derived from photoelectron spectroscopic measurements and CNDO/2 MO calculations [24]. According to this model, as the siloxane bond is compressed, the highest Si—O—Si σ bonding orbital is greatly destabilized. This factor, rather than decreased dative π-bonding, may mainly account for the increased basicity of the strained siloxanes.

Although the siloxane bond angle is normally large, it is quite easily compressed (or extended). Electron diffraction measurements on $Me_3SiOSiMe_3$ and related molecules show large amplitudes of internal motion in siloxanes [20] and far infrared spectroscopic measurements show that the force constant for Si—O—Si bending in disiloxane must be very low indeed [26], a fact which has important implications for the behavior of siloxane polymers *. Even in the weak hydrogen bonding interaction, some distortion of the siloxane bond to smaller angle may take place. If this effect is significant, we can predict that the relative base strength of siloxanes compared to ethers will increase as the acidity of the proton donor, and hence the energy of interaction, increases. At the same time the siloxane bond angle will become smaller.

Complete proton transfer to a siloxane to form the ion $(R_3Si)_2OH^+$ represents a limiting case for extreme distortion of the siloxane bond. Although the structure of the protonated siloxane is not known we believe the Si—O—Si angle must be greatly reduced in this species, probably to a value between 110 and 120°. Gas phase proton affinities of some siloxanes, alkoxysilanes and ethers have recently been studied in ion cyclotron resonance experiments by Pitt, Bursey and Chatfield [28]. These workers find that the relative basicity of siloxanes is indeed increased substantially in complete proton transfer, although they are still slightly less basic than isostructural ethers.

In agreement with earlier qualitative results [4], data in Table 1 show that the silicon—sulfur compounds $Me_3SiSCMe_3$ and $Me_3SiSSiMe_3$, with $-\Delta H$ (phenol) of only 1.9 and 0.8 kcal/mol respectively, are far weaker bases than dialkyl sulfides. This result is consistent with the earlier finding that $H_3SiSSiH_3$ is nonbasic toward diborane [29]. Much less is known of the orbitals involved in silicon—sulfur compounds. However, the data suggest that mesomeric electron withdrawal by silicon may be even more important in this mercaptosilane than it is in the alkoxysilanes. A possible rationalization is that energy match

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* Rochow and LeClair were the first to demonstrate abnormally great molecular motion at low temperatures in polysiloxanes [27], using wide line proton NMR spectroscopy. This low temperature motion is undoubtedly associated with the useful low-temperature properties of commercial silicone polymers. Displacements involving bending of the Si—O—Si bonds probably are responsible for most of this molecular motion in siloxanes, although other motions such as rotation and rocking of methyl groups must also contribute.

between the sulfur out-of-plane lone pair orbital and the π-acceptor orbitals is likely to be better than for the oxygen lone pairs.

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References

1 R.H. Baney, K.J. Lake, R. West and L.S. Whatley, Chem. Ind., (1954) 1129.
2 R. West, L.S. Whatley and K.J. Lake, J. Amer. Chem. Soc., 83 (1961) 761.
3 M. Horak, V. Bažant and V. Chvalovský, Coll. Czech. Chem. Commun., 25 (1960) 2822.
4 E.W. Abel, D.A. Armitage and D.B. Brady, Trans. Faraday Soc., 62 (1966) 3459.
5 K. Ulbrich, M. Jakoubkova and V. Chvalovský, Coll. Czech. Chem. Commun., 33 (1968) 1693.
6 A.N. Egorochkin, N.S. Vyzankin and S.D. Skoboleva, Zh. Obsch. Khim., 44 (1974) 1024.
7 S.G. Shevchenko, E.I. Brodskaya, Y.L. Frolov, A.M. Sklyanova, R.G. Mirsov and M.G. Voronkov, Zh. Obsch. Khim., 44 (1974) 1925.
8 H. Kelling, K. Dauber and E. Popowski, Z. Chem., (1975) 114.
9 B. Sternbach and A.G. MacDiarmid, J. Amer. Chem. Soc., 83 (1961) 3384.
10 R.M. Badger and S.H. Bauer, J. Chem. Phys., 5 (1937) 839.
11 W. Partenheimer, T.D. Epley and R.S. Drago, J. Amer. Chem. Soc., 90 (1968) 3886.
12 E.M. Arnett, L. Joris, E. Mitchell, T.S.S.R. Murty, T.M. Gorrie and P.R. Schleyer, J. Amer. Chem. Soc., 92 (1970) 2365.
13 R. West, D.L. Fowell, L.S. Whatley, M.K.T. Lee and P.v.R. Schleyer, J. Amer. Chem. Soc., 84 (1962) 3221.
14 R. West, D.L. Powell, M.K.T. Lee and L.S. Whatley, J. Amer. Chem. Soc., 86 (1964) 3227.
15 D.L. Powell and R. West, Spectrochim. Acta, 20 (1964) 983.
16 E.W. Abel, J. Chem. Soc., (1960) 4406.
17 M. Brandon, M. Tamres and S. Searles, J. Amer. Chem. Soc., 82 (1960) 2129.
18 E.A.V. Ebsworth in A.G. MacDiarmid (Ed.), Organometallic Compounds of the Group IV Elements, Vol. 1, Marcel Dekker, New York, 1968, p. 61—65 and ref. therein.
19 C.G. Pitt, J. Organometal. Chem., 61 (1973) 49.
20 W. Adcock, G.L. Aldous and W. Kitching, Tetrahedron Lett., 36 (1978) 3387.
21 B. Csákvári, Zs. Wagner, P. Gömöry, J.C. Mijlhoff, B. Rozsonodai and I. Hargittai, J. Organometal. Chem., 107 (1976) 287.
22 H. Oberhammer, W. Zeil and G. Fogarsi, J. Mol. Struct., 18 (1973) 309.
23 W.A. Piccoli, G.G. Haberland and R.L. Merker, J. Amer. Chem. Soc., 82 (1960) 1883.
24 H. Bock, P. Mollere, G. Becker and G. Fritz, J. Organometal. Chem., 61 (1973) 113.
25 C. Glidewell and D.C. Liles, Acta Cryst. B, 34 (1978) 124.
26 D.W. Robinson, W.J. Lafferty, J.R. Arouson, J.R. Durig and R.C. Lord, J. Chem. Phys., 35 (1962) 2248.
27 E.G. Rochow and H.G. LeClaire, J. Inorg. Nucl. Chem., 1 (1955) 92.
28 C.G. Pitt, M.M. Bursey and D.A. Chatfield, J. Chem. Soc. Perkin Trans., (1976) 434.
29 M. Onyszchuk, Can. J. Chem., 39 (1961) 808.