Journal of Organometallic Chemistry, 146 (1978) 1—5

VIBRATIONAL SPECTROSCOPIC STUDY OF TRIALKOXYSILANE—SOLVENT INTERACTIONS

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(Received August 30th, 1977)

Summary

The shifts in the stretching vibration frequencies of the Si—H bond recorded for $(RO)_3SiH$ (where R = CH_3, C_2H_5, C_3H_7, i-C_3H_7) in a number of solvents are interpreted in terms of trialkoxysilane—solvent interactions.

Introduction

Detailed kinetic studies of oxidative and solvolytic cleavage of the Si—H bond in the presence of copper(II) salts revealed a non-linear dependence of the observed rate constants on $[\text{copper(II)}]_0$ for trialkoxysilanes [1—3]. The different mechanistic pathways are readily accounted for by a pre-equilibrium step for the trialkoxysilane reaction involving an interaction of the solvent with silane [3]. Our preliminary study of the IR spectra and ^{1}H NMR chemical shifts of trialkoxysilane in DMF and methanol supports this assumption [3]. It is well-known that halogenosilanes form numerous complexes with electron-donating molecules, such as teriary amines and phosphines, as well as other organic compounds [4]; e.g. tetrahydrofuran forms a binary complex with trichlorosilane of the composition 1 : 1 melting at —91°C [5]. Such coordination of a solvent molecule to the silane takes place only when an electron-withdrawing substituent is present on the silicon atom. IR spectroscopic measurements by Voronkov and Lebedeva confirm intermolecular interactions of methyl (or ethyl) dichlorosilane and trichlorosilane with a number of solvents [6—8]. Since the electronegativity of alkoxy substituents is close to that of halogen (OCH_3 —0.727; Cl —0.745), solvation of alkoxysilanes by organic solvents seemed likely, and so we examined trialkoxysilane—solvent interactions. The results indicate the existence of the molecular complexes which are intermediates in reactions of the Si—H bond.

Results and discussion

The results of an IR study of the series $HSi(OR)_3$ (where R = CH_3, C_2H_5, C_3H_7, i-C_3H_7) in several polar and non-polar solvents are presented in Table 1. $\Delta\nu$-

TABLE 1

THE SHIFT ($\Delta\nu$) AND INTEGRATED INTENSITY (A) OF THE SILICON—HYDROGEN STRETCHING BAND OF TRIALKOXYSILANES IN SEVERAL SOLVENTS

Solvent	Donor number	Acceptor number	ϵ [a]	A [b] × 10^{-3} (M^{-1} cm^{-1}) for $(MeO)_3SiH$	$\Delta\nu$(Si—H) [c] (cm^{-1})			
					$(MeO)_3SiH$	$(EtO)_3SiH$	$(PrO)_3SiH$	$(i\text{-}PrO)_3SiH$
1 Dimethyl sulphoxide	29.8	19.3	45.0	0.62	53	24	2	—6
2 Dimethylformamide	26.6	16.0	36.1	0.74	12	12	6	—5
3 Trimethylphosphate	23.0		20.6	0.85	47	46	6	—2
4 Methanol	19.0	41.3	32.6	0.62	17	20	17	10
5 Ethanol	18.5	37.1	25.1	0.78	16	20	7	6
6 Acetone	17.0	12.5	20.7	0.98	57	4	0	—2
7 Acetonitrile	14.1	18.9	38.0	0.85	7	6	6	0
8 Nitrobenzene	4.4	14.8	34.8	0.95	10	14	14	6
9 Nitromethane	2.7	20.5	35.9	1.30	17	14	8	2
10 CH_2Cl_2		20.4	9.1	0.90	7	4	6	0
11 $CHCl_3$		23.1	4.8	0.88	7	6	6	3
12 Tetrahydrofuran	20.0	8.0	7.6	1.11	0	2	0	—2
13 Diethylether	19.2	3.9	4.3	1.15	—1	—1	0	—2
14 Dioxane	14.8	10.6	2.2	0.78	—1	—2	—4	—4
15 Benzene	0.1	8.2	2.3	1.30	2	2	0	—2
16 CCl_4		8.6	2.2	0.73	1	0	0	0
17 Cyclohexane			2.0	0.99	1	0	2	0
18 Hexane (reference solvent)		0	1.9	0.85				
η(Si—H) hexane (cm^{-1})					2203	2196	2194	2190

[a] ϵ = dielectric constant. [b] A = integrated intensity of Si—H bands. [c] $\Delta\nu$(Si—H) = ν(Si—H) (solvent) — ν(Si—H) (hexane).

(Si—H) expresses the shift of the stretching vibration frequency of the Si—H bond measured in a given solvent relative to ν(Si—H) in hexane (in cm^{-1}). A shows the integrated intensity of the Si—H bond of trimethoxysilane in a given solvent (in M^{-1} cm^{-1}). Also are given empirical parameters, expressing donor properties, (Donor number), acceptor properties (Acceptor number) and dielectric constants (ϵ) of the solvents examined [9].

From knowledge of the characteristics of the silicon atom and the Si—H bond [4,10], we can expect the following influences in trialkoxysilane—solvent interactions, leading to an increase (positive $\Delta\nu$) or decrease (negative $\Delta\nu$) of the Si—H vibration frequency in trialkoxysilane:

(1) nucleophilic attack of the solvent molecule on silicon leading to (*a*) a decrease in (*p*—*d*) π bond back donation and hence an increase of the electron-withdrawing character of the alkoxy group (+$\Delta\nu$), (*b*) increase of the electron density at the Si atom (+$\Delta\nu$).

(2) electrophilic attack of the acceptor solvent molecule on hydrogen causing an increase of hydridic character of the hydrogen (+$\Delta\nu$).

(3) interactions of the acceptor solvent molecule with *n*-electrons of oxygen atoms of the alkoxy group leading (as in case 1a) to a lower (*p*—*d*) π bond order in the silane (+$\Delta\nu$). (Such a redistribution of electrons presumably increases the degree of *s*-character of the hydrogen-directed silicon orbital resulting in a shortening of the Si—H bond [11]).

(4) hydrogen bond formation involving the *n*-electrons of oxygen (Si—H···O) or nitrogen of the solvent (—$\Delta\nu$). The last effect predominates in the case of methyl (or ethyl) dichlorosilane—solvent interactions [6,7].

(5) a dipole-dipole character of the interactions, proportional to $(\epsilon - 1)/(2\epsilon + 1)$ ($\pm\Delta\nu$).

The observed shifts $\Delta\nu$ may be considered as the sum of the above effects, mainly nucleophilic and electrophilic actions of the solvent molecules at the silicon. It is, however, important to recognize all the influences involved and to estimate their respective contributions.

The large over-all shift ($\Delta\nu$) of the Si—H vibration bond to higher frequencies for trimethoxysilane and triethoxysilane solvated by strongly nucleophilic solvents (DMSO, DMF, trimethylphosphate) arises from effect 1. The shift is partly compensated or overcompensated with propoxysilanes, presumably due to steric hindrance and the lower —*I* effect of propoxy substituents compared with methoxy and ethoxy groups and thus effect 4 is predominant in the case of isopropoxysilane. In addition to this nucleophilic attack, a strongly amphoteric solvent such as alcohol may interact at the same time as an electrophile (effects 2 and 3). The positive values of $\Delta\nu$(Si—H) for all trialkoxysilanes in alcohols indicate the dominant contribution of effects 1—3.

One of the most notable results presented in Table 1 is the extremely large positive $\Delta\nu$(Si—H) of trimethoxysilane solvated by acetone. Our preliminary ^{1}H NMR and UV-VIS spectroscopic measurements confirm the formation of a spectroscopic complex between $(MeO)_3SiH$ and acetone [12]. The composition of this complex is $(MeO)_3SiH \cdot 2$ acetone, as determined by the isomolar series method. Similar conclusions can also be drawn from analysis of ν(C=O) stretching band of acetone solvated by trimethoxysilane used as solvent (Table 2). The observed shift ν(C=O) to lower frequencies ($\Delta\nu = 5$ cm^{-1}) compared with

TABLE 2

ν(C=O) AND ν(C—D) STRETCHING BANDS OF ACETONE AND $CDCl_3$, RESPECTIVELY, IN TRIMETHOXYSILANE AND HEXANE SOLVENTS

Solvent	ν(C=O) (acetone)	ν(C—D) ($CDCl_3$)
Trimethoxysilane	1718	2240
Hexane	1723	2254

hexane solvent implies a coordination of the acetone molecules to the trimethoxysilane. The details of these unusual effects will be the subject of a separate publication.

The shift of ν(Si—H) to higher frequencies in solvents of low donor property and relatively high acceptor number such as nitromethane, nitrobenzene, dichloromethane, trichloromethane, and to a lesser extent acetonitrile, are mainly due to their electrophilic interactions with hydrogen (effect 2) and/or on n-electrons of the oxygen of the alkoxy groups (effect 3). This conclusion is supported by the observed decrease of the stretching frequency of the C—D bond of d-chloroform (Table 2, $\Delta\nu = 14$ cm^{-1}) solvated by trimethoxysilane (d-chloroform was used to avoid the overlapping of C—H bands of two substances).

The very small $\Delta\nu$(SiH) shift for solvents of relatively high donor property and poor electrophilic properties such as THF, diethylether, and to a lesser extent dioxan and acetone, may arise from either a combination of effects 1 and 4, with effect 4 predominating, or the dipole interactions (effect 5), observed with other non-polar solvents (benzene, CCl_4, cyclohexane). The increase in integrated intensity (A), given in Table 1 for trimethoxysilane as an example, may also point to hydrogen bond formation (effect 4) between alkoxysilane and, in particular, THF, diethylether and benzene.

We conclude that the stretching vibration frequency shift of the Si—H bond of trialkoxysilanes is markedly compensated in the following order of the substituents at the silicon: $CH_3O \geqslant C_2H_5O > C_3H_7O >$ i-C_3H_7O when the nucleophilic action of the solvent is predominant and a coordination of the solvent to the Si atom is anticipated. However, when trialkoxysilane is attacked predominantly by solvents of relative high acceptor number and weak donor property, the substituent effect is less appreciable. On the other hand, a close relationship exists between the observed $\Delta\nu$(Si—H) shift and the kinetic results of the Si—H bond reactivity. The rate of oxidation of the Si—H bond in trimethoxysilane in the presence of cupric salts varies in the following order [3,13]; DMSO $\geqslant CH_3OH \geqslant C_2H_5OH >$ DMF $\approx$ acetone $\gg$ dioxane, acetonitrile, that is, except for acetone, in the same sequence as $\Delta\nu$(Si—H).

Experimental

IR spectra were recorded with a Perkin—Elmer 580 spectrometer using a 0.0014 cm NaCl cell. Wavenumbers were read with an accuracy of 1 cm^{-1}. The concentration of trialkoxysilane was 0.15—0.30 M. The concentration of acetone and $CDCl_3$ in trimethoxysilane and hexane were 0.12—0.65 M. The integrated intensity was calculated for a one molar solution of the trimethoxysilane. The solvents used were purified by standard methods and dried carefully. The trialkoxysilanes used were prepared as previously described [3,14].

Each value was taken as the average of three measurements carried out when equilibrium between the trialkoxysilane and solvent had been established (after 5 min—3 h) and $\Delta\nu$(Si—H) was constant.

Acknowledgement

The authors wish to thank Dr Barbara Marciniec and Mrs Maria Włodarczak, M.Sc., for recording some of the spectra.

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