PROTON ACCEPTOR ABILITY OF HALOGENS
IN ORGANOSILICON COMPOUNDS* **

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IR absorption spectra of 0·02M phenol (proton donor)/substituted halogenosilane/CCl_4 (solvent) ternary mixtures prove that halogen atoms X (X = F, Cl, Br, I) act as proton acceptors. Their interaction with acidic hydrogen of phenol results in a broad IR band of the associate $v(OH \ldots X)$, similar to the carbon series. In (halogenoalkyl)silanes this interaction is affected by the distance between silicon and halogen X (X = Cl, F). If a given silane contains in addition to halogen also another proton acceptor center (*e.g.* oxygen), the spectrum shows besides the free OH absorption band $(v(OH)_{free})$ also absorption bands of both hydrogen bonds $v(OH \cdots OSiX)$ and $v(OH \cdots \cdots XSiO)$ or $v(OH \cdots OSiC_nX)$ and $v(OH \cdots XC_nSiO)$ (n = 1—3).

Proton acceptor ability of alkyl halogenides has been already established. Schleyer and West[1] measured $v(OH)$ shifts of phenol and methanol on interaction with n-butyl halogenides and cyclohexyl halogenides and Krueger and Mettee[2] investigated hydrogen bonds between methanol and aryl halogenides. Both groups of authors observed that the relative basicity of halogens is very low. In the present work we attempted to ascertain a similar interaction in the case of organosilicon compounds. The value of

$$\Delta v(\text{phenol}) = v(OH)_{free} - v(OH)_{assoc.}$$

was taken as a measure of formation of hydrogen bonds between phenol and alkyl-halogenosilanes, alkylhalogeno(halogenoalkyl)silanes and methylalkoxychlorosilanes.

EXPERIMENTAL

Compounds studied. With the exception of readily available compounds, the references to methods used to prepare other compounds are given in Tables I—III. The purity of the compounds was verified by gas chromatography and by IR and NMR spectra.

Spectroscopic measurements. IR spectra of hydrogen bonds were recorded on a double-beam Zeiss (Jena) spectrometer, Model UR 20, in $3\,700 - 3\,200\ cm^{-1}$ region (LiF prism), using 0·1 cm thick NaCl cells. Phenol was used in 0·02M concentration, a proton acceptor as 0·5M—1·5M solution in spectrograde CCl_4, with the exception of $(CH_3)_3SiO(CH_2)_nCl$ ($n = 1,2$) which were measured also without the solvent. $\Delta\nu$ values were determined with an accuracy of $\pm 3\ cm^{-1}$ as an average of three measurements.

Equilibrium of reactions between chlorosilanes and phenol. With a trimethylchlorosilane/phenol/ CCl_4 mixture, in addition to the hydrogen bond region the IR spectra in the $3\,800 - 400\ cm^{-1}$ region were measured without compensation in 0·01 cm KBr cells. Model systems $(CH_3)_3$. $.\ SiOC_6H_5$ or $(CH_3)_2Si(OC_6H_5)_2/HCl/CCl_4$ were measured analogously. Gaseous hydrogen chloride was introduced into a solution of a given phenoxysilane in CCl_4 immediately before measurements. Similar measurements of hydrogen bonds of trimethylphenoxysilane solutions were carried out in two solvents differing in dielectric constant, chloroform and dichloromethane. Attempted use of 0·03M methanol as a proton donor for trimethylchlorosilane resulted in a change in the spectrum with time which showed that the silicon-chlorine bond is rapidly cleaved in this mixture.

RESULTS AND DISCUSSION

Measurements of hydrogen bonds of some chloro derivatives of alkoxysilanes with phenol showed that in addition to the two absorption bands $\nu(OH)_{free}$ ($3\,611\ cm^{-1}$) and $\nu(OH \cdots O)$ an absorption band occurs in the $3\,700 - 3\,200\ cm^{-1}$ region whose maximum for the studied compounds is located at $3\,611$ to $3\,540\ cm^{-1}$. This band was

TABLE I

Proton Acceptor Ability of Alkyl Halogenides RX (X = F, Cl, Br, I)

R	$\Delta\nu^a$, cm^{-1}			
	F	Cl	Br	I
$(CH_3)_3Si$	39^b	52	64	^{c}
$(CH_3)_3SiCH_2$	50^d	62	68	73^e
$(CH_3)_3Si(CH_2)_3$	41^f	58	—	—
$CH_3(CH_2)_6$	41	60	68	70
$(CH_3)_3CCH_2$	37^d	—	69	—
$CH_3(CH_2)_3{}^g$	40	59	69	77
$C_6H_{12}{}^g$	53	66	82	—

^{a} $\Delta\nu$ denotes $\Delta\nu(OH \ldots X)$ of hydrogen bond of 0·02M phenol in CCl_4 with 1M alkyl halogenide RX; ^{b} R = $C_2H_5(CH_3)Si$; ^{c} the intensity of $\nu(OH)_{free}$ absorption band decreases rapidly with time so that $\Delta\nu$ can be recorded only immediately after addition of $(CH_3)_3SiI$ to the standard 0·02M phenol solution in CCl_4 and amounts to approx. 70 cm^{-1}; ^{d} the preparation and characterization of compounds see ref.[3]; ^{e} $\nu(OH \cdots I)_{assoc.}$ band is broad and very weak; ^{f} the preparation and characterization of compounds see ref.[4]; ^{g} taken from ref.[1].

found not only with the compounds containing a halogen attached to carbon but also with those possessing Si—X bond $(X = $ a halogen$)$ (Fig. 1 and Table I). With regard to the fact that at the concentration used $(0\cdot02\text{M})$ the phenol does not self-associate $(v(\text{OH})_{\text{dimer}}\ 3481\ \text{cm}^{-1},\ \text{ref.}^5)$ we believe that this absorption band can be ascribed to interaction of halogen with the acidic hydrogen of phenol $v(\text{OH}\cdots X)$.

For the phenol/trimethylchlorosilane/CCl$_4$ system under study formation of hydrogen bond solely with chlorine is surprising, since in view of the nature of the Si—Cl bond an equilibrium reaction (A) ought to be also considered.

$$\underset{/}{\overset{\backslash}{\text{Si}}}\text{—Cl} \ + \ C_6H_5OH \ \underset{\Longleftarrow}{\overset{CCl_4}{\Longrightarrow}} \ \underset{/}{\overset{\backslash}{\text{Si}}}\text{—OC}_6H_5 \ + \ HCl \qquad (A)$$

We have, however, proved by experiments that the above equilibrium in the medium given, *i.e.* nonpolar carbon tetrachloride, and under exclusion of air moisture is shifted completely to the left side. This was demonstrated above all by intensity of the $v(\text{OH})_{\text{free}}$ absorption band of phenol in the spectrum of chlorosilane/phenol/CCl$_4$ systems which did not decrease with time and further by the absence of a band corresponding to interaction of phenolic hydrogen with oxygen of an eventual phenoxy group $(\Delta v$ for $(CH_3)_3OC_6H_5$ is^6 175 cm$^{-1})$. A change in the intensity of the Si—Cl characteristic vibration $(550\ \text{cm}^{-1})$ cannot be followed reliably, since this band
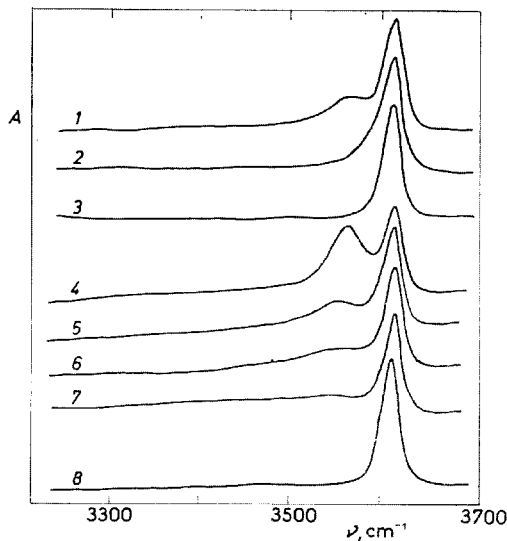

FIG. 1

$v(\text{OH})$ Stretching Vibrations of $0\cdot02\text{M}$ Phenol with 1M Methylchlorosilanes $(CH_3)_{4-n}\text{SiCl}_n$ and (Halogenomethyl)trimethylsilanes $(CH_3)_3\text{SiCH}_2X$ in CCl$_4$

1 $n = 1$, *2* $n = 2$, *3* $n = 3$, *4* X = F, *5* X = Cl, *6* X = Br, *7* X = I, *8* $0\cdot02\text{M}$ phenol in CCl$_4$.

overlaps with that of phenyl group[7]. Eventual $v(Si—O)$ absorption bands cannot be identified for analogous reasons.

Experiments in which hydrogen chloride was added to trimethylphenoxysilane as a model compound (see the right-hand side of equation (A)) have led to formation of phenol. This was demonstrated by occurence of characteristic absorption bands in the region of hydrogen bonds. The intensity and half-width of these bands changed proportionally with variation in the polarity of the medium.

Preliminary experiments with the use of methanol as a proton donor have been unsuccessful. With a methanol/trimethylchlorosilane/CCl$_4$ system an absorption band of methanol (either free or associated) is absent, by contrast to an analogous system with phenol. It is obvious that methanol reacts fastly with trimethylchlorosilane already during preparation of the solution[8].

Table I presents wavenumber shifts of the $v(OH)$ band of phenol upon its interaction with alkylhalogenosilanes, (halogenoalkyl)trimethylsilanes and some carbon analogues. The Δv's for the series of (halogenomethyl)trimethylsilanes increase in the order F $<$ Cl $<$ Br $<$ I. A similar sequence holds also for the series of n-heptyl halogenides and neopentyl halogenides, in agreement with Schleyer and West[1] (Table I). In a subsequent study by West[9] (and later also by Arnett and coworkers[10]) the opposite trend for basicities has been established on the basis of measurements of the equilibrium constants and enthalpies of n-butyl halogenides. In this connection it is worthy of note that, as we found, intensity of the absorption band of the associated component $v(OH \cdots X)$ of equimolar solutions of n-heptyl halogenides decreases also in the order F $>$ Cl $>$ Br $>$ I. If one compares Δv's for the isostructural series differing only in halogen, one can conclude that in all the series — carbon and silicon ones — Δv decreases with increasing electronegativity of halogen, the greatest change within a given series being always observed on going from the fluoro to chloro derivative. This trend is obviously retained also in alkylhalogenosilanes, as indicated by Δv's for trialkylhalogenosilanes which are presented in Table I. Replacement of an alkyl group by halogen atoms (F or Cl) brings about a strong decrease in Δv that is accompanied also by lowering of intensity of the absorption band due to the associated component. Thus, for example, in the case of diethyldifluorosilane and methyltrichlorosilane the above interaction leads only to slight broadening and a small decrease in the intensity of the $v(OH)_{free}$ of phenol (compare curves 3 and 8 in Fig. 1).

As to Δv's of models in which silicon and halogen atoms are separated by varying number of inserted methylene groups, the values for $n = 1-3$ and X $=$ F or Cl for the series $(CH_3)_3Si(CH_2)_nX$ are so similar that their interpretation would probably be possible only when they are compared with theoretical gas-phase basicities calculated by CNDO/2 method.

Let us proceed now to the compounds that possess two different basic centers: weakly basic chlorine and strongly basic oxygen. In Tables II and III are besides

$\Delta\nu(\text{OH} \cdots \text{Cl})$ presented also $\nu(\text{OH})$ wavenumber shifts for interaction of phenol with oxygen of the alkoxy group, $\Delta\nu(\text{OH} \cdots \text{O})$, methylalkoxychlorosilanes and methyl-(chloroalkoxy)silanes. Comparison of relative basicities of the oxygen in model series reveals that electron density at oxygen lowers with increasing number of chlorine atoms attached to silicon (Table II). (The same trend was observed also with the series $(\text{CH}_3)_n\text{Cl}_{3-n}\text{SiO}(i\text{-}\text{C}_3\text{H}_7)$, $n = 0-3$). The replacement of methyl groups by chlorine shifts $\nu(\text{OH} \ldots \text{Cl})$ band to higher wavenumbers and lowers its intensity. This decrease is so steep that only for dimethylalkoxychlorosilanes the wavenumbers shifts can be expressed numerically (Table II). The pattern of the spectra of di- and trichloro derivatives is similar to that of analogous methylchlorosilanes in the region below 3611 cm^{-1} (Fig. 1, curve 2 and 3).

The spectrum of $(\text{CH}_3)_2[(\text{CH}_3)_3\text{CO}]\text{SiCl}$ shows only one broad band $(\Delta\nu\ 33\ \text{cm}^{-1})$, and a band characteristic of interaction of oxygen of bulky tert-butoxy group with phenol is absent (Table II). This fact agrees with successive decrease in an intensity of the $\nu(\text{OH} \cdots \text{O})$ band for dimethylalkoxychlorosilanes with increasing steric demands of the alkoxy group $(\text{C}_2\text{H}_5\text{O} > i\text{-}\text{C}_3\text{H}_7\text{O} > (\text{CH}_3)_3\text{SiCH}_2\text{O} > (\text{CH}_3)_3\text{CO})$.

When turning to chloroalkoxy-substituted silanes (Table III) we can conclude that $\Delta\nu(\text{OH} \cdots \text{Cl}-\text{C})$ wavenumber shifts are nearly constant for all the members $(59 - 64\ \text{cm}^{-1})$. The exception is only $(\text{CH}_3)_3\text{SiOCH}_2\text{Cl}$ whose $\Delta\nu(\text{OH} \cdots \text{Cl}-\text{C})$

TABLE II

Proton Acceptor Ability of Methylalkoxychlorosilanes

Proton acceptor[a]	$\Delta\nu(\text{OH} \cdots \text{O})$, cm^{-1}	$\Delta\nu(\text{OH} \cdots \text{Cl}-\text{Si})$, cm^{-1}
$(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$	273[b]	—
$(\text{CH}_3)_2(\text{C}_2\text{H}_5\text{O})\text{SiCl}$	206	50[c]
$(\text{CH}_3)(\text{C}_2\text{H}_5\text{O})\text{SiCl}_2$	136	$+$[d]
$(\text{C}_2\text{H}_5\text{O})\text{SiCl}_3$	84	$+$[d]
$(\text{CH}_3)_3\text{SiOCH}_2\text{Si}(\text{CH}_3)_3$	293[b]	—
$(\text{CH}_3)_2[(\text{CH}_3)_3\text{SiCH}_2\text{O}]\text{SiCl}$	212	42
$\text{CH}_3[(\text{CH}_3)_3\text{SiCH}_2\text{O}]\text{SiCl}_2$	145	$+$[d]
$[(\text{CH}_3)_3\text{SiCH}_2\text{O}]\text{SiCl}_3$	121	$+$[d]
$(\text{CH}_3)_3\text{SiOC}(\text{CH}_3)_3$	265[b]	—
$(\text{CH}_3)_2[(\text{CH}_3)_3\text{CO}]\text{SiCl}$	—[e]	33

[a] 0·5—1·5M; for proton donor concentrations see Table I; the synthesis and physical constants of proton acceptors are reported in ref.[11]; [b] taken from ref.[12]; [c] $\nu(\text{OH} \cdots \text{Cl}-\text{Si})$ band is broad and very weak; [d] symbol $+$ denotes a hydrogen bond whose small $\Delta\nu$ cannot be expressed numerically; [e] the absorption band absent.

equals to 46 cm^{-1}. The lowering of the $\Delta v(\text{OH} \cdots \text{O})$ and intensity of this band compared to the β- and γ-derivative is also anomalous. It could be due to the more favourable influencing of both proton acceptor centers separated by one methylene group[12].

With model series $(\text{CH}_3)_n\text{Si}(\text{OCH}_2\text{CH}_2\text{Cl})_{4-n}$ ($n = 0-4$) we have observed characteristic changes in intensities of both associated bands: at the same proton acceptor concentration the intensity of $v(\text{OH} \cdots \text{Cl})$ increases while that of $v(\text{OH} \cdots \cdots \text{O})$ decreases with increasing n. The relative intensity of the $v(\text{OH} \cdots \text{Cl})$ band for the tetrakis-derivative even exceeds the intensity of the $v(\text{OH} \cdots \text{O})$ band, which could be due to the greater accessibility of vicinal chlorine atoms for interaction with phenol.

In addition to the compounds listed in Tables I to III we have measured also the greater number of chloro-substituted derivatives whose Δv values were not tabelated because of their difficult reading. The pattern of the spectra allows, however, to make several qualitative conclusions: an increase in the number of chlorine atoms in the ending group $-\text{CH}_2\text{Cl}$, $-\text{CHCl}_2$, and $-\text{CCl}_3$ brings about again a decrease in $\Delta v(\text{OH} \ldots \text{Cl}-\text{C})$, similarly as in the series of methylchlorosilanes. This is consistent

TABLE III

Proton Acceptor Ability of Methyl(chloroalkoxy)silanes and (Chloromethyl)methylethoxysilanes

Proton acceptor[a]	$\Delta v(\text{OH} \cdots \text{O})$, cm^{-1}	$\Delta v(\text{OH} \cdots \text{Cl}-\text{C})$, cm^{-1}
$(\text{CH}_3)_3\text{SiOCH}_2\text{Cl}$	176[b]	46[b]
$(\text{CH}_3)_3\text{SiO(CH}_2)_2\text{Cl}$	233[b]	60
$(\text{CH}_3)_3\text{SiO(CH}_2)_3\text{Cl}$	264[b]	62
$(\text{CH}_3)_3\text{SiOCH}_2\text{CHCl}_2$	193[b]	$+$[c]
$(\text{CH}_3)_3\text{SiOCH}_2\text{CCl}_3$	135[b]	$+$[c]
$(\text{CH}_3)_2\text{Si}[\text{O(CH}_2)_2\text{Cl}]_2$	206	64
$\text{CH}_3\text{Si}[\text{O(CH}_2)_2\text{Cl}]_3$	180	60
$\text{Si}[\text{O(CH}_2)_2\text{Cl}]_4$	154	59
$(\text{ClCH}_2)(\text{CH}_3)_2\text{SiOC}_2\text{H}_5$[d]	241	63[e]
$(\text{ClCH}_2)\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_2$[d]	226	64[e]
$(\text{ClCH}_2)\text{Si}(\text{OC}_2\text{H}_5)_3$[d]	206	61[e]
$\text{CH}_3\text{OCH}_2\text{Cl}$	132	56

[a] $0.5-1.5\text{M}$, $(\text{CH}_3)_3\text{SiOCH}_2\text{Cl}$ measured in the absence of the solvent; proton donor concentrations are given in Table I; the synthesis and physical constants of proton acceptors are reported in ref.[11]; [b] taken from ref.[12]; [c] symbol $+$ denotes a hydrogen bond whose small Δv cannot be expressed numerically; [d] the synthesis and characterization of compounds see ref.[13]; [e] a very weak band.

with *e.g.* a similar behaviour of "spectral" solvents such as CH_2Cl_2, $CHCl_3$, and CCl_4. The spectrum of phenol in these solvents shows one band whose half-width is however greatest for CH_2Cl_2. A sharp symmetrical band of phenol in CCl_4 is generally used as the standard $\nu(OH)_{free}$ for hydrogen bond measurements (Fig. 1, curve 8). We have also examined model compounds that contain varying number of chlorine atoms bonded in different ways: $(CH_3)_{3-n}Cl_nSiO(CH_2)_mCl$ ($n = 1-3$, $m = 2, 3$), $(CH_3)_{3-n}Cl_nSiOCH_2CHCl_2$ and $(CH_3)_{3-n}Cl_nSiOCH_2CCl_3$ ($n = 1-3$). Increasing number of chlorine atoms within these series resulted in a decrease in both $\Delta\nu$'s, a steep decrease in an intensity of the corresponding bands, and in an overlap between $\nu(OH \cdots Cl—C) + \nu(OH \cdots Cl—Si) + \nu(OH)_{free}$ bands, $\nu(OH \cdots \cdots Cl—C)$ and $\nu(OH \cdots Cl—Si)$ not being distinguished.

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