

A MULTINUCLEAR NMR SPECTROSCOPY STUDY OF ALKOXYSILANES

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Summary

^{17}O , ^{29}Si , and ^{13}C NMR spectra of more than 100 mono-, di-, tri- and tetra-alkoxysilanes $\text{R}_{4-n}\text{Si}(\text{OR}')_n$; $\text{R} = \text{C}_n\text{H}_{2n+1}$, Ph, CH_2Cl , CH_2Br ; $\text{R}' = \text{C}_n\text{H}_{2n+1}$, CH_2Ph , $\text{CH}_2\text{CH}_2\text{Cl}$, $\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CH}_2\text{C}\equiv\text{CH}$, CH_2CF_3 , $(\text{CH}_2)_3\text{Cl}$, $(\text{CH}_2)_3\text{CN}$ have been studied.

Linear relationships between the chemical shifts of ^{17}O , ^{29}Si , ^{13}C in alkoxy silanes and the inductive and steric constants of substituents R and R' were observed. Different transmission of electronic effects along the Si-O bond in various directions was revealed by means of ^{13}C , ^{29}Si , ^{17}O NMR spectroscopy and correlation analysis. The results are discussed in terms of $(p-d)_\pi$ -bonding between the oxygen and silicon atoms in compounds containing an Si-O bond.

Introduction

An atom of element M which has vacant d -orbitals, can function as an electron acceptor from a substituent X in an M-X fragment (X is a substituent with a lone electron pair or unsaturated π -system). The most widespread hypothesis explaining π -acceptor properties of element M is the one postulating $(p-d)_\pi$ -bonding between the lone electron pair or π -electron system of the substituent X and the vacant d -orbitals of element M [1-13].

Alkoxy silanes, which have already been studied by means of ^1H [14-24] and ^{29}Si [23,25-42] NMR spectroscopy also belong to this class of compounds. The data obtained have been generally discussed in terms of $(p-d)_\pi$ -interaction in the Si-O bond. The ^{13}C NMR spectroscopic data available in the literature [35-49] for alkoxy silanes demonstrate a certain lack of consensus in discussing the effects of substituents in these compounds. ^{17}O NMR spectra have been reported for only 4 ethoxy silanes $\text{Me}_{4-n}\text{Si}(\text{OEt})_n$ [41] and 3 (acetoxymethyl)ethoxy silanes $\text{Me}_{3-n}\text{Si}(\text{OEt})_n\text{CH}_2\text{OAc}$ [38].

There has been considerable discussion in the literature as to whether $(p-d)_\pi$ -back bonding occurs in the Si-O bond. It is with this point in mind that we have tried to

extend the existing NMR information by a multinuclear NMR spectroscopic study of a number of mono-, di-, tri- and tetra-alkoxysilanes. Since all the data were subjected to a correlation analysis, we also measured ^{13}C , ^{29}Si , ^{17}O chemical shifts (CS) for compounds, whose spectra have been previously reported in the literature, as they have been recorded under different experimental conditions.

Results and discussion

1. ^{17}O NMR spectroscopy

The parameters of ^{17}O NMR spectra for the compounds studied are listed in Tables 1–4. The position of ^{17}O resonance signals in alkoxysilanes varies over a 70 ppm range. The magnitude of β - and γ -effects on the screening of ^{17}O nuclei (substitution of the hydrogen atom by a CH_3 group in β - and γ -position with respect to oxygen) in silicon derivatives shows little difference from that in carbon analogues [50,51]: 30 and -5 ppm, respectively. The half-width of ^{17}O resonance signals ($\Delta\nu_{1/2}$) ranges from 110 Hz ($\text{Me}_3\text{SiOCH}_2\text{CF}_3$) to 680 Hz for $\text{Si}(\text{OC}_5\text{H}_{11})_4$. $\Delta\nu_{1/2}$ of ^{17}O resonances are generally limited by quadrupole relaxation time T_2 and are directly proportional to the rotational correlation time for the molecule (τ_c), which, for a given sample, decreases with the rising temperature and lowering solution viscosity [51,52]. An approximate relationship between the molecule size and $\Delta\nu_{1/2}$ for the studied compounds was observed: an increased molecular radius implies a greater linewidth of ^{17}O resonance.

Linear correlations were noted between ^{17}O CS in alkoxysilanes and those in the corresponding alcohols (Tables 5 and 6). The coefficient ρ in these equations shows little variation with different substituents at the silicon atom. A linear relationship has been found [53] to exist between the ^{17}O CS for methyl ethers (MeOR) and the OH stretching frequencies ($\nu(\text{OH})$) of the corresponding saturated alcohols ROH:

$$\delta(^{17}\text{O}) = 6413.7 - 1.7705 \nu(\text{OH}) \quad (r = 0.987; n = 11) \quad (1)$$

We have found that a similar correlation also exists between ^{17}O CS in the alkoxysilanes Et_3SiOR (eq. 2) and MePh_2SiOR (eq. 3) and the OH stretching frequencies of the corresponding alcohols [54] ROH:

$$\delta(^{17}\text{O}) = 3718(\pm 21) - 3.2(\pm 0.6) \nu(\text{OH}) \quad (r = 0.97; n = 6) \quad (2)$$

$$\delta(^{17}\text{O}) = 3722(\pm 21) - 3.2(\pm 0.6) \nu(\text{OH}) \quad (r = 0.97; n = 6) \quad (3)$$

As follows from correlations 1–3, ^{17}O CS in alkoxysilanes are more sensitive to the effects of substituents at the oxygen atom than in ethers, which may be due to partial π -bonding in the Si–O fragment of alkoxysilanes. Similar values of coefficients in correlations 2 and 3 suggest that the phenyl ring at the silicon atom insignificantly affects the properties of oxygen nuclei.

Our preliminary investigations showed that, apart from inductive effects, the steric effects of substituents are necessary for ^{17}O CS description. We failed to detect statistically significant multiple correlations for the entire data array. However, linear correlations do exist, within a more limited series of alkoxysilanes (Table 7). The correlation coefficients are comparatively small; therefore, in a number of cases we can only speak of certain tendencies in the variation of oxygen screening caused by different substituents. Correlations were found to deteriorate with the increasing number of alkoxy groups in the molecule within the series under study.

This may be due to two factors: (1) an increase in the molecule size implies broadening of ^{17}O resonances, thus affecting the accuracy of ^{17}O CS measurements; (2) the increasing complexity of molecules and the possibility of interactions between substituents cause the experimental points to deviate from the probable linear correlations. This is illustrated by the fact that the influence of the steric factor on ^{17}O CS increases with the number of alkoxy groups as is witnessed by increased ρ/ρ' ratios (Table 7). Inductive and steric constants alone appear insufficient to explain variations in ^{17}O CS under the influence of substituents in tri- and tetra-alkoxysilanes. The results of correlation analysis show that an increase in electron-acceptor properties of substituents at the oxygen causes highfield shift of the ^{17}O resonance (Table 7). The diamagnetic shielding contribution σ_{dia} decreases with decreasing electron density at the oxygen atom [55], thereby leading to a downfield shift of ^{17}O resonances. Therefore, the observed upfield shift of the ^{17}O resonance with increasing acceptor properties of the substituent at the oxygen confirms the dominant role of the paramagnetic term σ_{para} in ^{17}O nuclei screening in alkoxy derivatives of silicon. Coefficients ρ characterizing the sensitivity of ^{17}O CS to the effects of substituents at oxygen are the same for mono-, di-, tri- and tetra-alkoxy derivatives of silicon within the limits of error.

On the other hand, the sensitivity of ^{17}O CS to the influence of substituents at silicon is considerably smaller in magnitude and sometimes even opposite to that observed for the substituents at oxygen (Table 7). This may be indicative of additional opposite effects, acting along the Si-O bond, as compared with the C-O bond (cf. also coefficients ρ in eq. 4 and 5):

$$\delta(^{17}\text{O})(\text{Me}_2\text{RSiOEt}) = 14.7(\pm 2.8) + 3.6(\pm 2.6)\sigma^* + 8.1(\pm 4.1)E_s \quad (4)$$

$(r = 0.93; n = 6)$

$$\delta(^{17}\text{O})(\text{Me}_3\text{SiOCH}_2\text{R}) = 11.5(\pm 3.7) - 8.6(\pm 3.2)\sigma^* - 0.6(\pm 5.0)E_s \quad (5)$$

$(r = 0.98; n = 6)$

We have studied the dependence of ^{17}O CS on the number of alkoxy substituents within 9 series of alkoxy silanes, $\text{R}_{4-n}\text{Si}(\text{OR}')_n$ ($\text{R} = \text{Cl, Me, Et, Ph}$; $\text{R}' = \text{Et, Pr, CH}_2\text{CH}=\text{CH}_2, \text{CH}_2\text{C}\equiv\text{CH, CH}_2\text{CH}_2\text{OMe, CH}_2\text{CF}_3$). If inductive effects were only present in the $\text{X}_{4-n}\text{Si}(\text{OR})_n$ series, ^{17}O CS would increase smoothly with increasing n , because our CNDO/2 calculations of partial charges on oxygen nuclei demonstrate an increase in the negative charge for this sequence (Table 8). However, experimental data show (Fig. 1), that this is not the case. The transition $n = 1 \rightarrow 2$ inflicts appreciable downfield shift, whereas subsequent substitutions cause gradual upfield shifts.

These experimental curves could be explained if we assume that the position of ^{17}O resonances in alkoxy silanes is dominated by π -electron density at the oxygen nuclei and, consequently, by π -charge as well as partial double bonding between the oxygen and silicon atoms, which is represented by the term Q_{AB} [51] in the equation for paramagnetic shielding contribution. Enhanced $(p-d)_{\pi}$ -bonding between the oxygen and silicon atoms decreases π -electron charge on the oxygen atom and increases the order of the Si-O bond (consequently, Q_{AB} value). These two factors explain the observed downfield shift of ^{17}O resonances upon transition from $n = 1$ to $n = 2$. The degree of participation of each oxygen lone pair in $(p-d)_{\pi}$ -interaction

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TABLE 1
 ^{17}O , ^{29}Si , ^{13}C NMR PARAMETERS δ (ppm), $\Delta\nu_{1/2}$ (Hz) FOR MONOALKOXY-SILANES $\text{R}^1\text{R}^2\text{SiOR}$

No	R^1	R^2	R	^{17}O		$\delta(^{29}\text{Si})$	$\delta(^{13}\text{C})_{\text{R}^1}$				$\delta(^{13}\text{C})_{\text{R}^2}$				$\delta(^{13}\text{C})_{\text{R}}$			
				δ	$\Delta\nu_{1/2}$		C(1)	C(2)	C(3)	C(4)	C(1)	C(2)	C(3)	C(4)	C(1)	C(2)	C(3)	C(4)
1	Me	Me	Et	14.5	140	14.53	-0.45	-	-	-	-	-	58.30	18.65	-	-	-	
2	Me	Me	Pr	11.0	200	16.82	-0.45	-	-	-	-	-	64.28	26.13	10.38	-	-	
3	Me	Me	$\text{CH}_2\text{CH}=\text{CH}_2$	7.6	200	18.53	-0.39	-	-	-	-	-	63.76	137.52	114.40	-	-	
4	Me	Me	$\text{CH}_2\text{C}\equiv\text{CH}$	5.0	340	21.43	-0.32	-	-	-	-	-	50.95	82.41	73.50	-	-	
5	Me	Me	$(\text{CH}_2)_2\text{OMe}$	5.2	230	18.08	-0.45	-	-	-	-	-	62.13	74.28	59.01	-	-	
				-23.8 ^a	280													
6	Me	Me	CH_2CF_3	-10.1	110	23.48	-0.71	-	-	-	-	-	61.81	125.01	-	-	-	
7	Et	Et	Me	-30.8	220	20.23	^b	4.42	6.76	-	-	-	50.76	-	-	-	-	
8	Et	Et	Et	5.2	260	17.85	^b	4.81	6.89	-	-	-	58.62	18.85	-	-	-	
9	Et	Et	Pr	0.6	280	17.68	^b	4.82	6.88	-	-	-	64.86	26.45	10.40	-	-	
10	Et	Et	i-Pr	33.6	320	16.04	^b	5.13	6.95	-	-	-	64.93	26.10	-	-	-	
11	Et	Et	Bu	0.8	240	17.52	^b	4.87	6.89	-	-	-	62.91	35.55	19.43	14.04	-	
12	Et	Et	s-Bu	29.2	360	15.75	^b	5.32	6.95	-	-	-	69.99	32.85	10.06	-	-	
														23.50				
13	Et	Et	CH_2Ph^c	-0.4	320	19.95	^b	4.74	6.82	-	-	-	64.99	141.74	128.42	127.18	-	
14	Et	Et	$(\text{CH}_2)_2\text{Ph}^d$	3.0	400	18.59	^b	4.68	6.76	-	-	-	64.40	39.97	139.47	129.33	-	
15	Et	Et	$(\text{CH}_2)_2\text{Cl}$	0.6	420	20.19	^b	4.74	6.76	-	-	-	63.82	45.10	-	-	-	
16	Et	Et	$\text{CH}_2\text{CH}=\text{CH}_2$	-3.0	320	19.66	^b	4.81	6.82	-	-	-	64.08	137.91	114.19	-	-	
17	Et	Et	$\text{CH}_2\text{C}\equiv\text{CH}$	-5.4	300	22.68	^b	4.74	6.69	-	-	-	51.29	82.52	72.91	-	-	
18	Et	Et	$(\text{CH}_2)_2\text{CN}$	0.2	320	21.24	^b	4.48	6.62	-	-	-	58.50	21.82	119.20	-	-	
19	Et	Et	$(\text{CH}_2)_2\text{OMe}$	-5.8	280	19.21	^b	4.74	6.76	-	-	-	62.65	74.61	59.01	-	-	
				-25.0 ^a	300													
20	Et	Et	CH_2CF	-20.6	240	23.71	^b	4.68	6.50	-	-	-	62.23	125.01	-	-	-	
21	Me	Ph	Me	-26.4	300	-1.15	-3.34	136.02	134.59	128.09	130.04	-	51.02	-	-	-	-	

TABLE 2
 ^{17}O , ^{29}Si , ^{13}C NMR PARAMETERS δ (ppm), $\Delta\nu_{1/2}$ (Hz) FOR DIALKOXYSILOANES $\text{R}^1\text{R}^2\text{Si}(\text{OR})_2$

No	R ¹	R ²	R	^{17}O		$\delta(^{29}\text{Si})$		$\delta(^{13}\text{C})_{\text{R}^1}$		$\delta(^{13}\text{C})_{\text{R}^2}$		$\delta(^{13}\text{C})_{\text{R}}$					
				δ	$\Delta\nu_{1/2}$			C(1)	C(2)	C(3)	C(4)	C(1)	C(2)	C(3)	C(4)		
1	Me	H	Et	27.6	300	-16.99	-3.05	-	-	-	-	-	-	59.08	18.37	-	-
2	Me	Me	Et	27.7	280	-4.30	-2.78	-2.78	-	-	-	-	-	58.51	18.80	-	-
3	Me	Pr	Et	25.4	280	-5.31	-4.74	16.75	16.75	17.98	-	-	-	58.11	18.50	-	-
4	Me	C ₃ H ₁₁ ^a	Et	25.4	340	-5.09	-4.81	14.10	22.62	35.87	22.81	-	-	58.17	18.59	-	-
5	Me	<i>c</i> -C ₆ H ₁₁	Et	22.0	340	-7.27	-6.95	25.61	28.08	27.04	27.04	-	-	58.30	18.59	-	-
6	Me	CH ₂ Cl	Et	23.6	220	-15.67	-6.17	26.88	-	-	-	-	-	58.95	18.44	-	-
7	Me	(CH ₂) ₃ Cl	Et	25.4	310	-6.54	-4.80	11.95	26.94	47.40	-	-	-	58.24	18.50	-	-
8	Me	Ph	Et	24.2	360	-18.10	-4.25	134.60	135.69	128.01	130.22	-	-	58.90	18.71	-	-
9	Me	(CH ₂) ₂ CN	Et	25.2	300	-9.29	-4.84	10.79	11.11	121.14	-	-	-	58.56	18.46	-	-
10	Me	(CH ₂) ₃ CN	Et	25.4	340	-7.15	-4.74	13.90	20.08	20.21	119.71	-	-	58.43	18.52	-	-
11	Me	CH=CH ₂	Et	26.0	380	-18.80	-4.34	134.82	135.20	-	-	-	-	58.64	18.73	-	-
12	Me	Cl	Et	35.7	140	-28.80	-1.01	-	-	-	-	-	-	59.56	18.42	-	-
13	H	Ph	Et	24.4	400	-30.44	-	132.32	134.14	128.04	130.63	-	-	59.41	18.24	-	-
14	Ph	Ph	Et	21.4	480	-32.40	^b	133.96	135.52	128.44	130.78	-	-	59.35	18.80	-	-
15	4-Cl-Ph	4-Cl-Ph	Et	17.8	580	-33.40	^b	137.53	136.88	128.83	131.94	-	-	59.55	18.73	-	-
16	4-Me-Ph	4-Me-Ph	Et	19.2	580	-31.20	^b	140.46	135.65	129.22	130.71	-	-	59.22	18.80	-	-

TABLE 3
 ^{17}O , ^{29}Si , ^{13}C NMR PARAMETERS δ (ppm), $\Delta\nu_{1/2}$ (Hz) FOR TRIALKOXSILANES $\text{R}^1\text{Si}(\text{OR})_3$

No	R ¹	R	^{17}O		$\delta(^{29}\text{Si})$	$\delta(^{13}\text{C})_{\text{R}^1}$				$\delta(^{13}\text{C})_{\text{R}}$				
			δ	$\Delta\nu_{1/2}$		C(1)	C(2)	C(3)	C(4)	C(1)	C(2)	C(3)	C(3)	
1	Me	Et	23.8	260	-43.35	-7.02	-	-	-	-	-	58.43	18.46	-
2	Me	Pr	19.2	260	-43.35	-7.14	-	-	-	-	-	64.54	26.04	10.39
3	Me	$\text{CH}_2\text{CH}=\text{CH}_2$	17.0	330	-41.74	-6.95	-	-	-	-	-	63.76	136.80	114.66
4	Me	$\text{CH}_2\text{C}\equiv\text{CH}$	13.8	360	-39.73	-6.30	-	-	-	-	-	51.15	81.43	74.02
5	Me	$\text{CH}_2\text{CH}_2\text{OMe}$	14.2	460	-41.95	-7.15	-	-	-	-	-	62.13	73.89	58.81
			-23.8 ^a	380										
6	Me	CH_2CF_3	-1.1	270	-41.25	-7.99	-	-	-	-	-	61.78	124.43	-
7	H	Et	25.6	220	-58.77	-	-	-	-	-	-	58.56	18.33	-
8	Et	Et	20.0	280	-44.62	2.73	6.63	-	-	-	-	58.62	18.52	-
9	C_5H_{11} ^b	Et	22.4	210	-45.53	10.20	22.23	33.01	30.41	-	-	58.43	18.46	-
10	$\text{CH}_2\text{NC}_3\text{H}_{10}$	Et	20.4	290	-51.86	46.10	59.23	26.59	24.11	-	-	59.23	18.27	-
11	CH_2Cl	Et	19.2	260	-58.32	23.92	-	-	-	-	-	59.47	18.39	-
12	CHCl_2	Et	19.4	200	-70.62	56.80	-	-	-	-	-	60.44	18.20	-
13	$\text{CH}=\text{CH}_2$	Et	16.5	240	-58.73	130.05	137.06	-	-	-	-	58.75	18.39	-
14	$\text{CH}\equiv\text{CH}$	Et	23.3	190	-74.73	81.76	92.87	-	-	-	-	59.21	18.07	-
15	Ph	Et	19.8	340	-57.91	131.67	135.11	128.09	130.56	-	-	58.88	18.33	-
16	4-MePh ^c	Et	19.4	290	-57.21	127.12	135.24	129.00	140.38	-	-	58.82	18.39	-
17	Cl	Et	27.2	200	-70.4	-	-	-	-	-	-	60.25	17.79	-
18	F	Et	11.6	160	-88.61	-	-	-	-	-	-	59.79	18.23	-

^a $\delta(^{17}\text{O})_{\text{OMe}}$. ^b $\delta(^{13}\text{C})_{\text{C(S)}}$ 11.63 ppm. ^c $\delta(^{13}\text{C})_{\text{C(S)}}$ 21.64 ppm.

TABLE 4

 ^{17}O , ^{29}Si , ^{13}C NMR PARAMETERS δ (ppm), $\Delta\nu_{1/2}$ (Hz) FOR TETRAALKOXSILANES $\text{Si}(\text{OR})_4$

No	R	^{17}O		$\delta(^{29}\text{Si})$	$\delta(^{13}\text{C})$		
		δ	$\Delta\nu_{1/2}$		C(1)	C(2)	C(3)
1	Me	-26.5	200	-78.76	51.28	-	-
2	Et	12.4	280	-82.05	59.40	18.26	-
3	Pr	7.2	440	-82.13	65.38	25.87	10.27
4	i-Pr	42.6	380	-85.83	65.84	25.48	-
5	i-Bu	5.8	460	-82.67	70.12	30.78	18.96
6	s-Bu	39.0	460	-86.00	70.71	32.20	9.80
						22.72	
7	C_5H_{11} ^a	7.8	640	-82.05	63.69	32.43	28.27
8	$\text{CH}_2\text{CH}=\text{CH}_2$	4.2	340	-81.72	64.60	136.34	114.86
9	$\text{CH}_2\text{C}\equiv\text{CH}$	2.6	480	-82.09	52.12	80.85	74.41
10	CH_2CF_3	-12.6	290	-86.82	62.85	124.21	-
11	$\text{CH}_2\text{CH}_2\text{OMe}$	2.0	560	-82.59	62.98	73.63	58.75
		-24.4 ^b	380				

^a $\delta(^{13}\text{C})_{\text{C}(4)}$ 22.68, $\delta(^{13}\text{C})_{\text{C}(5)}$ 14.10. ^b $\delta(^{17}\text{O})_{\text{OMe}}$.

TABLE 5

 ^{17}O NMR PARAMETERS FOR ALCOHOLS ROH

No	R	$\delta(^{17}\text{O})$ (ppm)	$\Delta\nu_{1/2}$ (Hz)	Literature values
1	Me	-35.2	200	-37.0 ^a , -38 ^b , -37 ^c
2	Et	5.7	220	5.9 ^a , 8 ^b , 6 ^c
3	Pr	0.2	320	-0.5 ^a , 0 ^c
4	i-Pr	40.1	260	39.8 ^a , 39 ^b , 38 ^c
5	Bu	0.6	360	0 ^a , -1 ^b , -4 ^c
6	i-Bu	-1.5	360	-2.0 ^a , 0 ^c
7	s-Bu	33.1	300	34.0 ^a , 36 ^d , 41 ^c
8	CH_2CF_3	-22.0	240	-23.6 ^a
9	CH_2Ph	6.4	300	7.9 ^a , 4 ^d
10	$\text{CH}_2\text{CH}=\text{CH}_2$	-0.7	200	-1.6 ^a
11	$\text{CH}_2\text{C}\equiv\text{CH}$	-0.8	200	-1.9 ^a
12	$(\text{CH}_2)_2\text{Cl}$	-2.7	300	-1.8 ^a , -3 ^c
13	$(\text{CH}_2)_2\text{CN}$	-0.6	320	
14	$(\text{CH}_2)_2\text{Ph}$	3.0	580	
15	$(\text{CH}_2)_3\text{Cl}$	-3.8	480	

^a Ref. 61, pure sample, 65°C. ^b Ref. 62, pure sample, 34–36°C. ^c Ref. 63, ^{17}O -enriched pure sample.^d Ref. 62, 50% solution in CCl_4 , 70–80°C.

TABLE 6

CORRELATIONS BETWEEN ^{17}O CS IN ALKOXSILANES AND CORRESPONDING ALCOHOLS $\delta(^{17}\text{O})_{\text{R}_4-\text{nSi}(\text{OR})_4} = \delta_0 + \rho\delta(^{17}\text{O})_{\text{ROH}}$

No	Series	δ_0	ρ	r	n
1	Me_3SiOR	8.7(±1.7)	0.9 (±0.2)	0.98	5
2	Et_3SiOR	-0.8(±1.5)	0.87(±0.06)	0.99	13
3	MePh_2SiOR	3.0(±1.0)	0.85(±0.06)	0.99	11
4	$\text{Me}_2\text{Si}(\text{OR})_2$	21.4(±1.7)	0.9 (±0.2)	0.98	5
5	$\text{MeHSi}(\text{OR})_2$	20.2(±1.1)	1.0 (±0.1)	0.98	7
6	$\text{MeSi}(\text{OR})_3$	17.6(±1.6)	0.9 (±0.2)	0.98	5
7	$\text{Si}(\text{OR})_4$	6.4(±0.7)	0.93(±0.03)	0.99	9

TABLE 7

RESULTS OF CORRELATION ANALYSIS $\delta(^{17}\text{O}) = \delta_0 + \rho \Sigma \sigma^* + \rho' \Sigma E_s$ FOR ^{17}O CHEMICAL SHIFTS

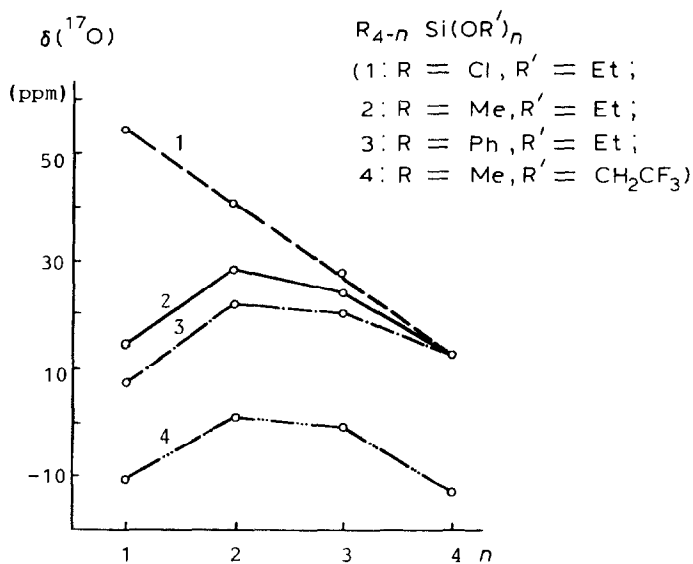
No	Series	δ_0	ρ	ρ'	r	n	$r^+{}^a$
1	Me_3SiOR	$9.7(\pm 4.9)$	$-23.3(\pm 5.4)$	$-4.5(\pm 4.3)$	0.95	7	0.423
2	$\text{Me}_2\text{Si}(\text{OR})_2$ ^b	$22.3(\pm 5.5)$	$-25.9(\pm 5.9)$	$-5.5(\pm 4.9)$	0.96	7	0.423
3	$\text{MeSi}(\text{OR})_3$ ^b	$17.8(\pm 5.1)$	$-26.4(\pm 5.8)$	$-7.1(\pm 4.8)$	0.96	7	0.423
4	$\text{Si}(\text{OR})_4$ ^b	$0.2(\pm 9.5)$	$-20.4(\pm 17.2)$	$-16.0(\pm 11.2)$	0.68	11	0.340
5	Me_2RSiOEt	$14.7(\pm 2.8)$	$3.6(\pm 2.2)$	$8.1(\pm 4.1)$	0.93	6	0.315
6	$\text{R}^1\text{R}^2\text{Si}(\text{OEt})_2$	$26.0(\pm 0.6)$	$-1.3(\pm 0.9)$	$1.4(\pm 0.5)$	0.76	14	0.351
7	$\text{RSi}(\text{OEt})_3$	$23.0(\pm 2.3)$	$-3.1(\pm 1.6)$	$3.0(\pm 2.4)$	0.75	8	0.233

^a Correlation coefficient for σ^*/E_s relationship. ^b The effects of substituents acting through system O-Si-O are neglected.

TABLE 8

NET ATOMIC CHARGES OF ALKOXYSILANE OXYGEN ATOMS

No	Compound	$\Delta q_{\text{O}}(e)$
1	Me_3SiOEt	-0.2675
2	$\text{Me}_2(\text{ClCH}_2)\text{SiOEt}$	-0.2698
3	$\text{Me}_3\text{SiOCH}_2\text{CF}_3$	-0.2494
4	$\text{Me}_2\text{Si}(\text{OEt})_2$	-0.2798
5	$\text{Me}(\text{ClCH}_2)\text{Si}(\text{OEt})_2$	-0.2752
6	$\text{Me}_2\text{Si}(\text{OCH}_2\text{CF}_3)_2$	-0.2555
7	$\text{MeSi}(\text{OEt})_3$	-0.2828
8	$\text{ClCH}_2\text{Si}(\text{OEt})_3$	-0.2807
9	$\text{MeSi}(\text{OCH}_2\text{CF}_3)_3$	-0.2609
10	$\text{Si}(\text{OEt})_4$	-0.2937
11	$\text{Si}(\text{OCH}_2\text{CF}_3)_4$	-0.2701

Fig. 1. The dependence of ^{17}O CS in alkoxy silanes $R_{4-n}\text{Si}(\text{OR}')_n$ on the number of alkoxy groups, n .

declines with the increasing number of alkoxy substituents, thereby leading to an increase in the partial π -charge on the ^{17}O nucleus. By analogy with systems containing a double-bonded oxygen atom, an increasing π -charge accounts for the observed upfield shift of ^{17}O resonance signals [56,57]. The upfield shift may also be partially caused by variation in the inductive effect of the RSi substituent as the number of alkoxy groups increases.

In chloroethoxysilanes $\text{Cl}_{4-n}\text{Si}(\text{OEt})_n$ upfield shifts of ^{17}O resonances were observed with increasing n . When considering only inductive effects of the chlorine atom and ethoxy group, an opposite slope of the relationship $\delta(^{17}\text{O})/n$ ($\sigma_{\text{Cl}}^* = 2.9$; $\sigma_{\text{OEt}}^* = 1.68$ [58]) would be expected. Therefore we must assume that $(p-d)_\pi$ -bonding in the Si–O bond is probably prevalent over the inductive effect of SiCl groups.

2. ^{29}Si chemical shifts

As has been noted earlier [29] an increase in the number of alkoxy groups causes a gradual shift of ^{29}Si resonance signals to higher fields in the studied alkoxy silane series $\text{R}_{4-n}\text{Si}(\text{OR}')_n$ (Tables 1–4). The contributions of each alkoxy group to ^{29}Si nuclei screening are not additive and are determined by substituent R at the silicon. For example, in $\text{Me}_{4-n}\text{Si}(\text{OR}')$ the transition $n = 1 \rightarrow 2$ results in an upfield shift of ^{29}Si resonance by 20 ppm, transitions $n = 2 \rightarrow 3$ and $n = 3 \rightarrow 4$ causing a further shielding of ^{29}Si nuclei by approximately 40 ppm; the transition $n = 1 \rightarrow 2$ in $\text{Ph}_{4-n}\text{Si}(\text{OEt})_n$ results in an upfield shift of ^{29}Si by 25 ppm, $n = 2 \rightarrow 3$ and $n = 3 \rightarrow 4$, in upfield shifts of ^{29}Si resonances by 25 and 24 ppm, respectively.

Equations characterising the dependence of ^{29}Si CS on the inductive and steric constants of substituents are summarized in Table 9.

Except for $\text{Si}(\text{OR}')_4$, the screening of ^{29}Si nuclei was found to be more sensitive to the inductive rather than steric effects of substituents in all studied compounds. A rise in electron-acceptor properties of substituents in the alkoxy radical implies deshielding of the silicon nucleus, whereas a rise in electron-acceptor properties of the substituent at the silicon atom, on the contrary, increases the shielding of the ^{29}Si nuclei. This indicates unequal transmission of electronic effects in different directions along the Si–O bond. This can be explained if we assume that the position of ^{29}Si resonance signals is determined, in the first approximation, by two factors: the inductive effect of the substituent and the effect of $(p-d)_\pi$ -interaction along the Si–O bond, which have been found to affect the screening of ^{29}Si nuclei in the opposite ways. A gain in the $-I$ effect of alkoxy groups with the increasing

TABLE 9

RESULTS OF CORRELATION ANALYSIS $\delta(^{29}\text{Si}) = \delta_0 + \rho \Sigma \sigma^* + \rho' \Sigma E_s$ FOR ^{29}Si CHEMICAL SHIFTS

No	Series	δ_0	ρ	ρ'	r	n	r^+
1	Me_3SiOR	17.1(± 1.1)	9.1(± 1.2)	1.5(± 0.9)	0.98	7	0.423
2	MePh_2SiOR	-2.2(± 0.6)	6.4(± 1.1)	1.9(± 0.9)	0.93	10	0.010
3	$\text{R}^1\text{R}^2\text{R}^3\text{SiOEt}$	17.1(± 1.3)	-10.0(± 1.3)	3.9(± 1.2)	0.97	13	0.515
4	$\text{Me}_2\text{Si}(\text{OR})_2$	-2.2(± 0.7)	6.1(± 0.4)	2.2(± 0.3)	0.99	7	0.423
5	$\text{R}^1\text{R}^2\text{Si}(\text{OEt})_2$	-6.1(± 1.8)	-17.9(± 2.6)	1.3(± 1.5)	0.92	14	0.351
6	$\text{MeSi}(\text{OR})_3$	-40.4(± 1.0)	3.7(± 0.4)	2.4(± 0.3)	0.99	7	0.423
7	$\text{RSi}(\text{OEt})_3$	-48.6(± 2.6)	-10.9(± 1.5)	0.6(± 2.1)	0.94	11	0.233
8	$\text{Si}(\text{OR})_4$	-78.3(± 1.3)	1.6(± 0.5)	2.2(± 0.3)	0.93	12	0.378

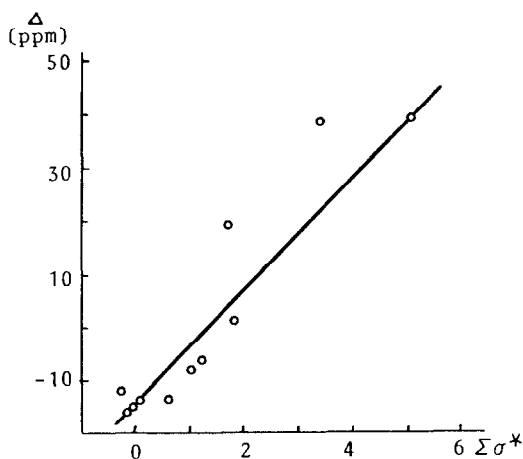


Fig. 2. Correlation of Δ values ($\Delta = \delta(^{29}\text{Si}_{\text{R}^1\text{R}^2\text{R}^3\text{SiMe}}) - \delta(^{29}\text{Si}_{\text{R}^1\text{R}^2\text{R}^3\text{SiOEt}})$) with Taft inductive substituent constants.

acceptor properties of the substituent at the oxygen weakens ($p-d$) $_{\pi}$ -bonding, whereas electron-acceptor substituents at the silicon, on the contrary, stimulate ($p-d$) $_{\pi}$ -interaction by increasing the positive charge on the silicon atom. The sensitivity of ^{29}Si CS to the effects of OR' substituents decreases with the increasing number of alkoxy groups in the molecule (cf. coefficients ρ in equations 1, 4, 6, 8; Table 9). The sensitivity of ^{29}Si CS to the influence of SiR substituents depends on the number of alkoxy substituents at silicon in a more complex way: transition from $n = 1$ to $n = 2$ increases coefficient ρ , whereas a further transition to $n = 3$ reduces the influence of the SiR substituent.

If we compare ^{29}Si CS of methylsilanes $\text{R}^1\text{R}^2\text{R}^3\text{SiMe}$ [31,32] with ^{29}Si CS of the corresponding ethoxysilanes $\text{R}^1\text{R}^2\text{R}^3\text{SiOEt}$ (Fig. 2), the difference in ^{29}Si CS $\Delta = \delta(^{29}\text{Si}(\text{R}^1\text{R}^2\text{R}^3\text{SiMe})) - \delta(^{29}\text{Si}(\text{R}^1\text{R}^2\text{R}^3\text{SiOEt}))$ is proportional to the sum of Taft constants $\Sigma\sigma^*$ for substituents $\text{R}^1\text{R}^2\text{R}^3$. The points corresponding to substituents $\text{R}^1\text{R}^2\text{R}^3 = \text{Me}_2\text{OEt}$ and $\text{Me}(\text{OEt})_2$ deviate from the linear relationship (eq. 6):

$$\Delta(^{29}\text{Si}) = -14.8(\pm 1.5) + 10.0(\pm 0.9)\Sigma\sigma^* \quad (r = 0.98; n = 9) \quad (6)$$

This suggests the existence of an additional bonding effect in alkoxy silanes, the extent of which depends on the electronic properties of other substituents in the molecule.

3. ^{13}C chemical shifts

We have noted several linear correlations between ^{13}C CS and the inductive and steric constants of substituents (Table 10). As would be expected, the transmission coefficient lowers with the increasing distance between the substituent and the indicator centre.

The behaviour of $\delta(^{13}\text{C})/\sigma^*$, E_s relationships for C_{α} and C_{β} -atoms of the ethoxy group is opposite in all studied ethoxysilanes. This contradicts the influence of substituent inductive effects, according to which it would be natural to expect a similar variation in the ^{13}C CS of ethoxy group carbons. Feshin [43,44] explains

TABLE 10

RESULTS OF CORRELATION ANALYSIS $\delta(^{13}\text{C}) = \delta_0 + \rho\Sigma\sigma^* + \rho'\Sigma E_s$ FOR ^{13}C CHEMICAL SHIFTS

No	Series	C*	δ_0	ρ	ρ'	r	n	r^+
1	Me ₃ SiOR	C _{Me}	-0.6(±0.3)	-0.8(±0.2)	-0.5(±0.2)	0.96	7	0.423
2	R ¹ R ² R ³ SiOEt	C _{OC_α}	58.6(±0.07)	0.5(±0.07)	-0.04(±0.07)	0.94	13	0.515
3	R ¹ R ² R ³ SiOEt	C _{OC_β}	18.8(±0.04)	-0.1(±0.04)	-0.04(±0.03)	0.85	13	0.515
4	Me ₂ Si(OR) ₂	C _{Me}	-3.3(±0.5)	-1.0(±0.3)	-0.7(±0.2)	0.96	7	0.423
5	R ¹ R ² Si(OEt) ₂	C _{OC_α}	58.4(±0.1)	0.8(±0.1)	0.2(±0.05)	0.94	14	0.351
6	MeSi(OR) ₃	C _{Me}	-7.5(±0.7)	-0.8(±0.2)	-0.5(±0.2)	0.94	7	0.423
7	RSi(OEt) ₃	C _{OC_α}	58.5(±0.1)	0.5(±0.08)	0.3(±0.05)	0.99	11	0.233

these discrepancies by the geminal interaction between the positive charge on the silicon and the O-C bond that results in an increase in the shielding of ethoxy group C_β carbon, observed experimentally.

The sensitivity of ethoxy group ^{13}C CS to the influence of substituents at the Si atom is practically independent of the number of ethoxy groups present. The sensitivity of the SiMe group ^{13}C resonances to the effect of the O-substituent shows no dependence on the number of alkoxy groups either (cf. entries 1, 4, 6, in Table 10). This may be due to the removal of indicator sites from the substituent. ^{13}C resonances of the SiMe carbon undergo upfield shifts with increasing electron-withdrawing properties of the O-substituent, which is opposite to the effect of the SiR substituent on the C_α carbon resonance. This also indicates that the Si-O bond in alkoxysilanes displays unequal transmission of substituent effects in different directions. This fact can be explained by considering the $(p-d)_\pi$ -bonding concept, as the polar effect of the substituent reduces the extent of $(p-d)_\pi$ -interaction in the direction from silicon to oxygen, whereas in the direction from oxygen to silicon the reverse is the case.

It has been found for ^{13}C CS of the aromatic ring in methyldiphenylalkoxysilanes that

$$\Delta = 22.9(\pm 1.9) - 0.15(\pm 0.01)\delta(^{13}\text{C}_i) \quad (r = 0.98; n = 11) \quad (7)$$

where $\Delta = \delta(^{13}\text{C}_p) - \delta(^{13}\text{C}_m)$.

According to ref. 59, relation 7 shows the prevailing π -inductive influence of the methylphenylalkoxy group on the ^{13}C CS of the aryl groups. Variations in the alkoxy radical cause only redistribution of π -electron density in the aromatic ring without any net charge transfer to or from the silicon atom. Hence, there is no need to consider the effect of $(p-d)_\pi$ -bonding between the Ph group and the silicon atom when discussing the properties of the MePhSiOR group with respect to the benzene ring. The aforesaid is confirmed also by the values of σ_{R}^0 -constants calculated for the MePhSiOR group. The data in Table 11 demonstrate that the values of σ_{R}^0 -constants alter negligibly with variation of the substituent R properties. The MePhSiOR group was found to show σ -electron-donor and π -electron-acceptor properties with respect to the aromatic ring. In view of the above facts, it can be assumed that the oxygen lone pair is favoured for the $(p-d)_\pi$ -bonding with the vacant d -orbitals of the silicon atom over the π -electron system of the phenyl ring, the other conditions being equal.

TABLE 11

VALUES OF σ_1 AND σ_R^0 CONSTANTS FOR SiMePh(OR) GROUPS ^a

No	R	σ_1	σ_R^0
1	Me	-0.22	0.10
2	Et	-0.25	0.10
3	Pr	-0.25	0.10
4	i-Pr	-0.31	0.09
5	Bu	-0.25	0.10
6	i-Bu	-0.25	0.10
7	s-Bu	-0.31	0.09
8	CH ₂ Ph	-0.24	0.10
9	(CH ₂) ₂ Cl	-0.30	0.10
10	CH ₂ C≡CH	-0.30	0.10
11	CH ₂ CF ₃	-0.06	0.11

^a Values have been derived as in ref. 49.

Thus a combined use of ¹³C, ¹⁷O, ²⁹Si NMR served to reveal unequal transmission of electronic effects of substituents in different directions along the Si-O bond, which can be qualitatively explained within the framework of the hypothesis of (*p-d*)_π-bonding between oxygen and silicon atoms. The lone pairs of the oxygen atom are favoured for the above-mentioned interaction over the π-electron system of the phenyl ring.

Experimental

¹⁷O NMR spectra were obtained using a Bruker WM-360 spectrometer operating at 48.82 MHz, pulse width 40 μs, number of scans 10⁴-10⁵; CS were measured and reported relative to external H₂O, accuracy ±0.3 ppm.

²⁹Si NMR spectra were obtained using a Bruker WH-90/DS spectrometer operating at 17.88 MHz with proton decoupling, pulse width 5 μs, delay between pulses 3-10 s, number of scans 500-1000; CS were measured relative to internal TMS, accuracy ±0.04 ppm.

¹³C NMR spectra were obtained using a Bruker WH-90/DS spectrometer operating at 22.63 MHz with complete proton decoupling, pulse width 5 μs; CS were measured relative to internal TMS, accuracy ±0.07 ppm. All spectra were obtained for 50% solutions in CDCl₃, the temperature of samples being 313 K.

The studied di-, tri-, and tetra-alkoxysilanes were prepared by standard proce-

TABLE 12

PHYSICAL PROPERTIES OF MONOALKOXYLANES R¹R²SiOR

No	R ¹	R ²	R	M.p. (°C/mmHg)	n_D^{20}	d_4^{20}
1	Et	Et	(CH ₂) ₂ Ph	102-103(2)	1.4825	0.9166
2	Et	Et	(CH ₂) ₂ CN	107-112(20)	1.4360	0.9132
3	Et	Et	CH ₂ CF ₃	146-148(758)	1.3830	0.9948
4	Me	Ph	CH ₂ Ph	173-175(1)	1.5810	1.0735
5	Me	Ph	(CH ₂) ₂ Cl	146-148(2)	1.5560	1.1145
6	Me	Ph	CH ₂ C≡CH	130-135(2)	1.5571	1.0510
7	Me	Ph	CH ₂ CF ₃	101(1)	1.5060	1.1641
8	Ph	Me	CH ₂ CF ₃	72-74(10)	1.4400	1.1161
9	Me	i-Bu	Et	180-185(760)	1.4200	0.7995

TABLE 13
PHYSICAL PROPERTIES OF DIALKOXYSILANES $R^1R^2Si(OR)_2$

No	R ¹	R ²	R	M.p. (°C/mmHg)	n_D^{20}	d_4^{20}
1	Me	C ₃ H ₁₁	Et	92–94(25)	1.4078	0.8494
2	Me	c-C ₆ H ₁₁	Et	110–112(25)	1.4355	0.9130
3	Me	H	CH ₂ Ph	152–154(5)	1.5270	1.0510
4	Me	H	(CH ₂) ₂ Ph	159–160(3)	1.5188	1.0241
5	Me	H	(CH ₂) ₂ OMe	90–93(15)	1.4108	0.9783
6	Me	H	CH ₂ CF ₃	125–130(760)	1.3150	–
7	Me	CH ₂ Cl	CH ₂ CF ₃	47–49(12)	1.3480	–
8	Me	Ph	CH ₂ CF ₃	86–86.5(10)	1.4055	1.2760
9	Pr	Ph	CH ₂ CF ₃	100.5–101.5(10)	1.4100	1.2366
10	Ph	Ph	CH ₂ CF ₃	128–129(5)	1.4620	1.2862

dures from the corresponding chlorosilanes and alcohols in the presence of triethylamine. Trimethylalkoxysilanes and triorganylpropargyloxy- and -2-cyanoethoxysilanes were prepared similarly. The other triorganylalkoxysilanes were obtained by triorganylhydrosilane alcoholysis in the presence of $H_2PtCl_6 \cdot 6H_2O$. Physical constants of the known compounds corresponded to literature data [60]; the constants of new compounds are listed in Tables 12 and 13. Partial charges were calculated by the CNDO/2 method with the aid of a standard computer program on an ES-1045 computer.

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