

THE INFRARED SPECTRA
OF MONOALKOXY(METHYL)CHLOROSILANES
AND MONO(CHLOROALKOXY)METHYLCHLOROSILANES*

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The infrared absorption spectra of the organosilicon compounds $(\text{CH}_3)_{3-n}(\text{RO})\text{SiCl}_n$, where $\text{R} = \text{C}_2\text{H}_5$, $(\text{CH}_3)_2\text{CH}$, $(\text{CH}_3)_3\text{SiCH}_2$, $\text{Cl}(\text{CH}_2)_2$, $\text{Cl}(\text{CH}_2)_3$, Cl_2CHCH_2 , Cl_3CCH_2 and $n = 0-3$, were measured and analysed. The absorption band assignment to the characteristic vibrations of the substituents OR was carried out.

Within the framework of a study of organosilicon compounds we measured and analysed the infrared spectra of the compounds having together with the methyl groups and the chlorine atoms always one alkoxy (ethoxy, isopropoxy, trimethylsilylmethoxy), or chloroalkoxy (2-chloroethoxy, 3-chloropropoxy, 2,2-dichloroethoxy, 2,2,2-trichloroethoxy) group attached to silicon. On the grounds of the experience obtained from the analysis of other compounds¹⁻¹², and on the grounds of the "isolation effect" of the relatively heavy and voluminous central silicon atom we have attempted to determine the absorption bands belonging to the characteristic group vibrations of the alkoxy (or chloroalkoxy) groups in all the series of compounds with the same alkoxy (or chloroalkoxy) group and with variable number of the methyl and chlorine substituents.

EXPERIMENTAL

Compounds used. All the compounds $(\text{CH}_3)_{3-n}\text{ROSiCl}_n$, where $\text{R} = (\text{CH}_3)_3\text{SiCH}_2$, $(\text{CH}_3)_2\text{CH}$, C_2H_5 , $\text{Cl}(\text{CH}_2)_2$, $\text{Cl}(\text{CH}_2)_3$, Cl_2CHCH_2 , Cl_3CCH_2 were prepared by the reaction of a chlorosilane $(\text{CH}_3)_{3-n}\text{SiCl}_{n+1}$ with an appropriate alcohol in diethyl ether. The alcohol was always added to the solution of the chlorosilane (10% excess) and the reaction mixture was then heated 1 h to reflux. Methyl (chloro)alkoxysilanes were obtained by rectification. All the operations were carried out under nitrogen. The purity of all products was checked by gas-liquid chromatography and ¹H-NMR spectroscopy. Table I gives analysis and some physical properties of methyl(chloro)alkoxysilanes. Worth mentioning is a regular change of the refraction indices

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with the substitution on silicon: the n_D^{20} value increases with the increasing number of the chlorine atoms in the $(CH_3)_{3-n}Cl_nSi$ -group about equally in all the series of the compounds $(CH_3)_{3-n}Cl_n \cdot SiOR$ (for all the groups R), while the increment value decreases with increasing number of chlorines roughly in order 0.180, 0.060, and 0.030.

IR spectra were recorded with Model UR 20, double-beam spectrophotometer (Zeiss, Jena) in the $4000-400\text{ cm}^{-1}$ region. The compounds studied were measured as approximately 1M solutions in CCl_4 and CS_2 using KBr cell of 0.01 cm thickness. The frequency scale of the instrument was checked by polystyrene.

TABLE I

Analysis and Physical Properties of the $(CH_3)_{3-n}(RO)SiCl_n$ Compounds

Compound	% Cl		n_D^{20}		B., p., °C/Torr		Yield %
	found	calculated	found	lit. ¹³	found	lit. ¹³	
$(CH_3)_2(RO)SiCl$							
R = $(CH_3)_3SiCH_2$	18.68	18.01	1.4112	—	87/96	—	88
$(CH_3)_2CH$	23.20	23.22	1.3925	1.3917	105.5	102–104	67
C_2H_5	26.18	25.56	1.3908	—	95	94–95	65
$Cl(CH_2)_3$	19.32	18.94	1.4315	—	112/100	—	59
$Cl(CH_2)_2$	23.33	20.48	1.4285	—	85/74	—	86
Cl_2CHCH_2	17.10	17.08	1.4448	—	103/80	—	63
Cl_3CCH_2	14.87	14.65	1.4542	—	114/60	—	42
$CH_3(RO)SiCl_2$							
R = $(CH_3)_3SiCH_2$	32.14	32.64	1.4172	—	91/83	—	88
$(CH_3)_2CH$	40.99	40.96	1.3991	1.3990	111	111/731	83
C_2H_5	44.35	44.57	1.3972	1.3973	98	99–99.5	67
$Cl(CH_2)_3$	34.20	34.16	1.4382	—	116/105	—	82
$Cl(CH_2)_2$	39.21	36.63	1.4351	—	92/97	—	65
Cl_2CHCH_2	30.64	31.10	1.4492	—	100/64	—	64
Cl_3CCH_2	27.02	27.03	1.4594	—	105/37	—	37
$(RO)SiCl_3$							
R = $(CH_3)_3SiCH_2$	43.74	44.75	1.4202	—	84/70	—	69
$(CH_3)_2CH$	54.97	54.96	1.4037	1.4045	115	116	74
C_2H_5	58.20	59.26	1.4017	1.4045	102	102.4	65
$Cl(CH_2)_3$	46.65	46.65	1.4410	—	116/110	—	56
$Cl(CH_2)_2$	51.54	49.71	1.4380	—	152.5	151–152	83
Cl_2CHCH_2	42.79	42.82	1.4512	—	86/68	58–63/10	60
Cl_3CCH_2	37.32	37.60	1.4624	—	106/40	76–78/16	64

RESULTS AND DISCUSSION

The graphical survey of all the absorption bands observed in the infrared spectra of the monoalkoxy(methyl)chlorosilanes and mono(chloroalkoxy)methylchlorosilanes recorded under given conditions is seen on Figs 1 and 2 respectively. The positions of the individual lines relate to the wavenumbers of the absorption bands, the heights of the lines correspond to the approximate intensity of the absorption bands. Those absorption bands that were assigned empirically are illustrated by thick lines. The regions of the occurrence of the wavenumbers of these characteristic bands are, together with their assignment, summarized in Table II.

The absorption band assignment in the infrared spectra of the compounds studied in this work is based on the fact, that model compounds are of similar structure, which is reflected in analogous occurrence and shape of their characteristic absorption bands. Having discussed the spectra we could have made use in some cases also of the local symmetry of the individual groups.

With all the monochlorosilanes the absorption band between $491-479\text{ cm}^{-1}$ can be undoubtedly ascribed to the stretching vibration of the Si—Cl bond. Monochlorosilanes moreover possess the low intensity absorption band at 536 cm^{-1}

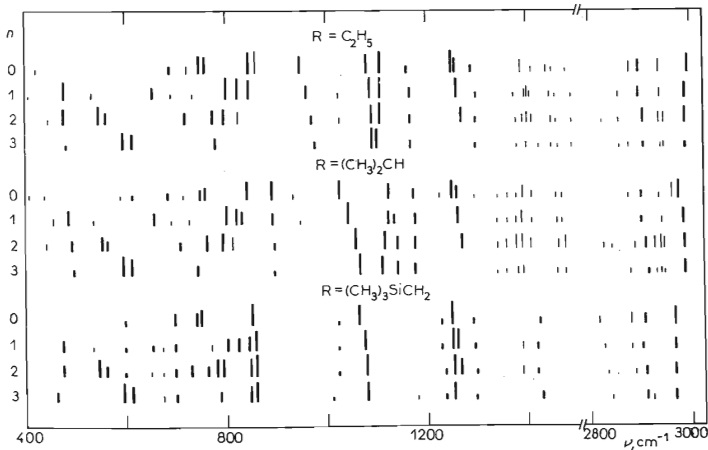


FIG. 1

Graphical Survey of the Infrared Spectra of Monoalkoxy(methyl)chlorosilanes $(\text{CH}_3)_{3-n}(\text{RO})\cdot\text{SiCl}_n$, $n = 0-3$

(Fig. 1 and 2), that we leave for the time being unassigned. Assuming C_{2v} local symmetry of the SiCl_2 grouping with dichlorosilanes we may assign the absorption band of medium intensity between $496-476\text{ cm}^{-1}$ to the symmetric stretching vibration (*A*), and more intensive absorption band between $558-547\text{ cm}^{-1}$ with shoulder at higher wavenumbers ($577-560\text{ cm}^{-1}$) to the antisymmetric stretching vibration (*B*). As for trichlorosilanes, we observed three absorption bands due to the stretching vibration of the SiCl_3 group. A weak band between $500-465\text{ cm}^{-1}$ we assign to the symmetric vibration (in phase), an intensive doublet at $609-578\text{ cm}^{-1}$ and 628 to 591 cm^{-1} we ascribe to other stretching vibration of the SiCl_3 group (out of phase). The doublet occurrence can be explained by the interaction of the chlorine atoms with the alkoxy group, *i.e.* by the removal of degeneracy of both vibrations of the SiCl_3 group (with C_{3v} local symmetry), or by the rotamer population (the rotation

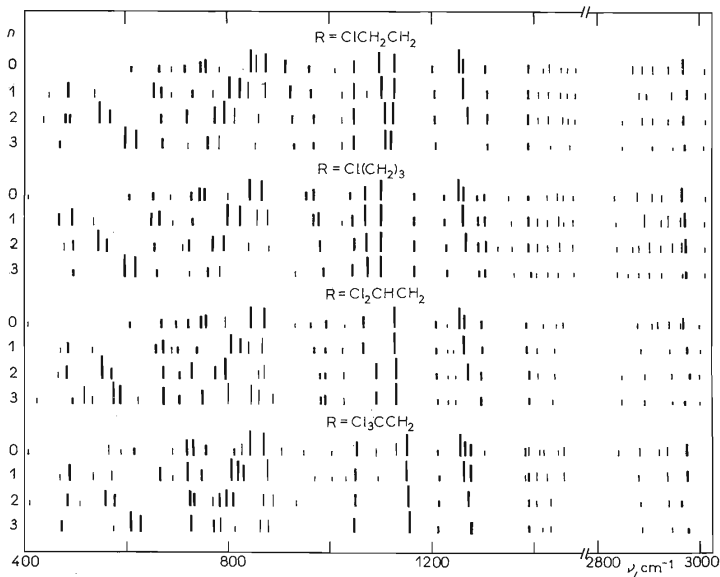


FIG. 2

Graphical Survey of the Infrared Spectra of Mono(chloroalkoxy)methylchlorosilanes $(\text{CH}_3)_{3-n} \cdot (\text{RO})\text{SiCl}_n$, $n = 0-3$

TABLE II

Wavenumbers of the IR Absorption Bands Belonging to the Characteristic Vibrations of the Monoalkoxy(methyl)chlorosilanes and Mono(chloroalkoxy)methylchlorosilanes

Grouping ^a	Vibration	Wavenumber cm ⁻¹	Intensity ^b
SiCl ₁	ν	491—479	s
	?	535	w
SiCl ₂	ν^s	495—476	m
	ν^{as}	558—547 ^c	s
		577—560	s
SiCl ₃	ν^{as}	609—578 ^d	vs
		628—591	vs
	ν^s	500—465	w
SiCH ₃	$\rho(\text{CH}_3)$	785—766 ^d	vs
		799—795	vs
	$\nu(\text{SiC})$	735—710	s
Si(CH ₃) ₂	$\rho^{as}(\text{CH}_3)$	828—820	vs
	$\rho^s(\text{CH}_3)$	810—803	vs
	$\nu^{as}(\text{SiC}_2)$	750—725	m
	$\nu^s(\text{SiC}_2)$	668—654	m
Si(CH ₃) ₃	$\rho^{as}(\text{CH}_3)$	848—842	vs
	$\rho^s(\text{CH}_3)$	758—756 ^d	vs
		750—735	vs
	$\nu^{as}(\text{SiC}_3)$	730—686	w
	$\nu^s(\text{SiC}_3)$	618—612	vw
SiCH ₃	$\delta^s(\text{CH}_3)$	1 271—1 268	vs
Si(CH ₃) ₂	$\delta^s(\text{CH}_3)$	1 265—1 261	vs
Si(CH ₃) ₃	$\delta^s(\text{CH}_3)$	1 257—1 253 ^d	vs
		1 265—1 262	m
		1 392—1 386 ^e	w
Si(CH ₃) _m	$\delta(\text{CH}_3\text{Si})$	1 392—1 386 ^e	w
	$\nu^{as}(\text{CH}_3)$	2 990—2 965 ^f	m
	$\nu^s(\text{CH}_3)$	2 925—2 900 ^e	m
SiOC	$\nu^{as}(\text{CO})$	1 158—1 029 ^{f,g}	vs
SiOC—C	$\nu(\text{CC})$	1 075—890	s
	$\nu^s(\text{SiO})$	780—745	w
CH ₂	δ	1 311—1 278	m
	δ	1 240—1 200	w
	δ sciss	1 465—1 452 ^f	vw
	δ^s	1 398—1 380	vw
	ν^{as}	2 982—2 970 ^f	w
	ν^s	2 950—2 928 ^h	w
CH ₃ C	δ^s	~ 1 380 ^{f,g}	m
	ρ	1 232—1 167	w

^a Grouping with C—Cl bonds see Table III. ^b vs very strong, s strong, m medium, w weak, vw very weak. ^c Shoulder. ^d Doublet. ^e Overlap with other bands. ^f See Discussion. ^g Broad band. ^h Occurrence of another band in the 2 910—2 888 cm⁻¹ region.

of R group about O—Si bond). One can generally observe the increase of the intensity of the absorption bands due to the Si—Cl stretching vibrations with increasing number of chlorines attached to silicon.

A comparison of the spectra of the compounds with the same number of the methyl groups bonded to silicon from the different series enabled us to find out the characteristic absorption bands due to the Si—(CH₃)_m, ($m = 1-3$) grouping in the 900 to 600 cm⁻¹ region. The tentative assignment of the wavenumbers of these bands is shown in Table II and it was carried out on the grounds of analogous absorption band occurrence in this region for the same m , what follows from Figs 1 and 2. Expectedly increasing number of the absorption bands due to the rocking vibration appears for $m = 3$ (compare interaction or rotation assumed above): doublet between 758–735 cm⁻¹ (Table II), and another band between 848–842 cm⁻¹. Asymmetric and symmetric stretching vibration of SiC₃ grouping is shifted to lower wavenumbers (730–686 cm⁻¹, resp. 618–612 cm⁻¹) compared to the vibration of SiC₂ grouping.

The most characteristic absorption band of the Si—(CH₃)_m grouping is a sharp narrow band at 1271–1253 cm⁻¹ belonging to the symmetric deformation vibration, the band being always splitted into doublet when $m = 3$ except for the (CH₃)₃.OCH₂Si(CH₃)₃ compound. The shift of the maximum of this band to higher wavenumbers with gradual substitution of the methyl groups by chlorine is apparent even in very narrow wavenumber region. The asymmetric deformation vibration of Si(CH₃)_m group is not characteristic for the organosilicon compounds. With all the models there exists an overlap of this absorption with other bands, as *e.g.* with the band of the symmetric deformation vibration of the methyl group attached to carbon (Table II). The same is true for the stretching vibration of the C—H bonds in the Si(CH₃)_m grouping. It is known, that organosilicon compounds possess larger absorptivity and their spectra are of simpler character with respect to carbon analogous compounds. (Transfers of the vibration interaction are depressed because of the isolation effect of silicon¹¹.) Figures 1 and 2 therefore give only relatively intensive bands of the asymmetric stretching vibration of the (Si)—C—H bonds; the intensity of these bands is deeply diminished in all the region of the C—H stretching vibration with increasing number of chlorines on silicon.

Dominant absorption band in the 2925–2900 cm⁻¹ region is perhaps that of the symmetric stretching vibration of the (Si)CH₃ group, while the antisymmetric stretching vibration of the alkoxy CH₂ group absorbs in its close proximity (Table II). Several weak absorption bands overlapping one another arise in the 1500–1350 cm⁻¹ region, that are practically of no diagnostic purpose. These are the absorption bands of the deformation vibrations of the CH₃ and CH₂ groups attached both to silicon and carbon.

The Si—O—C grouping shows an absorption band of significant intensity and

TABLE III
Wavenumbers (in cm^{-1}) of the IR Absorption Bands of the $(\text{CH}_3)_3-n(\text{RO})\text{SiCl}_n$ ($n = 0-3$) Compounds Belonging to the Characteristic Vibrations of the Chloroalkoxy and Alkoxy Groups

Grouping ^a	$\text{Cl}_3\text{CCH}_2\text{O}$	$\text{Cl}_2\text{CHCH}_2\text{O}$	$\text{Cl}(\text{CH}_2)_3\text{O}$	$\text{Cl}(\text{CH}_2)_2\text{O}$	ClCH_2O^b	$\text{CH}_3\text{CH}_2\text{O}$	$(\text{CH}_3)_2\text{CHO}$	$(\text{CH}_3)_3\text{SiCH}_2\text{O}$
$(\text{Si})\text{OCR}$	1 052-1 050	1 068-1 066	1 048-1 044	1 050-1 043	1 020	1 092-1 075	1 068-1 029	1 080-1 068
	1 158-1 153	1 133-1 128	1 076-1 072	1 110-1 103	1 056	1 112-1 101	1 128-1 111	—
	—	—	1 107-1 104	1 129-1 121	1 103	—	—	—
CH_2^c	<i>d</i>	984-964	970-958	935-913	943	978-947	898-890	<i>d</i>
	—	996-990	989-971	971-959	965	—	—	—
	1 216-1 210	1 215-1 210	1 168	1 207-1 201	1 165	1 168	1 146-1 128	—
	1 279-1 271	1 301-1 296	1 232-1 226	1 311-1 305	1 240	1 298-1 290	1 179-1 174	1 300-1 290
	1 390-1 387	1 391-1 386	1 292-1 288	1 390	1 285	1 390-1 380 ^e	1 380 ^e	1 430-1 420
—	—	1 306-1 300	—	1 330	—	—	—	—
—	—	1 398-1 392	—	—	—	—	—	—
2 980 ^f	2 970 ^f	2 974 ^f	2 972 ^f	2 968 ^f	2 992 ^f	2 990 ^f	—	—
CCI	728-720 ^g	675-671 ^g	670-659 ^h	678-668 ^h	685 ^h	—	—	—
	820-812 ⁱ	708-702 ⁱ	—	—	—	—	—	—

^a Attemptive assignment of the vibrational mode see Table II. ^b Wavenumber values obtained only for $n = 0$ (see discussion). ^c Grouping CCH_3 in case of $\text{R} = (\text{CH}_3)_2\text{CH}$. ^d No absorption bands were observed under given conditions in the $1\ 000-900\ \text{cm}^{-1}$ region. ^e Overlap with the bands of the SiCH_3 grouping. ^f Wavenumber values $\nu_{\text{as}}\text{CH}_2$ were obtained from the spectra of the trichlorosubstituted compounds. ^g $\nu_s\text{CCl}_3$ and $\nu_s\text{CCl}_2$ respectively. ^h νCCl_1 , $\nu_{\text{as}}\text{CCl}_3$ and $\nu_s\text{CCl}_2$ respectively.

half-width. This band is considered to be characteristic for the Si—O—C grouping despite that its assignment is not unambiguous. Most of all it is ascribed to the stretching vibration of the C—C bond (ref.^{1,2,4,14}). The possibility of the effect of rotamers is not excluded either¹⁵. The wavenumber of this broad band is strongly influenced by the interaction with a molecular rest: for monoalkoxy(methyl)chlorosilanes it appears in the 1130–1029 cm^{-1} region, for mono(chloroalkoxy)methylchlorosilanes it appears in the 1158–1095 cm^{-1} region. This band is splitted into doublet in case of the ethoxy and 2-chloroethoxy derivatives (Fig. 1). A broad isolated absorption band between 1080–1065 cm^{-1} was observed with the series of the compounds having $R = (\text{CH}_3)_3\text{SiCH}_2$ (Fig. 2). The fragment Si—O—(C)_x possess likely also the absorption bands in the 1075–915 cm^{-1} region. The derivatives containing SiCl₃ group have low intensity band at 780–745 cm^{-1} belonging to the stretching vibration of the Si—O bond. This band is overlaped by strong bands of the rocking vibrations of the SiCl₃ group with methyl derivatives (Fig. 1).

Having analysed the spectra of the compounds studied we made eventually use of the model compounds to attempt to find the characteristic group vibrations of the substituents OR. The wavenumbers of the absorption bands due to the vibration of the groupings (Si)—OR, CH₃C, (CH₂)_x, and CCl_n of the individual alkoxy, resp. chloroalkoxy groups are summarized in Table III. An interesting model (CH₃)₃.SiOCH₂Cl is introduced in this table for the sake of comparison. We hope the data in Table III to be of usage for the identification of the groups mentioned above also in the spectra of other compounds than organosilicon.

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