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Hydrogen Bonding Studies. V. The Relative Basicities of Ethers, Alkoxysilanes and Siloxanes and the Nature of the Silicon–Oxygen Bond[1,2]

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The relative Lewis basicities of a number of ethers, alkoxysilanes and siloxanes as proton acceptors in hydrogen bond formation have been measured. Ethers are slightly stronger bases than alkoxysilanes, and both of these classes of compounds are much stronger bases than siloxanes. The chemical and structural evidence is interpreted as indicating that dative pi bonding takes place from oxygen to silicon involving only one of the unshared electron pairs on oxygen.

Partial double-bonding involving *d* orbitals of silicon was first suggested in 1934 by Brockway and Wall[4] to explain the abnormally short bond distances in silicon tetrahalides. That this concept might be generally applicable to organosilicon chemistry was indicated by the striking discovery that the substance trisilylamine is non-basic[5] and has a planar structure.[6] In a paper on dative pi bonding Craig, *et al.*,[7] suggested that the silicon–oxygen sigma bonds in siloxanes might also be accompanied by pi bonding from oxygen to silicon, and this suggestion was amplified and extended in a review by Stone and Seyferth.[8] More recently, the cyclic siloxanes have been suggested as examples of "aromatic" dative pi bonded systems in papers by Craig.[9]

Structural evidence indicates that pi bonding does take place in silicon–oxygen compounds. Both in the simple molecule disiloxane[10] and in organosiloxanes[11] the Si–O–Si bond angle is larger than would be expected if only sigma bonding of the normal sp^3 (or p^2) type were taking place at oxygen.

Pi bonding of oxygen to silicon should also be expected to influence the chemical reactivity of siloxanes. In particular, the basicity of the oxygen in siloxanes might be reduced by such pi bonding. The reactions of disiloxane and some methyldisiloxanes with strong Lewis acids have been studied recently. Emeleus and Onyszchuk have investigated reactions with boron halides, hydrogen iodide and methyl iodide,[12] while Sujishi has studied the reaction of disiloxane with diborane, boron trifluoride and trimethylaluminum.[13] The fact that stable complexes of disiloxane with these Lewis acids were not isolated was interpreted as indicating weaker basicity for siloxanes than for ethers, due to oxygen–silicon pi bonding.[12,13] However, the evidence is qualitative at best and is complicated by the fact that disiloxane is cleaved rapidly by the more powerful Lewis acids.[14]

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(2) Previous paper in this series: R. West, R. H. Baney and D. L. Powell, THIS JOURNAL, **82**, 6269 (1960).

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To gain a clearer understanding of the nature of bonding in siloxanes, it seemed desirable to have a quantitative measure of the basicity of these compounds. The present paper reports the study of the Lewis basicity of a variety of siloxanes, alkoxysilanes and ethers as proton acceptors in hydrogen bond formation. Phenol was used as the principal reference acid, and the shift of the phenol O–H stretching frequency upon hydrogen bond formation to the various oxygen compounds served as a measure of their relative Lewis basicity. The trends in basicity were checked by determining the N–H frequency shift for pyrrole upon hydrogen bonding to many of the compounds. A similar method has been used by previous workers to determine relative basicity of ethers.[15] A discussion of the theoretical background of the method and additional references to earlier work may be found in previous publications in this series.[2,16]

Experimental

Spectra.—The infrared spectra were determined using a Perkin–Elmer Model 112 single-beam recording spectrophotometer with a lithium fluoride prism, calibrated with water vapor and ammonia. A path length of 3 mm. was used. The spectrum of each compound was determined alone in solution in carbon tetrachloride (a); in solution in CCl_4 containing 0.01 *M* phenol (b); and in solution in CCl_4 containing 0.013 *M* pyrrole (c). The concentration of the compound was maintained constant in runs a, b and c and is given in Table I. The ratios of the per cent. absorption of a/b and a/c then were determined for closely spaced points in the region of interest. Values of log a/b and log a/c were then replotted *versus* frequency. The frequency difference ($\Delta\gamma$) between the free and associated O–H or N–H peaks was determined from the resulting plots. Data so obtained are tabulated in Table I. The reproducibility of the band maxima was ± 1 cm.$^{-1}$ for free peaks and ± 3 cm.$^{-1}$ for associated bands.

Solvent and Reference Compounds.—Reagent grade carbon tetrachloride from freshly-opened bottles was used as a solvent without purification. The phenol was Mallinckrodt Co. reagent grade, fractionally crystallized and fractionally distilled *in vacuo*, b.p. 85.5–86° (20 mm.). Pyrrole from the Eastman Kodak Co. was purified by careful fractional distillation; the fraction used boiled at 131°.

Ethers.—Diethyl ether, Mallinckrodt analytical reagent grade, was dried over calcium hydride and distilled, b.p. 34.6°. 1,1,1-Triethoxyethane obtained from Aldrich Chemical Co. was dried over sodium sulfate and distilled, b.p. 144°. Tetraethoxymethane obtained from Delta Chemical Co. was dried over sodium sulfate and distilled, b.p. 159°. Dibenzyl ether obtained from Matheson, Coleman and Bell was used without further purification. Acetone diethylacetal prepared by the method of Claisen[17] had b.p. 112–114°; lit.[17] 112–114°. Ethyltriphenylmethyl ether was prepared from trityl chloride and sodium ethoxide.[18] After several recrystallizations from petroleum ether (60–70°), the compound had m.p. 83°; lit.[18] 81.3°. Dibenzhydryl ether donated by Dr. Harlan Goering was recrystallized from ethanol and from petroleum ether (60–70°); m.p. 109–109.5; lit.[19] 108–109°. Di-*t*-butyl ether was prepared by a modification of the method of Erickson and Ashton[20] which will be described separately. The compound had b.p. 104.5° (747 mm.); lit.[20] 106.5–107° (760 mm.).

TABLE I

Compound	Concn., *M*	$\Delta\nu_{OH}$ Phenol	$\Delta\nu_{NH}$ Pyrrole
Et_2O	0.25	282	149
Me_3COEt	0.25	300	149
Me_3COCMe_3	0.25	329	163
$Me_2C(OEt)_2$	0.13	257	138
$MeC(OEt)_3$	0.17	201	107
$C(OEt)_4$	0.09	164	98
Ph_3COEt	0.5	54	
$PhCH_2OCH_2Ph$	0.25	225, 57	
$Ph_2CHOCHPh_2$	0.5	55	
Me_3SiOEt	0.5	271	138
$Me_3SiOCMe_3$	1.0	261	125
$Me_2Si(OEt)_2$	0.25	257	129
$MeSi(OEt)_3$	0.17	237	114
$Si(OEt)_4$	0.13	219	97
Ph_3SiOEt	0.5	222, 52	
$ClCH_2Me_2SiOEt$	0.25	238	111
$(Me_3Si)_2O$ (MM)	1.0	169	75
MD_2M	1.0	142	58
MD_6M	0.5	137	54
D_3	0.4	166	79
D_4	1.0	144	54
D_5	0.8	147	52
D_6	0.65	141	48
$(Me_2HSi)_2O$	1.0	156	
$(MeHSiO)_4$	1.0	101	
$(MeHCO)_4$	Insol.		
$(ClCH_2Me_2Si)_2O$	0.25	59	
$(PhSiH_2)_2O$	0.75	51	
$(Ph_2SiH)_2O$	0.26	52	
$(PhMe_2Si)_2O$	1.0	55	

Alkoxysilanes and Siloxanes.—Ethoxytrimethylsilane, methyltriethoxysilane, hexamethyldisiloxane (MM), decamethyltrisiloxane (MD_2M), octadecamethyloctasiloxane (MD_6M), hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5) and dodecamethylcyclohexasiloxane (D_6) were kindly donated by Dr. Charles M. Huggins of the General Electric Research Laboratories. They were dried over sodium sulfate and distilled. The observed boiling points agreed with those listed by Rochow.[21] Reagent grade diethyldiethoxysilane was obtained from the Dow Corning Corp and used without purification. Practical grade tetraethoxysilane from Eastman Kodak Co. was purified by fractional distillation, b.p. 168°. Tetramethylcyclotetrasiloxane was prepared by H.-Y. Niu in these Laboratories by the hydrolysis of methyldichlorosilane,[22] b.p. 134.5°, n^{25}D 1.3838; lit.,[22] b.p. 134.5–134.9°, n^{20}D 1.3870. Chloromethyldimethylethoxysilane and *sym*-bis-(chloromethyl)-tetramethyldisiloxane were prepared from chloromethyldimethylchlorosilane according to the method of Andrianov and Golubenko[23]; for *sym*-bis-(chloromethyl)-tetramethyldisiloxane, b.p. 92° (21 mm.), n^{25}D 1.4393; lit.,[23] b.p. 92° (21 mm.), n^{20}D 1.4389; for chloromethyldimethylethoxysilane, b.p. 131–132° (745 mm.); lit.,[23] b.p. 131–132° (745 mm.). Ethoxytriphenylsilane was prepared by refluxing sodium ethoxide and chlorotriphenylsilane in absolute ethanol for 20 hr., filtering the resulting suspension and distilling the product *in vacuo* and recrystallizing the resulting solid from petroleum ether, m.p. 65–66°; lit.[24] 65–66°. The *t*-butoxytrimethylsilane was prepared from trimethylchlorosilane and *t*-butyl alcohol in the presence of pyridine,[25] b.p. 100° (750 mm.), n^{23}D 1.3881; lit.,[25] b.p. 101° (754 mm.), n^{20}D 1.3913. The *sym*-diphenyldisiloxane, obtained by hydrolysis of phenylbromosilane,[26] in turn obtained by

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the action of bromine in carbon tetrachloride on phenylsilane, had b.p. 100–110° (0.25 mm.), n^{25}D 1.541; lit.,[26] 86–90° (0.15 mm.), n^{25}D 1.541. The *sym*-tetraphenyldisiloxane, m.p. 46.5–57.5°, was obtained as a by-product in the synthesis of diphenylsilanol reported earlier.[16b] *sym*-Diphenyltetramethyldisiloxane was prepared by the dehydration of the corresponding silanol and had b.p. 106–108° (3 mm.), n^{23}D 1.5157; lit.,[27] b.p. 106–108° (3 mm.), n^{20}D 1.5176. The *sym*-tetramethyldisiloxane was a purified sample kindly donated by Dr. R. Baney.

Discussion

Results.—The simple ethers are the most basic class of oxygen compounds studied. As expected, the basicity increases with increasing alkyl substitution at the carbon alpha to the oxygen. The great basicity of di-*t*-butyl ether toward phenol and pyrrole is remarkable in view of previous findings that this compound is not basic toward the Lewis acid dinitrogen tetroxide.[28] It is apparent that the steric requirements of phenol and pyrrole for hydrogen bonding are low. The ethers with several oxygens bonded to a single carbon atom show regularly decreasing basicity as the number of alkoxyl groups attached to a single carbon atom increases (Table I). Qualitatively similar trends are found using pyrrole as the reference acid.

The compounds trityl ethyl ether and dibenzhydryl ether show greatly reduced basicity, giving phenol O–H shifts of only about 55 cm.$^{-1}$. Our interpretation is that the 55 cm.$^{-1}$ shifts represent hydrogen bonding to the aromatic rings,[29] which takes place in preference to hydrogen bonding to the relatively hindered oxygen atoms in these ethers. This interpretation is strengthened by the observations that both dibenzyl ether and triphenylethoxysilane give *two* hydrogen bonded O–H bands with phenol. The frequency shifts of about 55 and 225 cm.$^{-1}$ observed for the two bonded bands in each of these compounds indicate competing hydrogen bonding to the aromatic rings and to the oxygen atom, respectively.

Toward both phenol and pyrrole, the alkoxysilanes are slightly weaker bases than are ethers. In this they resemble silanols, which have previously been shown to be only slightly less basic than carbinols with analogous structure.[16b] However, it should be noted that the Lewis basicities of both alkoxysilanes and silanols are very much less than might be expected considering the inductive effect of the electropositive silicon atom. Trialkylsilyl groups are powerfully electron releasing when back-donation by pi bonding to silicon cannot take place.[30] Such dative pi bonding must therefore take place in alkoxysilanes and silanols, reducing the basicities of these substances below those of analogous ethers and carbinols.

In the compound chloromethyldimethylethoxysilane, the inductive effect of the chlorine atom operates normally to reduce the basicity of the compound. On the other hand, the basicity does not seem to be increased by increasing alkyl substitution at the alpha carbon, since trimethyl *t*-butoxysilane shows slightly smaller O–H and N–H shifts than trimethylethoxysilane. As the number of alkoxyl groups on silicon increases, the basicity declines, but less so than in the case of the polyalkoxymethanes. The result is that methyltriethoxysilane and tetraethoxysilane are more basic than their carbon analogs. Apparently the pi bonding capacity of silicon tends to become saturated as the number of donor atoms increases, as predicted by Jaffé.[31] Hence the effectiveness of the pi bonding in reducing electron density at a given oxygen declines as the number of alkoxy groups increases.[32] This effect alone should lead to increased basicity as the number of alkoxy groups increases, but the opposing inductive effect of the additional oxygen bonded to the silicon appears to be slightly more important, and the net result is a slight decrease in basicity.

The siloxanes are very much weaker as Lewis bases than any of the other classes of compounds studied (Table I). Pi bonding from oxygen to silicon therefore seems to be much stronger in siloxanes than in alkoxysilanes. The two linear methylpolysiloxanes, and the cyclic dimethylsiloxanes with ring size greater than six-membered, all showed $\Delta\nu$ in the range 137–147 cm.$^{-1}$ with phenol. Hexamethyldisiloxane (MM) and hexamethylcyclotrisiloxane (D_3) are slightly more basic, giving OH band shifts of 169 and 166 cm.$^{-1}$, respectively. The increased basicity of hexamethyl disiloxane may be due to the fact that it is unique among the polysiloxanes studied in containing an oxygen atom bonded to *two* trimethylsilyl groups. The enhanced basicity of hexamethylcyclotrisiloxane can be attributed to bond strain in this molecule (*vide infra*). Phenyl substituted siloxanes show only bands characteristic of hydrogen bonding to the phenyl rings, discussed above for phenyl ethers. With bis-(chloromethyl)-tetramethyldisiloxane, phenol gives an O–H shift of only 59 cm.$^{-1}$, indicating that in this compound hydrogen bonding takes place to the chlorine atom rather than to the siloxane oxygen.[33]

The Nature of the Silicon–Oxygen Bond.—In a tetrahedral molecule MAB_3 (C_{3v} symmetry), where B is a ligand incapable of pi bonding and A is a ligand with two pi orbitals available, if the z axis is taken along the M–A bond, the d_{xy} and d_{yz} orbitals of M are suitably disposed to form bonds with the p_x and p_y orbitals of A, respectively, to give maximum overlap.[31] The pi bonding thus involves both of these p electron pairs on A to the same extent. The remaining unshared pair of electrons on A is localized in a non-bonding orbital. Silicon-containing species which would fall into the class MAB_3 include the trialkylsilyl halides, R_3SiX, and the trialkylsilanolate anions, R_3SiO^-.

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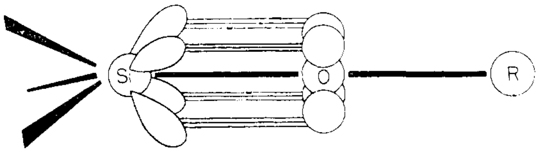

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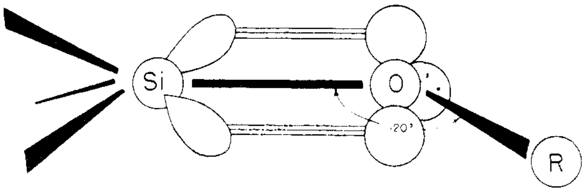

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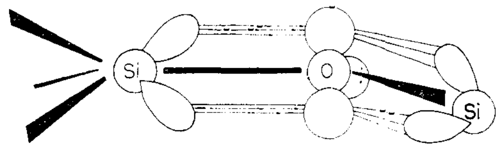

III

The trialkyl silanols, alkoxysilanes and disiloxanes, R_3SiOH, R_3SiOR and $R_3SiOSiR_3$, differ in that one electron pair on oxygen, instead of remaining unshared, is used in sigma bonding to another atom. The over-all symmetry in these molecules is low, but the local symmetry at silicon is still C_{3v}. One might expect that the bonding in these compounds would be the same as in MAB_3, with equal participation of both *p* electron pairs on oxygen in pi bonding to silicon and sp hybridization at oxygen (I). However, the fact that alkoxysilanes are nearly as basic as ethers suggests that an unshared pair of electrons must be present on oxygen in alkoxysilanes. We favor a model in which only one *p* electron pair on oxygen is involved in pi bonding to silicon, leaving the other electron pair essentially unshared (II).[34]

If only one electron pair were involved extensively in pi bonding, as in II, the sigma bond hybridization would be sp^2, and the Si–O–X angle should be near 120°. Model I on the other hand predicts sp hybridization at oxygen and an Si–O–X angle of 180°. However, this strictly linear arrangement does not seem to be found in any silicon–oxygen compounds. The first spectral study of disiloxane reported a linear structure,[10b] but later reports indicate that the molecule is bent with an Si–O–Si angle of 140–160° [10a,c,d] The polysiloxanes have similar bent structures.[11] No detailed structural studies have been carried out on monoalkoxysilanes or monosilanols, but the Si–O–C bond angle in tetramethoxysilane is reported to be only 113°,[11c] and the structures of solid silanediols indicate a bent Si–O–H group.[35] Finally, the disilicate anion $Si_2O_7^{-6}$, formerly thought to be linear in hemimorphite and thortveitite, recently has been shown to be angular in both these minerals.[36] On the other hand, several cases of colinear bonding at oxygen are known, in which dicovalent oxygen utilizes both of its *p* orbitals for pi bonding and attains the linear arrangement characteristic of sp sigma bond hybridization.[37] That it does not do so in silicon-oxygen compounds must mean that *oxygen forms a strong pi bond to silicon using only one of its two p orbitals*, occupying only a single 3d orbital of silicon.

The reasons for the conclusion stated above are not entirely clear. In the species showing sp hybridization at oxygen, the oxygen is bonded to two transition metal atoms. In these species, $(n - 1)d$ orbitals of the metals are used, and pi bonding from oxygen to metal undoubtedly contributes much more to the total bond energy than it does in silicon–oxygen compounds. In the latter the sigma bonding is relatively more important, and the pi bonding less important than in the transition metal species. In the special case of silicon–oxygen compounds, increased sigma bond energy may perhaps be realized with sp^2 hybridization at oxygen.

We believe that the Si–O–Si pi bonding in disiloxanes is best viewed as a three-center bond involving principally a single *d* orbital on each silicon atom and *one* of the 2*p* oxygen orbitals (III).[37] The lowered basicity of the siloxanes is interpreted as resulting from the increased electron withdrawal from oxygen by pi bonding to two silicon atoms. Although according to this view, the formal sigma bond hybridization at oxygen would still be sp^2, the unshared *p* electron pair would be drawn in closely toward the oxygen atom and would have both lowered basicity and lowered steric requirements. As a result, the Si–O–Si angle could spread out to somewhat more than the predicted 120° angle, perhaps with some consequent increase in pi orbital overlap. Hence when the Si–O–Si angle is constrained to less than the preferred angle of about 140°, as it is in hexamethylcyclotrisiloxane, the oxygen becomes slightly more basic. A similar theory can be applied to the bonding in polysiloxanes, except that the pi bonding may now be multi-center, as proposed by Craig.[9]

Acknowledgments.—The authors are grateful to Drs. Ronald H. Baney of the Dow Corning Corporation and Lawrence F. Dahl of these Laboratories for many helpful discussions.

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