INTERACTIONS OF TRIALKOXYSILANES WITH SOME ORGANIC SOLVENTS

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Summary

Changes in proton chemical shift δ (downfield) for the hydrogen bonded directly to the silicon atom of the trialkoxysilanes $(RO)_3SiH$ (where $R = CH_3$, C_2H_5, C_3H_7, iso-C_3H_7) in several, mainly aromatic, solvents as well as changes in $\delta(C—H)$ of the aromatic ring (downfield), $\delta(C—H)$ of chloroform (downfield) and in $\delta(C—H)$ of the alkoxy groups (in aromatic solvent upfield, in $CHCl_3$ downfield) were observed for the trialkoxysilane—aromatic (and $CHCl_3$) solvent systems. The results obtained are interpreted mainly in terms of interaction of Si—O—C bonds in trialkoxysilane with organic solvent molecules, particularly for n-electrons of the alkoxy groups, with the benzene ring functioning as a π-electron acceptor (and with protonic hydrogen of chloroform).

Introduction

Kinetic studies of heterolytic cleavage of the Si—H bond in the presence of cupric salts have shown the existence of a non-linear dependence of the observed rate constants on $[Cu^{II}]_0$ for trialkoxysilanes, while for trialkylsilanes a linear dependence was observed [1—3]. The different mechanisms are readily accounted for by a pre-equilibrium step for the trialkoxysilane reaction involving an interaction of the solvent with the silane [3]. Our detailed measurements of the IR and UV-Vis spectra, specific conductivity and other physico-chemical properties, have proved the existence of molecular complexes of trialkoxysilane (trimethoxy-, triethoxy-, tripropoxy-, triisopropoxysilanes) with a variety of organic, mainly electron-donor and electron-acceptor solvents [4,5].

On the grounds of our previous study and of the characteristics of the silicon atom and the Si—H bond [4], the observed shifts of the Si—H vibration frequency ($\Delta\nu$) appear to be a result of the combination of the following trialkoxysilane—solvent interactions: (1) a nucleophilic attack of the solvent molecule on silicon, leading to (a) a decrease in $(p—d)\pi$ bond back donation and hence an increase in the electron-withdrawing character of the alkoxy group, (b) an

increase in the electron density on the Si atom; (2) an electrophilic attack of the acceptor solvent molecule on hydrogen (particularly when another solvent molecule is coordinated to Si atom), causing an increase in hydridic character of the hydrogen, (3) interactions of the acceptor solvent molecule with n-electrons of oxygen atoms of the alkoxy groups, leading (as in the case mentioned in 1a) to a lower $(p-d)\pi$ bond order in the silane; (4) hydrogen-bond formation involving the n-electron of oxygen (Si—H⋯O) or nitrogen as well as the π-electrons of the solvent; (5) a dipole—dipole character of the interactions, proportional to $(\epsilon - 1)(2\epsilon + 1)$.

In order to extend our study on the solvation of alkoxysilanes by organic solvents, ^{1}H NMR chemical shift measurements for Si—H and C—H of trialkoxysilane and for C—H of the solvent were undertaken. The ^{1}H NMR technique seems to be very useful for a characterization not only of the Si—H bond but of the whole trialkoxysilane molecule. The present study of molecular complexes of trialkoxysilanes with different organic solvents aims at the identification of intermediates in the numerous chemical reactions of trialkoxysilanes.

Results and discussion

Proton chemical shifts, $\Delta\delta$, for four trialkoxysilanes (trimethoxysilane, triethoxysilane, tripropoxysilane and triisopropoxysilane) in different solvents are presented in Table 1. In addition, several concentration dependences of the proton chemical shift for Si—H and C—H of trimethoxysilane and for C—H of the solvent in a trimethoxysilane-solvent mixture are plotted in Fig. 1.

The following conclusions concerning the trialkoxysilane—solvent interactions can be drawn from the results of the ^{1}H NMR study. Most interesting are the large changes ($\Delta\delta = 0.11—0.31$) in proton chemical shift for the hydrogen bonded directly to the silicon atom of the trialkoxysilane, appearing downfield in all aromatic solvents examined as compared with hexane solvent or without solvent, regardless of the nature of the ring substituent. The effects point to electronic deshielding of the hydrogen of Si—H. Simultaneous increase in δ(C—H) of the aromatic ring and a decrease in δ(C—H) of the alkoxy groups were observed for all trialkoxysilane—aromatic solvent systems.

Electronic and d_π—p_π effects of the trialkoxy substituents bonded to silicon would favour $Si^{\delta-}$—$H^{\delta+}$ bond polarity [6], at least in trimethoxysilane and triethoxysilane. The low-field shift is quite characteristic for all hydrogen atoms involved in hydrogen bonding with n-type donors, e.g. diethyl ether, while in aromatic solvents, which function as π-electron donors a high-field shift for solute protons is usually observed [7]. The latter arises predominantly from the large diamagnetic anisotropy of aromatic solvent molecules [7,8]. Hydrogen bonding of solute protons to the ring has been suggested to account for the solvent shift in many cases [7,9]. We observe, however, that the trialkoxysilane Si-bonded proton resonance is shifted in aromatic solvents to lower field and no effect in the hydrogen (Si) atom shielding in diethyl ether. Therefore, we can exclude such hydrogen bond formation in the system examined. Moreover, a small vibration frequency shift of the Si—H bond in benzene solutions does not confirm such specific interactions either [4].

On the contrary, the relative basicity of the oxygen in siloxanes and particu-

TABLE 1

THE CHANGE OF ^{1}H NMR SHIFT OF TRIALKOXYSILANES IN VARIOUS SOLVENTS ($\Delta\delta$(Si—H))

Solvent	$\Delta\delta$ (ppm) [a,b]			
	(MeO)$_3$SiH	(EtO)$_3$SiH	(PrO)$_3$SiH	(i-PrO)$_3$SiH
Benzene	0.31	0.32	0.31	0.28
Toluene	0.26	0.25	0.26	0.19
Chlorobenzene	0.22	0.22	0.21	0.18
Acetophenone	0.20	0.19	0.15	0.14
Benzonitrile	0.19	0.16	0.17	0.11
Nitrobenzene	0.18	0.15	0.15	0.11
CHCl$_3$	0.14	0.10	0.10	0.06
CH$_2$Cl$_2$	0.08	0.05	0.02	0.02
Propanol	0.13	0.05	0.04	
Ethanol	0.13	0.04	0.02	
NMF	0.06	0.02	0.00	
DMF	0.04	0.02	0.00	
δ(Si—H) (hexane) (ppm)	4.06	4.16	4.19	4.26

[a] $\Delta\delta$(Si—H) = δ(Si—H) (solvent) — δ(Si—H) (hexane).
[b] For acetone, DMSO, diethyl ether, acetonitrile, nitromethane, THF, dioxane, CCl$_4$, cyclohexane, $\Delta\delta$ ≈ 0—0.03 ppm.

larly in alkoxysilanes $(RO)_n Si(CH_3)_{4-n}$ measured usually as $\Delta\nu$(OH) of phenol or $\Delta\nu$(NH) of pyrrol [10,11], show interactions of n-electrons of the oxygen bound to silicon with protons. The donor-acceptor properties of organoalkoxysilanes in the presence of aromatic compounds as examined by Voronkov et al. [12,13] indicate that the aromatic ring would be the electron acceptor in the
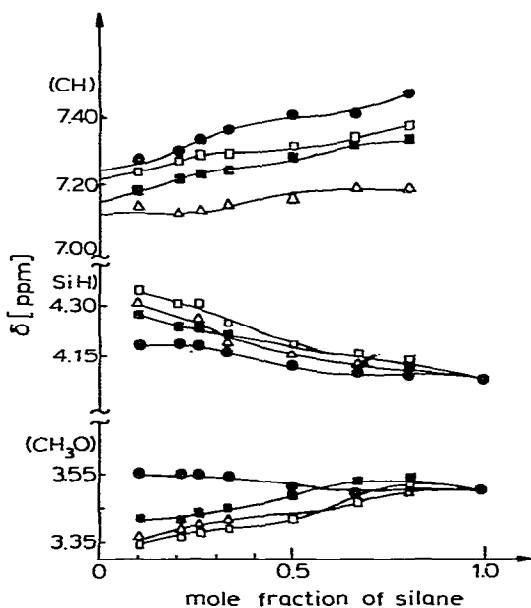

Fig. 1. Concentration dependence of proton chemical shifts for C—H and Si—H of trimethoxysilane and for C—H of solvent in the trimethoxysilane—solvent systems (benzene, □; toluene, △; chlorobenzene, ■; chloroform, ●).

alkoxysilane—solvent intermolecular complex, while the oxygen of the alkoxy substituent at silicon would be the electron donor. Our supplementary examination of the tetramethoxysilane—solvent system (Table 2) confirms Voronkov's observations as regards benzene solvent and shows that the proton chemical shift of the methoxy group is upfield (in the case of chloroform-downfield) and of the solvent downfield. Thus, the direction change and $\Delta\delta$ values are very similar to those of the trimethoxysilane-solvent complex (Fig. 1).

A significant change in δ(H—Si), occurring in the same direction (downfield), was observed for trialkoxysilanes interacting with halogenated hydrocarbons. Since the composition of such complexes of $(RO)_3SiH$ with $CHCl_3$ and with aromatic solvents are 1:1 and 1:2 [5,15], the change in ν(Si—H) [4] as well as in δ(H—Si) can be explained by interactions between the protonic hydrogen of chloroform and n-electrons [14] of the oxygen of one or two alkoxy groups.

On the other hand, the slight high-field shift of hydrogen atoms of the methoxy group observed in all aromatic solvents examined (contrary to in chloroform — Fig. 1), may be interpreted roughly in terms of weak hydrogen bond formed by C—H of methoxy group with π-electrons of another molecule of solvent interacting with the solute. Nevertheless, π-electron-acceptor behavior of the benzene ring seems to predominate in specific interactions with trialkoxysilanes.

In the interpretation of the absence of a change in the hydrogen (on Si) atom shielding in solvents of relatively high donor properties (DMSO, acetone, DMF, acetonitrile and some alcohols), the suggested coordination of the solvent to Si atom, suggested on the basis of the IR study appears also to be supported in the case of ^{1}H NMR chemical shift measurements.

The most evident confirmation comes from a comparison of the NMR and IR spectral data of the trialkoxysilane—acetone and trialkoxysilane—acetophenone systems. The experimental shift of the stretching vibration of trimethoxysilane in acetone and acetophenone ($\Delta\nu = 57$ and 49 cm^{-1}, respectively) as well as the observed shift of ν(C=O) of the solvent to lower frequency, imply coordination of the C=O group to the trimethoxysilane [4]. However, the different values of $\Delta\delta$(H—Si) of trimethoxysilane for the above solvents is brought about by π-acceptor interaction of the aromatic ring of acetophenone with n-electrons of the oxygen of the alkoxy group. The latter interaction with silane is exclusively sp^3d and/or sp^3d^2 complex formation which does not influence the H(Si) shielding. The increase in O—Si—O angles and the increase in the electron density on

TABLE 2

THE CHANGE IN ^{1}H NMR SHIFT OF TETRAMETHOXYSILANE IN VARIOUS SOLVENTS $(\Delta\delta_1)$ AND OF THE SOLVENT IN TETRAMETHOXYSILANE $(\Delta\delta_2)$ [a]

Solvent	$\Delta\delta_1$ (ppm)	$\Delta\delta_2$ (ppm)
Benzene	—0.05	0.12
Toluene [b]	—0.04	0.08
CHCl$_3$	0.03	0.20

[a] $\Delta\delta_1 = \delta(Si(OCH_3)_4)$ (solvent) — $\delta(Si(OCH_3)_4)$ (hexane). $\Delta\delta_2 = \delta$(C—H) $(Si(OCH_3)_4)$ — δ(C—H) (neat).
[b] δ(C—H) = 7.13.

silicon, causing the change in the configuration from sp^3 to sp^3d, slightly influence the H(Si) shielding, as was already explained in the ^{1}H NMR study of triethoxysilane in some, mainly nucleophilic, N-containing solvents [16].

We can conclude that trimethoxysilane forms two kinds of intermolecular complexes with acetophenone (1:1 and 1:2) as a result of C=O coordination to the silicon atom, as well as bonding of the aromatic ring with n-electrons of oxygen atoms of the silane, while the aliphatic ketone (acetone) can interact with the trimethoxysilane only as a result of coordination to silicon which leads to the formation of complexes of sp^3d and sp^3d configuration. On the contrary, we would like to emphasize that the absence of a change in the H(Si) atom shielding and the high $\Delta\nu$(Si—H) vibrational frequency of the trimethoxysilane observed simultaneously might be indirect evidence for coordination of the given electron-donor solvent molecule to the silicon atom.

All the effects mentioned earlier [1—5], may be combined in the case of trialkoxysilane—alcohol interactions, with predominating coordination of one or two molecules of alcohol to the silane (in analogy to such intermolecular complexes as $(MeO)_4Si \cdot 2$ ROH [17]) and competitive hydrogen bonding with the oxygen of the alkoxy substituents.

Experimental

The trialkoxysilane and tetramethoxysilane used were prepared as described previously [1,3]. The solvents under study were purified by standard methods and dried carefully. Measurements of proton chemical shifts for the trialkoxysilanes in different solvents were carried out using a Tesla spectrometer with 600 Hz sweep for full scale and with TMS as the internal standard. The concentration of trialkoxysilane and tetramethoxysilane in the given solvent was 10%. The concentration of the selected solvent in tetramethoxysilane was also 10%.

Each value of proton chemical shift (δ) was taken as an average of three measurements carried out when equilibrium between trialkoxysilane and solvent was established (after 5 min—3 h) and $\Delta\delta$(Si—H) was constant. These values were obtained with an estimated accuracy of at least ±0.02 ppm.

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