Translated from *Uspekhi Khimii*, 45, 2253-2273 (1976) U.D.C. 678.84.044

Complexes of Organosilicon Compounds Containing a Siloxane Bond

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The ability of various classes of organosilicon compounds containing a siloxane (Si-O) bond to form intra- and inter-molecular complexes, by hydrogen bonding and otherwise, is surveyed, and several physicochemical properties of the complexes are discussed. A list of 264 references is included.

CONTENTS

I. Introduction 1167
II. Complexes without hydrogen bonding 1167
III. Hydrogen bonding 1170

I. INTRODUCTION

Compounds containing a siloxane bond occupy an important place in the chemistry of silicon. Several monographs and reviews[1-3] have dealt with the physical and chemical properties of these compounds, as well as aspects of their practical use. Nevertheless, no survey has yet appeared of the tendency of various classes of such organosilicon compounds to form complexes, with a discussion of their properties. A probable reason is that most studies of complexes of oxygen-containing silicon compounds have appeared during the past decade, although the first compounds of this type were obtained as early as the beginning of the present century[4-6]. Not only are complexes of organosilicon compounds containing a siloxane bond of obvious theoretical interest but attention has recently been paid to them as products of practical promise. Several of them are specific catalysts[7], biologically active compounds[8,9], or intermediates in the production of siloxane oligomers and polymers[10-12].

In contrast to a carbonyl bond, both atoms forming a siloxane bond can act as centres of complex formation. The presence on the silicon atom of five vacant $3d$ orbitals is responsible for the possible existence of five- and six-coordinated silicon compounds. Of the five d orbitals only the d_γ orbitals ($3d_{Z^2}$ and $3d_{X^2-Y^2}$) are used for the formation of σ bonds, probably for steric reasons. In five-coordinated silicon compounds, which have a trigonal bypyramid structure, p orbitals of other atoms are bonded with the d_{Z^2} orbital of the silicon atom (hybridisation of the latter sp^3d). In six-coordinated complexes, with an octahedral structure, the silicon atom has sp^3d^2-hybridised orbitals[13,14].

Besides σ bonding, the d orbitals of the silicon atom (d_e orbitals) can be used to form p_π–d_π bonds with π systems or with atoms having unshared p electrons (halogens, oxygen, nitrogen, etc.) The latter type of bonding is very characteristic of the siloxane bond itself[2], but this does not prevent several compounds containing this bond from forming intra- and inter-molecular complexes by additional $p_\pi - d_\pi$ interaction, as will be shown below.

The oxygen atom acts as another centre of complex formation by the siloxane bond. Owing to $p_\pi - d_\pi$ interaction with the adjacent silicon atom the basicity of a siloxane oxygen atom is usually weak. The degree of $p_\pi - d_\pi$ interaction depends significantly on the structure of the molecule containing the siloxane bond. In the series of compounds CH_3OCH_3, SiH_3OCH_3, SiH_3OSiH_3, for example, the El–O–El′ angle (El, El′ = C, Si) is respectively 111.43°, 120.6°, and 144°, so that the hybridisation of the oxygen atom in methoxysilane can be assessed as intermediate between sp^3 and sp^2, and that in disiloxane as intermediate between sp^2 and sp. In the latter case both lone pairs of electrons of the oxygen atom may take part in $p_\pi - d_\pi$ interaction with d orbitals of the two attached silicon atoms[2]. These compounds, of course, exhibit different tendencies to complex formation both with electron acceptors and with electron donors, as well as with compounds containing active hydrogen or deuterium. One of the main tasks of this Review will be to examine such regularities.

II. COMPLEXES WITHOUT HYDROGEN BONDING

1. Intramolecular Complexes

The first intramolecular oxygen-containing organosilicon compounds were obtained in 1903 by Dilthey[4,5], who found that silicon tetrachloride acted on acetylacetone and its methyl derivative to form crystalline substances, which were regarded as "siliconium salts"

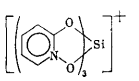
$$\{[RCOCH{=}C(CH_3)O]_3Si\}Cl \cdot HCl$$

containing a sexivalent silicon atom (R = CH_3 (I), C_2H_5). These compounds were converted further into salts $[A_3Si]^+M^nCl_{n+1}$, where M = Sn^{2+}, Fe^{3+}, Au^{3+}, Pt^{5+} and A = RCOCH : C(CH$_3$)O.[4-6] Corresponding derivatives of other β-diketones were obtained later[6,15-17]. The octahedral structure of compound (I) has been proved by resolving its racemate into optically active stereoisomers[15,18]. The chelate structure of (I) has been indicated also by its infrared spectrum, from which the carbonyl band in the region of 1700 cm^{-1} is absent, and has been replaced by a wide band at 1555 cm^{-1}.[19] Absorption in the range 1500–1600 cm^{-1}, which is characteristic of all chelate acetylacetonates of metals, is due to stretching vibrations of C=C bonds, and in some cases also C=O bonds[20-24].

In the proton magnetic resonance spectrum of (I) the signals from protons attached to carbon atoms are displaced down-field relative to the enolic form of pure pentane-2,4-dione, which was initially interpreted as proof of benzoid resonance in the chelate ring[25]. It was shown later, however, that an analogous shift occurs on passing from chelate diketonate cationic complexes of

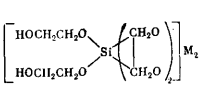
various metals (as well as silicon) to the corresponding neutral diketonates [26,27]. Thus this phenomenon does not indicate the development of aromatic structure in acetylacetonates, and can be satisfactorily explained as an effect of the electric field produced by the charge on the ion [26].

Reports have appeared also of other β-diketonate cationic complexes, having the structure $[SiRdik_2]^+[M^nCl_{n+1}]^-$, where $M = H^+$, Fe^{3+}, Sn^{4+}, and R is a hydrocarbon group [19,24,28], as well as non-ionic compounds dik_2SiX_2, where X is an organic substituent [19], chlorine [19,23,24,29], or an acyloxy-group [21,22,30], and also $dikSiR_3$, in which R is a hydrocarbon group [21,31-33]. The valency of the silicon atom depends on the composition of the β-diketonates. Chelate rings are present in the cationic complexes $[dik_3Si]X$ and $[dik_2SiR]X$, as well as in those of types dik_2SiX_2 and dik_2SiRX (where X represents chlorine on an acyloxy-group) [21-24,28-30,34,35]. Under ordinary conditions stable chelate rings are not formed when two or three organic substituents R are attached to the silicon atom [19,31-33]. Thus expansion of the electron octet with the formation of additional σ bonds occurs only when a sufficient number of electronegative substituents are attached to the silicon atom. In chelate compounds having two diketonate ligands silicon is quinquevalent (trigonal–bipyramidal structure) in the case of ionic compounds, or sexivalent (octahedral structure) when all bonds in the molecule are covalent in character. With dika SiR_3 a chelate structure may merely be intermediate in a *cis–trans* rearrangement [31,32]. A similar structure to cationic β-diketonates is possessed also by siliconium ions having tropolonato-ligands $[(C_7H_5C)_3Si]^+$ [36,37] and the trispyridine-1,2-dioxysiliconium ion [34]

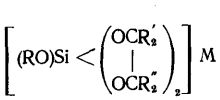


Several other stable ionic complexes are known in which the electron octet of the silicon atom is expanded by the formation of additional SiO bonds. The central silicon atom is attached only to electronegative atoms or in an extreme case may be attached to a single organic group. Typical complexes of this type are derivatives of arylene-o-diols having the structure $[(C_6H_4O_2)_3Si]M_2.H_2O$ (where $M = NH_4$ [38,39], K, C_5H_5NH [38], CN_3H_6 [40]), $[(C_6H_4O_2)_3Si]H_2$ or $[RSi(O_2C_6H_4)_2]H$ and their alkali-metal salts [41], $[(C_6H_4O_2)_2Si]Mg.9H_2O$ and $[(C_6H_4O_2)_3Si]Mg$ [40], $[RSi(O_2C_6H_4)_2]NR'_4$ [34,42,43], and $[RSi(O_2C_6H_{4-n}R'_n)_2]PR''_4$.[7] When an organic substituent is attached, the silicon atom is in a five-coordinated state, but in other cases it is six-coordinated. The molar conductance of aqueous solutions of silicon(V) complexes indicates that they are salts formed by a univalent anion and a cation [44].

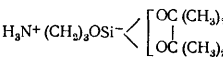
In 1929 Meerwein discovered [45] that orthosilicic esters of glycols and glycerol on titration with caustic alkalis give salts of intramolecular alkoxo-acids, for which a structure of type



was suggested. Later other complexes of similar type

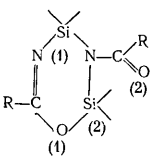


were obtained, in which R, R′, R″ = H, Alk and M represents an alkali metal or an ammonium cation [46,47], compounds of corresponding structure with biscyclohexane-1,1-dioxy- and bistetramethylethylenedioxy-substituents attached to the silicon atom [48], and several alkylammonium zwitterions derived from 1,2-diols [49], e.g.



All complexes of the above type are sparingly soluble in non-polar organic solvents. Several of them are very stable (e.g. the above zwitterion melts at 190°C); others decompose even at 100°C. The formation of complexes is favoured energetically, and often takes place with the evolution of heat. Salts of similar structure have been obtained also from orthosilicic esters of α-hydroxycarboxylic acids [50].

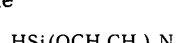
Crystalline adducts of derivatives of monohydric alcohols with five-coordinated silicon, e.g. $[(CH_3O)_5Si]K$, $\{[(CH_3O)_4Si]_2O\}K_2$, are stable only at low temperatures [51]. Other examples of intramolecular complex formation by means of additional silicon–oxygen bonds are cyclobisbenzamidodimethylsilane



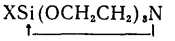
in which the distance between the $Si_{(2)}$ and $O_{(2)}$ atoms is 2.613 Å,[52] and also 2,2,5-trimethyl-5-nitro-2-sila-1,3-dioxan, the chair structure of which is assumed to be stabilised by transannular Si ← O interaction [53].

Thus, despite the well defined tendency of the siloxane bond to $p_\pi - d_\pi$ interaction, leading to diminished electron unsaturation of the silicon atom, the presence of such bonds in the molecule does not prevent involvement of *d* orbitals of the silicon atom in the formation of intramolecular coordinate bonds with oxygen or nitrogen atoms.

A typical example of intramolecular complexes of the latter type is silatrane

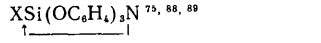


with its derivatives

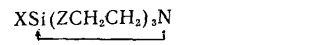


where X = Alk, Ar, Hal, etc.[54-80]. These compounds are usually crystalline solids with high-melting points (153°C for silatrane), although several liquid silatranes have been obtained recently [72,74,75]. The presence of a transannular Si ← N bond in the molecules has been proved by measurements of dipole moments [59-62,81,82], determinations of nuclear magnetic resonance [58,64,65,83,84] and ultraviolet [84] spectra, quantum-chemical calculations [81], and X-ray structural examination [85,86]. According to the latest estimates the transfer of electron density from the nitrogen to the silicon atom in a silatrane molecule is relatively small (0.1–0.2e).[81,82] X-Ray examination indicates that the phenylsilatrane [86] and *m*-nitrophenylsilatrane [85] molecules contain the silicon atom at the centre of a distorted trigonal bipyramid with three equatorial oxygen atoms, whil the axial positions are occupied by the group X and the nitrogen atom. The Si ← N bond lengths in the two derivatives are respectively 2.193 and 2.116 Å, much shorter than the sum of the van der Waals radii of the silicon and nitrogen atoms (~3.5 Å), but exceeding appreciably the length of a normal silicon–nitrogen single bond (~1.83 Å).

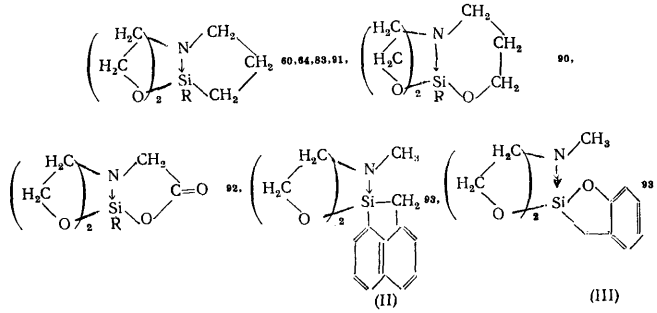
A dative bond Si ← N is formed also in *C*-substituted silatrane derivatives $XSi(OR)_n(OR')_{3-n}N$, where $n = 0-2$, $R = CH_2CH_2$, $R' = CH(CH_3)CH_2$ [60,75,82,87], etc.[75], substituted triphenoxysilatranes



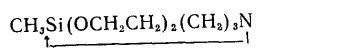
and other related heterocyclic sytems



(Z = S or NH)[90].



Available X-ray data indicate that the Si ← N bond length has the values 2.336, 2.344, 2.263, and 2.297 Å respectively for the compound[91]



for triphenylene-phenylsilatrane[89], and for the above methylbishydroxyethylamine derivatives (II) and (III).[93]

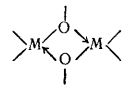
The presence of the Si ← N dative bond is assumed also in phthalocyanine derivatives of siloxanes[94-97].

Transannular Si ← N interaction is almost completely absent from alkyl-2-aminoethoxysilanes $R_nSi(OCH_2CH_2.NR'_2)_{4-n}$.[98-101]

2. Intermolecular Complexes

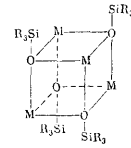
When dissolved in non-polar solvents the overwhelming majority of compounds containing siloxane bonds (other than silanols) show little tendency to associate or to undergo donor–acceptor interaction with the solvent. This is indicated by numerous determinations of molecular weight and other physicochemical results.

Many heterosiloxanes—compounds containing "foreign" atoms in the siloxane chain—exhibit systematic departures from this rule. Intermolecular coordination of such compounds is due to dative interaction of oxygen atoms with the heteroatoms. The stability of the autocomplexes of heterosiloxanes varies between wide limits. In several cases this type of complex formation is not clearly evident, and is apparent only from some increase in molecular weight. The nature and the valency state of the heteroatom are of decisive importance in the molecular association of heterosiloxanes. Sometimes, however, other substituents attached to the heteroatom and to the silicon atom have an appreciable effect. For example, compounds of the types $[R_3SiOMX_2]_2$ (where R represents H or an organic radical, X = Hal, H, or an organic radical, and M = Al, Ga, In) [102-111] and $[(R_2SiO)_3M]_2$ (R represents an organic radical and M = Al, Ga, Fe) [112-115] form stable dimers having the almost planar four-membered ring



The stability of the coordinate bonds is indicated by that of the ring in $[(CH_3)_3SiOAlCl_2]_2$ (up to 200°C).[108]

An analogous cyclic structure is suggested for $[(CH_3)_3.SiOAu(CH_3)_2]_2$,[116] $[(CH_3)_3SiOTl(CH_3)_2]_2$,[117] and $\{[(CH_3)_3.SiO]_4Zr\}$.[118,119] The presence of three bonds involving the bridging oxygen atoms in the dimers diminishes the strength of $p_\pi - d_\pi$ interaction between silicon and oxygen atoms and confers a coordinatively unsaturated character on the systems. With silanolates of alkali and pseudo-alkali metals, therefore, the above compounds form salts of type $[(R_3SiO)_4M]M'$, whose molecules contain only uncoordinated oxygen atoms, while the heteroatoms M retain their high coordination number[112,114,115,120-125]. The compounds $(CH_3)_3POM[OSi(CH_3)_3]_3$ and $(CH_3)_3NOM[OSi(CH_3)_3]_3$ (M = Al, Ga) probably have the zwitterion structure .[123] In the crystalline phase potassium, rubidium, and caesium trimethylsilanolates resemble $[(CH_3)_3COM]_4$ in being trameric, with the Si–O–M angle 123 ± 2°[126]; trialkylsiloxy-derivatives of mercury, zinc, and cadmium have an analogous structure:



where M = K, Rb, Cs [126] or HgR, ZnR, CdR.[119]

Potassium, rubidium, and caesium trimethylsilanolates are almost insoluble in organic solvents[127-129]. Sodium and lithium silanolates are associated in organic solvents, the degree of association increasing with decrease in the dielectric constant of the medium[128-134]. Potassium trimethylsilanolate dissolves immediately on addition to a solution of lithium or sodium trimethylsilanolate. Pure crystalline double salts $K\{M[OSi(CH_3)_3]_2\}$ (where M = Na, Li), having a narrow melting range, can be isolated from the resulting solutions[127].

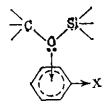
Several permethylsiloxy-derivatives of metals have higher molecular weights in solution (degree of association usually ≯1.5–1.7). When the methyl groups are replaced by ethyl, however, the degree of association falls to 1.0, probably owing to steric factors[132]. This is typical of compounds of type $U(OSiR_3)_5$ [132], $Zr(OSiR_3)_4$ [118,132], and $Ti(OSiR_3)_4$ [118,133]. Whereas trialkylsiloxy-derivatives of boron, phosphorus, and arsenic are monomeric, the unusual viscosity properties of siloxane polymers containing atoms of these elements suggest that they form unstable donor–acceptor association complexes, which decompose completely on dissolution[134-138].

Besides the above aggregates, complexes of siloxanes with several foreign ligands are also known. The formation of such complexes has been studied systematically by various physicochemical methods (mainly refractometrically)[139-160]. Compounds containing an Si–O–Si group show little tendency to form complexes either with donor or with acceptor solvents. The tendency to complex formation by alkoxysilanes $R_{4-n}Si(OR')_n$ depends on the number and structure of the substituents R and R'. In general the ability of alkoxysilanes to form labile complexes with ligands of any type falls with increase in the

number of alkoxy-groups in the molecule and also as their structure becomes more complicated. The weakening of the electron-donating properties of the oxygen atoms observed with increase in n in the alkoxysilanes is due to diminished steric accessibility and mainly to diminished polarity of the Si–O(C) bonds caused by the introduction of new electronegative alkoxy-substituents into the molecule. The latter effect is associated with simultaneous increase in $p_\pi - d_\pi$ interaction in the silicon–oxygen bonds. The weakening of the bonds of alkoxysilanes with electron-donating ligands as n increases is probably caused mainly by the more difficult steric accessibility of the silicon atom.

Phenoxysilanes, in which substituents more electronegative than alkoxysilanes are attached to silicon, exhibit a greater tendency to complex formation with organic bases, and less tendency with acids [141,146,155]. Oxalyldioxysilanes form stable complexes (up to 80–100°C) with oxolan, dioxan, and pyridine of general formula $[Si(C_2O_4)_2.2X]_n$, and with dioxan also $[C_6H_5Si(C_2O_4H)C_2O_4.1.5diox]_n$. [161]

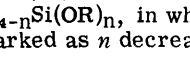
Alkoxysilanes associate with several benzene derivatives of type C_6H_5X. The stability of such complexes increases with the electron-accepting properties of the aromatic ring in the C_6H_5X molecule. Consequently the oxygen atom of the alkoxy-group acts as donor in the charge-transfer complexes formed, and the aromatic compound as acceptor [141,144,146,162]:



Various physicochemical methods have been used to establish the formation of complexes by alkoxysilanes with the tetrachlorides of tin [157,163–168], titanium [169,170], and silicon [171], but not with phosphorus halides [172,173]. Heats of complex formation q per donor–acceptor bond in complexes of tin(IV) chloride with $R'Si(OR)_3$ correlate satisfactorily with the sum of the Taft polar σ^* constants of the substituents R′ [166,167]:

$$q = 7.849 - 1.03\,\Sigma\sigma^*;\ r = 0.95\ . \qquad (1)$$

Increase in the $+I$ effect of substituents attached to the silicon atom leads to a decrease in the heat of complex formation. The same tendency is evident in the systems formed by titanium(IV) and tin(IV) chlorides with alkoxychlorosilanes $Cl_{4-n}Si(OR)_n$, in which complex formation becomes less marked as n decreases [164,166,170]. Silatranes



form 1:1 and 2:1 complexes with titanium(IV) chloride, and an equimolecular complex with aluminium bromide. These complexes are assumed to have an octahedral structure [174].

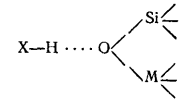
Labile complexes are formed by the interaction of $(CH_3O)_4SiSO_3$, [175] $(C_6H_5O)_4Si$, [176] and $(R_3SiO)_3PO$ (where R = CH_3, C_2H_5, C_6H_5) [177] with dioxan, of alkoxysilanes with iodine [141,156,178], and of alkylalkoxy- and acetoxysilanes with tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)europium and other paramagnetic shift reagents [179]. Complex formation by aminoalkoxysilanes [180–182] and alkoxyaminosilanes [183,184] with metal halides [181–184] and with silthianes [180] involves the nitrogen atoms, not oxygen.

Donor–acceptor interaction involving a phosphoryl group develops in mixtures of tristrialkylsilyl phosphates with tin(IV) and tellurium(IV) chlorides [185,186] and also with chloroform [177,186].

III. HYDROGEN BONDING

1. Intermolecular Association of Siloxanes and Alkoxysilanes with Proton Donors

The energy of the hydrogen bond in the associated complexes



(M = Si or C) does not exceed 5–6 kcal mole^{-1}. Hydrogen bonds of this type have been studied by infrared spectroscopy [187–220], nuclear magnetic resonance [221], refractometry [140,141,146,152,155,170,199], dielectric measurements [199,220,222,223], and viscosimetry [140,220]. The proton donors used have been phenol [187–212], pyrrole [188,189,198,212,215], chloroform [141,221,223] or deuterochloroform [214,217], alcohols [140,141,146,198–200,215,220,222], and other compounds containing mobile hydrogen [141,144,211,216].

Table 1. Shifts in hydroxyl-stretching band of phenol on hydrogen bonding with organo-silanes and -siloxanes.

No.	Formula	$\Delta\nu_{O-H}$, cm^{-1}	Ref.	No.	Formula	$\Delta\nu_{O-H}$, cm^{-1}	Ref.
1	H_3SiOCH_3	183	196	36	$[(CH_3)_3Si]_2O$	169	187
		185	200			170	194
2	$CH_3SiH_2(OCH_3)$	221	196			162	204
3	$(CH_3)_2SiH(OCH_3)$	251	200	37	$(CH_3)_2SiOSi(CH_3)_2$-n-C_3H_7	164	204
4	$(CH_3)_3SiOCH_3$	278	200	38	$(CH_3)_2SiOSi(CH_3)_2$ i-C_3H_7	159	204
5	$(CH_3)_3COC_2H_5$	300	187	39	$(CH_3)_3SiOSi(CH_3)_2CH_2CH_2CF_3$	154	192
6	$(CH_3)_3SiOC_2H_5$	271	187	40	$(CH_3)_2SiOSi(CH_2CH_2CF_3)_2CH_3$	147	192
		281	203	41	$(CH_3)_2SiOSi(C_6H_5)_3$	170	192
7	n-$C_3H_7(CH_3)_2SiOC_2H_5$	286	203	42	$(CH_3)_2SiOSi(C_6H_5)_3$	53	194
8	i-$C_3H_7(CH_3)_2SiOC_2H_5$	285	203	43	$(CH_3)_2SiOSi(CH_2CH_2CF_3)_2$	*	192
9	$C_6H_5CH_2(CH_3)_2SiOC_2H_5$	270	205	44	$[(CH_3)_2SiH]_2O$	156	187
10	$CF_3CH_2CH_2(CH_3)_2SiOC_2H_5$	255	192	45	$[C_2H_5(CH_3)_2Si]_2O$	190	194
11	$ClCH_2(CH_3)_2SiOC_2H_5$	238	187	46	$[CF_3CH_2CH_2(CH_3)_2Si]_2O$	145	192
12	$CH_3(CF_3CH_2CH_2)_2SiOC_2H_5$	235	192	47	$[ClCH_2(CH_3)_2Si]_2O$	59	187
13	$(CF_3CH_2CH_2)_2SiOC_2H_5$	210	192			65	194
14	$(C_6H_5)_2SiOC_2H_5$	222	187	48	$[Cl_2CH(CH_3)_2Si]_2O$	55	194
15	$(CH_3)_2SiOC_6H_5$	177	209	49	$[BrCH_2(CH_3)_2Si]_2O$	75	194
16	$(CH_3)_2SiOCH_2C{\equiv}CH$	227	209	50	$[ICH_2(CH_3)_2Si]_2O$	85	194
17	$(CH_3)_2C(OC_2H_5)_2$	257	187	51	$[CH_3(CF_3CH_2CH_2)_2Si]_2O$	*	192
18	$(CH_3)_2Si(OC_2H_5)_2$	257	187	52	$[(C_6H_5)_3Si]_2O$	200	194
19	$CH_3(CH_2{=}CH)Si(OC_2H_5)_2$	249	202			*	189
20	$(CF_3CH_2CH_2)_2Si(OC_2H_5)_2$	217	192	53	$(C_2H_5)_2SiOSn(C_2H_5)_3$	375	211
21	$(CH_3)_2Si(OC_6H_5)_2$	154	209	54	$[(n\text{-}C_4H_9)_2Si]_2O$	210	194
22	$CH_3Si(OCH_3)_3$	226	209	55	$(CH_3)_3SiO[Si(CH_3)_2O]_2Si(CH_3)_3$	142	187
23	$CH_3C(OC_2H_5)_3$	201	187	56	$(CH_3)_3SiO[Si(CH_3)_2O]_3Si(CH_3)_3$	137	187
24	$CH_3Si(OC_2H_5)_3$	237	187	57	$[(CH_3)_2SiO]_3$	167	204
25	$C_6H_5CH_2Si(OC_2H_5)_3$	232	212	58	$[(CH_3)_2SiO]_3CH_3$-n-$C_3H_7SiO]$	167	204
26	$ClCH_2Si(OC_2H_5)_3$	214	212	59	$[(CH_3)_2SiO](CH_3$-n-$C_3H_7SiO)_3$	170	204
27	$C_6H_5Si(OC_2H_5)_3$	224	212	60	$[CH_3$-n-$C_3H_7SiO]_3$	172	204
28	$CH_2{=}CHSi(OC_2H_5)_3$	229	202	61	cis-$[CH_3(CF_3CH_2CH_2)SiO]_3$	131	192
29	$CH_3Si(OC_6H_5)_3$	115	209	62	$trans$-$[CH_3(CF_3CH_2CH_2)SiO]_3$	129	192
30	$C(OC_6H_5)_4$	164	187	63	$[(CH_3)_2SiO]_4$	144	187
31	$Si(OC_2H_5)_4$	219	187			145	204
32	$Si(OC_6H_5)_4$	105	209	64	$[(CH_3)_2SiO]_3[CH_3$-n-$C_3H_7SiO]_3$	149	204
33	$(H_3Si)_2O$	*	200	65	$[CH_3$-n-$C_3H_7SiO]_4$	160	204
34	$[(CH_3)_2C]_2O$	329	187	66	$[CH_3(CF_3CH_2CH_2)SiO]_4$	*	192
35	$(CH_3)_2SiOC(CH_3)_2$	261	187	67	$[(CH_3)_2SiO]_5$	147	187
				68	$[(CH_3)_2SiO]_6$	141	187

*The basic properties of the oxygen atom do not develop under the conditions of the determination.

Infrared spectroscopy is the most sensitive method for studying a hydrogen bond, whose strength is assessed from the shift $\Delta\nu_{X-H}$ in the X–H or X–D stretching vibrations (X = O, N, etc.) due to interaction of the hydrogen (or deuterium) atom with the siloxane oxygen. According to the absolute frequency shift $\Delta\nu_{X-H}$ proton donors can be

arranged in the sequence [189] *p*-bromophenol > phenol > 2,3-dimethylphenol > indole > benzyl alcohol > pyrrole. In interpreting the infrared spectra, however, we must bear in mind that proton donors can form a hydrogen bond not only with the siloxane oxygen atom but also with π-electron systems (aromatic rings, multiple bonds) and halogen atoms present in the proton acceptor [188,224].

Selected values of $\Delta\nu_{O-H}$ for the systems formed by phenol with siloxanes are given in Table 1 together with comparative data for some isostructural organic compounds. Alkoxysilanes are evidently weaker bases than the corresponding dialkyl ethers, and siloxanes are still weaker bases. Thus the oxygen compounds of silicon are much less basic than might be expected from the induction effect of the silicon atom, which is less electronegative than carbon. This is explained by the presence of a donor–acceptor π bond, which diminishes the basicity of the siloxane oxygen atom.

Table 2. Values of $\Delta\nu_{C-D}$, $\Delta\nu_{O-H}$, and $\Delta\nu_{N-H}$, in systems comprising a base and a proton (deuteron) donor, accompanying the hydrogen bonding of compounds of subgroup IV*b* elements with deuterochloroform [214], phenol [216], and pyrrole [215].

General formula	$\Delta\nu_{C-D}$, cm^{-1}				$\Delta\nu_{O-H}$			$\Delta\nu_{N-H}$, cm^{-1}	
	C	Si	Ge	Sn	Si	Ge	Sn	Si	Ge
$(CH_3)_3MOCH_3$	—	—	—	—	153	245	329	163	258
$(CH_3)_3MOC_2H_5$	29	21	38	56	—	—	—	—	—
$(CH_3)_3M]_2O$	33	13	55	84	73	274	—	76	285

Table 2 illustrates the basicity of isostructural oxygen-containing compounds of elements in subgroup IVb. The shifts $\Delta\nu$ are minimal for compounds in which M = Si, owing to the substantial contribution by $p_\pi - d_\pi$ conjugation. Yet the variation in electronegativity of the atom M would suggest that the basicity should increase regularly from carbon to tin. The fall in basicity from compounds in which M = C, Ge, Sn to the isostructural silicon compound is especially large in the $[(CH_3)_3M]_2O$ series.

The departure from this rule observed with $n = 3$, 4 in the series $R_{4-n}M(OC_2H_5)_n$, where M = C, Si, and R = CH_3 (No. 23, 24, 30, and 31 in Table 1) must be attributed to the great steric hindrance to hydrogen bonding presented by the ethoxy-groups in compounds in which M ≠ C. [198]

Depending on the nature of the compounds the basicity of siloxane oxygen falls in the sequence (Table 1)

$$C_{Alk}OSi > C_{Ar}OSi > SiOSi > SiOSiOSi\ ,$$

which is probably governed by increasing electronegativity of the substituents attached to the oxygen atom and increasing degree of $p_\pi - d_\pi$ interaction in the molecules. A noteworthy feature is the unexpected enhanced basicity of cyclotrisiloxanes (No. 57–62 in Table 1), which is confirmed by nuclear magnetic resonance data [221]. The cause is the lower degree of $p_\pi - d_\pi$ conjugation in the strained planar molecules [188], as well as the greater steric accessibility of the oxygen atoms in them than in higher cyclosiloxanes or linear siloxanes [192].

In series of compounds with the same number of siloxane bonds in the molecule the induction effect of groups attached to the silicon atom has a decisive influence on the basicity. Statistical treatment of experimental data for trialkylethoxysilanes, alkyltrialkoxysilanes, and hexa-alkyldisiloxanes by means of the Taft equation

$$\Delta\nu_i = \Delta\nu_0 + a\Sigma\sigma_i^* \qquad (2)$$

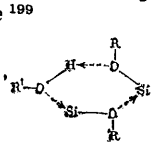
gave the results listed in Table 3. A good linear dependence of $\Delta\nu_i$ on $\Sigma\sigma_i^*$ was shown graphically [207] for phenol complexes of compounds of general formula $(CH_3)_{2-m}(X_nC_6H_{4-n})_mSi(OC_2H_5)_2$. The variation in the parameter a (Table 3) suggests that the induction effect of the substituents has the greatest influence on the basicity of trialkylethoxysilanes, and the least on that of alkyltrialkoxysilanes, with disiloxanes occupying an intermediate position. Hence the ability of the silicon atom to transmit the induction effect of substituents to oxygen diminishes with increase in the number of siloxane bonds in the molecule. Study of the hydrogen bonding of phenol and pyrrole with compounds of general formula $R_{4-n}M(OC_2H_5)_n$ (where R = CH_3, C_3H_7, n = 1–4, and M = C, Si, Ge) has established that the $\Delta\nu_i$–n lines have smaller slopes for the silicon derivatives than for the carbon and germanium compounds, where p_π–d_π conjugation is either absent or slight [198]. Thus there are grounds for supposing that the diminution in sensitivity to the induction effect of substituents on passing from ethers or alkoxygermanes to alkoxysilanes, or with increase in the number of siloxane bonds in the molecule, is due to increase in $p_\pi - d_\pi$ conjugation in the same sequence [205].

Table 3. Parameters in the Taft equation (2) for complexes of phenol with alkoxysilanes and disiloxanes.

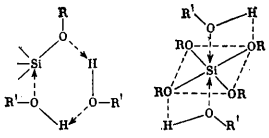
Formula	$\Delta\nu_0$	a	Correlation coefficient	Ref.
$R_3SiOC_2H_5$	275±2	−61.3±3.9	0.980	205
$RSi(OC_2H_5)_3$	237	−24.7	0.992	212
$RSi(OCH_3)_3$	266	−31.8	0.965	212
$(R_3Si)_2O$	162±3	−42.9±3.2	0.954	205

The steric effect of substituents is quite clear in the hydrogen bonding of phenol with siloxanes [189,192,204]. On passing from alkoxysilanes to disiloxanes the influence of steric factors on association with phenol is apparent also in a decrease in the number of hydrogen-bonded hydroxy-groups [192,204]. Differences in tendency to hydrogen bonding depending on steric features of substituents in siloxanes and alkoxysilanes have been revealed also by refractometry [139,141,144] and n.m.r. spectroscopy [221].

Depending on the nature of the components siloxanes and alkoxysilanes may form with proton donors 1 : 2, 1 : 1, and 2 : 1 complexes [145,199,213,220,223]. For example, tetra-alkoxysilanes give only 1 : 2 complexes [220] with the corresponding alcohols, methyltrialkoxysilanes and dimethyldialkoxysilanes 2 : 1 and 1 : 1, [199,213,220], and ethoxytrimethylsilane forms a 2 : 1 complex [195,213]. An ordinary hydrogen bond is undoubtedly present in the 1 : 1 complexes. In other cases silicon atoms may also be involved in complex formation, with an increase in their coordination number to 5 or even 6. For example, a 2 : 1 complex is assigned the structure [199]



and a 1:2 co.. .plex the structure



The latter st.. ure is supported by the ability of complexes of tetra-alkoxysilanes with alcohols to dissociate as very weak monobasic acids[199]:

$$Si(OR)_4 \cdot 2\,ROH + ROH \rightleftarrows [Si(OR)_6H]^- + ROH_2^+ \ .$$

Table 4. Enthalpy of hydrogen bonding of siloxanes and alkoxysilanes with phenol.

Base	$-\Delta H$, kcal mole^{-1}		
	expt.	Ref.	calc. from Eqn.(4)
$[(CH_3)_3C]_2O$	5.9	190	5.9
	7.4	191	
$[(CH_3)_3Si]_2O$	2.9	190	3.3
	4.0	191	
$(CH_3)_3SiO[(CH_3)_2SiO]_2Si(CH_3)_3$	4.3	191	—
$(CH_3)_3SiO[(CH_3)_2SiO]Si(CH_3)_3$	4.3	191	—
$[(CH_3)_2SiO]_3$	4.4	191	3.3
$[(CH_3)_2SiO]_4$	3.2	190	2.9
	3.8	191	
$(CH_3)_3SiOC(CH_3)_3$	6.7	191	4.8
$(CH_3)_3SiOC_2H_5$	6.0	191	5.0

Energetic characteristics published for the hydrogen bond between proton donors and oxygen-containing silicon compounds have been few and contradictory[190,191,195]. Table 4 gives existing values for the enthalpy of formation of the hydrogen bond. A linear relation exists between the frequency shift of the absorption by phenol and the enthalpy of formation of the hydrogen bond, the latter calculated from the association equilibrium constant[190]†:

$$-\Delta H\,(\pm 0.5 \text{ kcal mole}^{-1}) = 0.016\,\Delta\nu_{OH} + 0.63 \ . \qquad (4)$$

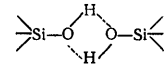
2. Hydrogen Bonds formed by Silanols

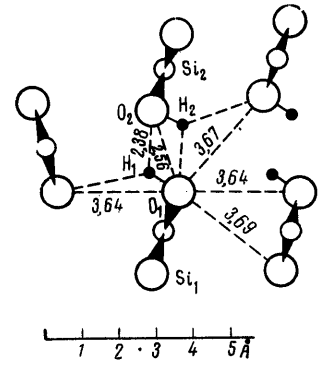
Silanols are associated by hydrogen bonding even in very dilute solutions[225-228], so that complete absence of association can be expected only in the gas phase[225,229]. The hydroxyl-stretching frequencies in the infrared spectra of dilute solutions of silanols in relatively inactive solvents (carbon disulphide and tetrachloride) lie in the range 3670–3695 cm^{-1}, being little affected by the nature of the substituents attached to the silicon atom[201,225,229-238]. Absorption by a free hydroxy-group occurs at frequencies 60–80 cm^{-1} higher in silanols than in alcohols[230,239], and is thus closer to the region of vibrations by the hydroxide ion (4200 cm^{-1})[240]. Together with the greater intensity of the band due to a silanol than to a carbinol hydroxyl[238] this indicates that the oxygen–hydrogen bond is more stable in silanols than in their carbon analogues. Hydroxy-groups in gaseous trimethylsilanol[225], as well as those in Aerosil and glass[241-244], absorb at 3735–3749 cm^{-1}. The infrared spectra of concentrated solutions, liquids, or crystals of silanols show a frequency shift to ν_{OH} = 3200 to 3300 cm^{-1},[225,226,229,238,245]. This band due to hydrogen-bonded hydroxysilyl groups has considerable width and greater integral intensity than in the corresponding carbinols.[228] The frequency shift due to association is $\Delta\nu_{OH}$ = 200–400 cm^{-1}, considerably larger than in carbinols, and caused by the enhanced acidity of silanols[187,225,230,231,235,238-240,245]. The absorption frequencies of free and associated OD groups in the infrared spectra of deuterosilanols R_3SiOD are respectively 2710–2730 and 2435–2455 cm^{-1}.[225,229,246]

An interesting example of association due to the hydrogen bonding of silanol groups is heptacyclohexyltricyclo-[7,3,3,1]heptasiloxane-3,7,14-triol, which forms a strongly associated dimer having K_{diss} = 0.0037. This dimer is soluble in benzene and in tetrachloromethane. Its infrared spectrum does not show vibrations of free hydroxy-groups, but contains a broad band with its maximum at 3230 cm^{-1}. It is assumed that all six hydroxyls of the two associated molecules of this triol are hydrogen-bonded in pairs[226].

Still stronger hydrogen bonds are present in the crystals of many inorganic hydrosilicates[241,247-251].

The infrared spectra of crystalline and liquid silanols contain only one wide band due to hydrogen-bonded hydroxysilyl groups[228,235,238,239,245,252], which indicates the cyclic character of the molecular association, in which almost all the hydroxy-groups are involved[228,252]:





Schematic arrangement of hydroxy-groups in the structure of diethylsilanediol.[255]

X-Ray[253,254] and electron[255] diffraction indicates that crystalline dialkylsilanediols $R_2Si(OH)_2$ (where R represents ethyl or allyl) consist of layers and chains of molecules joined by hydrogen bonds. The accompanying diagram shows schematically the arrangement of hydroxy-groups in diethylsilanediol molecules. The Si–O(H) distance is comparable with the siloxane bond length in polysiloxanes. Some contraction of the $O_{(1)}$–$O_{(2)}$ bond (2.56 Å) in comparison with the sum of the van der Waals radii can be attributed to the formation by dipoles of a group having a fixed hydrogen bond[225].

†Values given[191] for ΔH differ substantially from the probably more reliable values in Ref. 190 and from those calculated by means of Eqn. (4).

The infrared spectra of dilute solutions of certain trialkylsilanols containing π-type proton acceptors (phenyl, vinyl) and of all dialkylsilane- and siloxane-diols contain two or more overlapping bands in the region of absorption by hydroxy-groups [232-235,245,252,256]. Their presence can be explained satisfactorily in terms of rotational isomerism [233-235]. The staggered isomers predominate over the gauche isomers (the higher-frequency bands are usually more intense than those at lower frequencies) in $HO[SiR_2O]_nH$ molecules in which $n = 1, 2$ and R = CH_3, C_2H_5, whereas with R = C_6H_5, $CH_2:CH$ the predominant gauche structure is stabilised by weak interaction of one of the hydroxy-groups with the π electrons of the R substituents. The existence of rotational isomers leads to a certain restriction of freedom of rotation in siloxanediol molecules. The most stable intramolecular bond in hexaphenyltrisiloxane-1,5-diol is due to the steric effect of the phenyl groups, which promote the formation of cyclic, but not linear, molecules. Intermolecular association of polydialkylsiloxanediols is governed by the dimensions of the substituents, and in the case of di- and tri-siloxane-$\alpha\omega$-diols diminishes in the sequence

$$(CH_3)_2 > CH_3(C_6H_5) > CH_3(CH_2:CH) > (C_6H_5)_2.$$

Silanols not only associate but also form complexes with other proton-donating compounds—phenol [187,231,232,257], alcohols [242,243], and water [242,244]—as well as with several electron donors—ethers and esters [200,201,218,219,230-232,257,258], amines [10-12,243,248,258], benzene derivatives [218,219,242,243], dimethyl sulphoxide [201,259,260], ketones [219,243], and others [218,219,242,261,262]—among which study of the complexes with diethyl ether and with phenol gave valuable information on their acid–base properties. Table 5 lists experimental data for the most representative series of silanol complexes. Formation of the complexes with ether and similar compounds undoubtedly involves the hydroxyl hydrogen atom of the silanol, so that their stability is directly dependent on the degree of protonation of the latter. It follows from Table 5 that silanols are significantly stronger acids than analogous hydroxy-derivatives of carbon, germanium, and tin. Similar results have been obtained from a study of complexes formed by these compounds with dimethyl sulphoxide and with oxolan. [200,231] The abnormally high acidity of silanols indicates $p_\pi - d_\pi$ conjugation between silicon and oxygen atoms with enhancement of the polarity of the oxygen–hydrogen bond [187,196,200,201,230,231,251,263].

The variation of the frequency shift $\Delta\nu_{OH}$ accompanying the hydrogen bonding of silanols with ether indicates that the acidity of the silanols decreases with increase in the $+I$ effect of substituents attached to the silicon atom (e.g. with the lengthening of alkyl groups), but increases with increase in the $-I$ effect. For disubstituted silanediols $R_2Si(OH)_2$ (R = Alk, Ar) the logarithm of the ratio of $\Delta\nu_{OH}$ for the diol–ether to that for the dimethylsilanediol–ether complex is linearly dependent on the Taft σ constants, which confirms the comparatively small contribution by conjugation for most substituted diphenylsilanediols. [257]

The stability of the ether complexes increases somewhat on passing from trialkylsilanols to the corresponding dialkylsilanediols, which is consistent with replacement of an organic radical by the more electronegative hydroxy-group. Passing from the disubstituted silanediols to the corresponding siloxane-1,3-diols causes little or no (for the methyl or phenyl derivatives respectively) increase in acidity, which remains almost constant on further lengthening of the siloxane chain. These results suggest that the total induction and mesomeric effects of R_2SiO groups (R = CH_3, C_6H_5) in the series of compounds $HO[SiR_2O]_nH$ ($n = 1-5$) are close to zero [232].

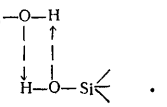
Values of $\Delta\nu_{OH}$ for adducts of phenol with hydroxylated compounds (Table 5) indicate that the oxygen atom in the hydroxysilyl group is only slightly less basic than that in a carbinol group, although silanols are significantly stronger acids than are the corresponding alcohols. Triphenylgermanol and triphenylstannol are appreciably stronger bases than is triphenylsilanol, in conformity with the arrangement of the elements in Group IV of the Periodic System. Thus here, too, data for silicon compounds are not consistent with the general rule, probably because of $p_\pi - d_\pi$ conjugation [201]. In the association of phenol with trialkylsilanols increase in the length of an alkyl group attached to the silicon atom causes an increase in basicity of the hydroxysilyl oxygen atom and hence an increase in the phenolic $\Delta\nu_{OH}$ shift. Replacement of alkyl by more electronegative groups (phenyl, benzyl) leads to diminished basicity. Hence in this series of compounds the more acidic silanols are weaker bases, as might have been expected.

Table 5. Values of $\Delta\nu_{OH}$ in the spectra of silanols (and some of their analogues) in the presence of ether or phenol.

No.	Formula	$(C_2H_5)_2O$		C_6H_5OH	
		$\Delta\nu_{M-OH...O}$, cm^{-1}	Ref.	$\Delta\nu_{C_6H_5OH...O}$, cm^{-1}	Ref.
1	2	3	4	5	6
1	$(CH_3)_3COH$	122	230	271	187
2	$(CH_3)_3SiOH$	238	230	216	230
3	$(C_2H_5)_3SiOH$	230	230	216 228	230
4	$(C_6H_5)_3SiOH$	317	201 231	175	231
5	$(C_6H_5)_3COH$	174	201 231	—	—
6	$(C_6H_5)_3GeOH$	196	201 231	288	231
7	$(C_6H_5)_3SnOH$	10	231	477	231
8	$(C_6H_5)_2HSiOH$	332	230	194	230
9	C_6H_5OH	280	230	132	230
10	$(CH_3)_2Si(OH)_2$	270	232 257	230	232
11	$[HO(CH_3)_2Si]_2O$	275	232 257	268	257
12	$HO[(CH_3)_2SiO]_3H$	274	232	291	232
13	$HO[(CH_3)_2SiO]_4H$	274	232	291	232
14	$HO[(CH_3)_2SiO]_5H$	270	232	230	232
15	$CH_3(C_6H_5)Si(OH)_2$	290	257	—	—
16	$HO[CH_3(C_6H_5)SiO]_2H$	291	257	226	257
17	$(C_6H_5)_2Si(OH)_2$	328	257	—	—
18	$HO[(C_6H_5)_2SiO]_2OH$	328	232	190	257
19	$HO[(C_6H_5)_2SiO]_3OH$	325	232	243	232
20	$CH_3(CH_2=CH)Si(OH)_2$	275	257	—	—
21	$HO[CH_3(CH_2=CH)SiO]_2H$	271	257	249	257
22	$HO[CH_3(CH_2=CH)SiO]_3H$	275	257	292	257
23	$(C_2H_5)_2Si(OH)_2$	272	257	—	—
24	$(C_3H_7)_2Si(OH)_2$	270	257	—	—
25	$(C_6H_5CH_2)_2Si(OH)_2$	302	257	169	257

On the introduction of new siloxane bonds into silanols the basicity of the latter is not inversely proportional to their acidity, as is always observed with alcohols [257,264]. Thus replacing methyl or phenyl in a trisubstituted silanol by hydroxyl yields the more acidic silanediols, which, however, also possess greater basicity. Acidity remains roughly constant in the series $HO[SiR_2O]_nH$, while basicity increases from $n = 2$ to $n = 3$ (Table 5). The shift $\Delta\nu_{OH}(C_6H_5OH)$ suggests that the hydrogen bonding involves hydroxysilyl oxygen atoms, since the shifts produced by the association of phenol with Si–O–Si bonds do not exceed 150–160 cm^{-1}. These results were interpreted in terms of multicentre $p_\pi - d_\pi$ conjugation, whose

development with growth of the siloxane chain may lead to weakening of $p_\pi - d_\pi$ interaction of the hydroxyl oxygen atoms with the terminal silicon atoms[232,257]. However, the unusual apparent relations between the acidity and the basicity of siloxane-$\alpha\omega$-diols may be due to variation in the acidity of phenol itself, resulting from coordination of its oxygen atom with the hydroxy-groups of the siloxane-diol, which are more strongly acidic than phenl itself (Table 5):



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