

THE STRUCTURE AND IR SPECTRA OF OXYGEN-CONTAINING CARBOFUNCTIONAL TRIMETHYLGERMANES*

J. POLA, M. JAKOUBKOVÁ and V. CHVALOVSKÝ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

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The wavenumbers of $\nu(\text{C}=\text{O})$, $\nu(\text{C}-\text{O}-(\text{Si}))$, and $\nu(\text{O}-\text{H})$ of the series $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3$, and $\text{C}(\text{O})\text{CH}_3$; $n = 1-4$) were measured. The lower values of $\nu(\text{C}-\text{O}-(\text{Si}))$ and $\nu(\text{O}-\text{H})$ for the members with $n = 1$, compared to the derivatives with $n = 2-4$ and their carbon analogues, were explained by labilisation of the $\text{C}-\text{O}$ bond due to the α -effect. Relative basicities of the oxygen of the compounds $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ ($\text{M} = \text{C}, \text{Ge}$; $n = 1-4$), determined by IR spectroscopy, are in harmony with the electron-donating effect of $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n$ ($n = 1, 2$) groups. The data obtained indicate an easy polarisability of the $(\text{CH}_3)_3\text{GeCH}_2$ -group in the compounds $(\text{CH}_3)_3\text{GeCH}_2\text{OX}$.

A systematic study of IR spectra of oxygen-containing carbofunctional germanes has not yet been performed. The present work is an extension of our previous study of IR spectra of oxygen-containing carbofunctional silanes¹ to analogous germanium compounds $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3$, and $\text{C}(\text{O})\text{CH}_3$; $n = 1-4$). The low wavenumbers of $\nu(\text{C}-\text{O}-(\text{X}))$ and $\nu(\text{O}-\text{H})$ observed in the series $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OX}$ for $n = 1$, relative to the members with $n = 2-4$ or to their carbon analogues were ascribed to back donation of electrons from oxygen to silicon, *i.e.* to the so called α -effect¹. On the contrary, the higher relative basicity of the oxygen of the α -derivatives compared to the other members of the series $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OX}$ is consistent with prevailing electron-donating effect of the $(\text{CH}_3)_3\text{SiCH}_2$ -group which is stronger than similar effect of $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n$ -groups ($n > 1$)²⁻⁴. With the aim of ascertaining whether $(\text{CH}_3)_3\text{GeCH}_2$ -group is similarly polarisable, in the present work the IR spectra of the compounds $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3$, and $\text{C}(\text{O})\text{CH}_3$; $n = 1-4$) were studied and the relative basicities of the oxygen of the compounds $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ were determined.

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EXPERIMENTAL

Preparation of the compounds $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OX}$ ($\text{M} = \text{C}, \text{Ge}$; $\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3$, and $\text{C}(\text{O})\text{CH}_3$) was reported earlier^{1,5-7}. IR spectra of the compounds studied were recorded with a double-beam spectrophotometer Model UR-20, (Zeiss, Jena, GDR) in the regions of KBr prism ($400-850 \text{ cm}^{-1}$), NaCl prism ($650-1700 \text{ cm}^{-1}$), and LiF prism ($1600-4000 \text{ cm}^{-1}$). The instrument was calibrated in the usual way. The spectra were measured of the compounds *in subst.*, using composed KBr cells, and of their solutions (c. 7%) in spectrograde CCl_4 . KBr cells were 0.01 cm thick. The $\nu(\text{O}-\text{H})_{\text{free}}$ absorption band of isoconcentration solutions of 0.005M alcohols, CH_3OH and $(\text{CH}_3)_3\text{MCH}_2\text{OH}$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}$), in CCl_4 was further recorded at a constant temperature of the instrument (35°C), using infrasil cells thick 1 cm. With the compounds $(\text{CH}_3)_3\text{MCH}_2\text{OH}$, the above band was recorded also at varying temperatures (10, 20, 35, 45, and 60°C); its temperature dependence was measured in 1 cm cells (infrasil) placed in a special metallic block whose temperature was maintained constant by a temperature controlled bath. Measurements of hydrogen bonding between the compounds $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OSi}(\text{CH}_3)_3$ ($\text{M} = \text{C}, \text{Ge}$) and phenol (0.02M) were made in the usual way, using 0.5M solutions of these compounds in CCl_4 . NaCl cells were 0.1 cm thick and $\Delta\nu$ were determined with the accuracy of $\pm 3 \text{ cm}^{-1}$.

RESULTS AND DISCUSSION

The wavenumbers of some characteristic vibrations of compounds of the type $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3, \text{C}(\text{O})\text{CH}_3$; $n = 1-4$) are presented in Table I, along with the wavenumbers of their carbon analogues. The wavenumber of the $\nu(\text{C}=\text{O})$ vibration is essentially identical for all trimethylgermylalkyl acetates and is comparable with the wavenumber of $\nu(\text{C}=\text{O})$ of carbon analogues, while the wavenumbers of $\nu(\text{O}-\text{H})$ and $\nu(\text{C}-\text{O}(\text{X}))$ vibrations of the compounds $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OX}$ with $n = 1$ are lower compared to those with $n = 2-4$ or to the compounds $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OX}$.

The above decrease of the wavenumbers of $\nu(\text{C}-\text{O}-\text{X})$ vibrations in α -carbofunctional trimethylgermanes is difficult to interpret in terms of the difference between electronic effects of $(\text{CH}_3)_3\text{GeCH}_2-$ and $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n-$ groups, because of different interaction between $\nu(\text{C}-\text{O}-\text{X})$ and $\nu(\text{M}-\text{C})$ vibrations in the compounds $(\text{CH}_3)_3\text{MCH}_2\text{OX}$ when $\text{M} = \text{C}$ and Ge . (The greater difference between kinematic, and apparently also dynamic, coefficients can make $\nu(\text{C}-\text{O})$ vibrations in germanium (and also silicon) compounds more characteristic). The greater mass of the atom attached to the $\text{C}-\text{O}$ bond of compounds CH_3-OX (*i.e.* substitution of hydrogen for a methyl group) is accompanied by an increase of the wavenumber of the stretching vibration of the $\text{C}-\text{O}$ bond⁸. Different values of $\nu(\text{C}-\text{O})$ for the alcohols $\text{R}-\text{CH}_2-\text{OH}$ (CH_3OH 1030 cm^{-1} , $\text{C}_2\text{H}_5\text{OH}$ 1050 cm^{-1} , $n\text{-C}_3\text{H}_7\text{OH}$ 1060 cm^{-1} , $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ 1040 cm^{-1} , $(\text{CH}_3)_3\text{CCH}_2\text{OH}$ 1030 cm^{-1} , $\text{CH}_2=\text{CHCH}_2\text{OH}$ 1030 cm^{-1} , and $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ 1030 cm^{-1}) (ref.⁹) are obviously due to the mass and electronic effects of substituent R. It is further evident that electron-attracting groups^{10,11} decrease the wavenumber of $\nu(\text{C}-\text{O})$ due to

the decrease of bond order, and thus also of force constant. Correlation of the wavenumbers of $\nu(\text{C—O})$ of the alcohols with polar effects of substituent $R(\sigma^*)$ is of qualitative character¹². The decrease of $\nu(\text{C—O})$ of the compounds $(\text{CH}_3)_3\text{GeCH}_2\text{OX}$ therefore seems to be the result of labilisation of the C—O bond, which cannot be caused by the electron-donating effect of $(\text{CH}_3)_3\text{GeCH}_2$ -group, but is to due electron withdrawal from the C—O group oxygen.

A more detailed discussion of this may be based on the lowering of the $\nu(\text{O—H})$ of trimethylgermylmethanol (Table I), whose $\nu(\text{C—O})$ absorption band is furthermore deformed on the lower wavenumber side. Graphical separation yielded two absorption bands with maxima at 3 628 and 3 615 cm^{-1} and with the ratio of their intensities 3 : 1. The best explanation of the doublet character of the $\nu(\text{O—H})$ band is conformational heterogeneity^{13,14}. In accordance with the studies by Krueger and Mettee^{15,16} and by Kuhne and coworkers¹⁷ the $\nu(\text{O—H})$ band at 3 615 cm^{-1} can be assigned to a rotamer with synclinal arrangement of the trimethylgermyl group and the hydroxylic hydrogen and the band at 3 628 cm^{-1} to a rotamer in which the trimethylgermyl group and hydrogen are in the *trans* position. The lower $\nu(\text{O—H})$ of the *trans* rotamer compared to $\nu(\text{O—H})$ of the *trans* rotamer of alcohols $\text{R—CH}_2\text{OH}$ ($\text{R} = \text{alkyl}$, $\nu(\text{O—H})$ 3 636–3 644 cm^{-1}) (ref.¹³) is similar to the decrease of $\nu(\text{O—H})$ in the *trans* rotamer of the alcohols $\text{X}(\text{CH}_2)_2\text{OH}$ ($\text{X} = \text{halogen}$, CN , NO_2 , etc.; cf.^{15–17}) and confirms the electron attracting effect of the $(\text{CH}_3)_3\text{Ge}$ -group. This follows also from comparison of integrated intensities (the area below the extinction curve) of the $\nu(\text{O—H})$ band of the alcohol ROH : $\text{CH}_3\text{OH} < (\text{CH}_3)_3\text{CCH}_2\text{OH} \approx (\text{CH}_3)_3\text{GeCH}_2\text{OH}$, since this quantity is sensitive to changes in electronic character of the substituent on the C—O bond and increases with increasing electron-accepting ability of the substituent¹⁸. A significant lowering of the $\nu(\text{O—H})$ of *gauche* rotamer could be described to a weak interaction between $\sigma(\text{O—H})$ bond and germanium *d*-orbitals.

The $\sigma(\text{O—H}) - d$ interaction was suggested as the reason of the lower $\nu(\text{O—H})$ of trimethylsilylmethanol and of alcohols of the type $\text{L}_n(\text{CH}_3)_{3-n}\text{SiCH}_2\text{OH}$ ($\text{L} = \text{C}_2\text{H}_5$, C_6H_5) (ref.¹). Additional temperature measurements of IR spectra confirmed that the assymetry of the $\nu(\text{O—H})$ band of the alcohols $(\text{CH}_3)_3\text{MCH}_2\text{OH}$ ($\text{M} = \text{C}$, Si , and Ge) decreases with increasing temperature. A graphical separation of the $\nu(\text{O—H})$ band of trimethylsilylmethanol gave two bands with maxima at 3 627 and 3 614 cm^{-1} and with the ratio of their intensities 10 : 1. We regard it more correct to interpret the lowering of the $\nu(\text{O—H})$ vibration of this compound similarly as in the case of trimethylgermylmethanol. (The area below the extinction curve of the $\nu(\text{O—H})$ of trimethylsilylmethanol equals to the areas for the compounds $(\text{CH}_3)_3\text{MCH}_2\text{OH}$ ($\text{M} = \text{C}$, Ge).

The relative basicity of the oxygen in the compounds $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OX}$ ($\text{M} = \text{C}$, Ge , $n = 1-4$; $\text{X} = \text{H}$, $\text{Si}(\text{CH}_3)_3$), presented in Table I, seems in this connection

TABLE I

Wavenumbers (cm^{-1}) of Some Vibrations of the Trimethylgermanes $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3$, and $\text{C}(\text{O})\text{CH}_3$; $n = 1-4$) and of Their Carbon Analogues, and the Values of $\Delta\nu(\text{O}-\text{H})$ (cm^{-1}) for the $(\text{CH}_3)_3\text{M}(\text{CH}_2)_n\text{OX}$ ($\text{M} = \text{C}, \text{Ge}$; $\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3$; $n = 1-4$) /Phenol/ CCl_4 System

Compound	<i>n</i>	X = H			X = Si(CH ₃) ₃		X = C(O)CH ₃	
		$\nu(\text{O}-\text{H})$	$\Delta\nu(\text{O}-\text{H})^a$	$\nu(\text{C}-\text{O})$	$\Delta\nu(\text{O}-\text{H})$	$\nu(\text{C}-\text{O}-\text{Si})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O}-\text{C})$
$(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OX}$	1	3 628	243	1 000	290	1 072	1 738	1 228
	2	3 629	240	1 042	287	1 072 ^b	1 738	1 246 ^c
	3	3 636	231	1 050	281	1 103	1 739	1 244 ^c
	4	3 636	232	1 065 ^d	281	1 103	1 738	1 241 ^c
$(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OX}^e$	1	3 640	228	1 052 ^f	255 ^g	1 094	1 740	1 238
	2	3 633	236	1 036	279 ^g	1 102 ^g	1 738	1 240
	3	3 636	234	1 058	279 ^g	1 092 ^g	1 740 ^g	1 240 ^g
	4	3 637	233	1 063	277	1 099	1 738 ^g	1 235 ^g

^a Ref.¹⁹. ^b Additional band at $1\,088\text{ cm}^{-1}$. ^c Partially overlapped with $\delta(\text{CH}_3(\text{Ge}))$. ^d Additional band at $1\,025\text{ cm}^{-1}$. ^e Ref.¹ ^f Ref.⁹ $1\,030\text{ cm}^{-1}$. ^g This work.

to be apparently contradictory. Generally higher relative basicity of the oxygen of the compounds with $\text{X} = \text{Si}(\text{CH}_3)_3$ indicates that the trimethylsilyl group, when bonded to the oxygen, is stronger electron donor than hydrogen atom. In view of the ability of silicon to form ($p-d$)_n bond with oxygen this fact seems surprising, but it was already observed with the compounds $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{OX}$ ($\text{X} = \text{H}, \text{Si}(\text{CH}_3)_3$) (ref.^{2,4}). The minimum change of the wavenumber of the $\nu(\text{O}-\text{H})$ of phenol, $\Delta\nu(\text{O}-\text{H})$ observed in the series $(\text{CH}_3)_3\text{C}(\text{CH}_2)_n\text{OX}$ for $n = 1$ is due to the steric effect of the $(\text{CH}_3)_3\text{CCH}_2$ group. The relative basicity of the oxygen of the compounds $(\text{CH}_3)_3\text{Ge}(\text{CH}_2)_n\text{OX}$ with $n = 1, 2$ is higher than the basicity of the other members of the carbon and germanium series. Practically identical relative basicities of α - and β -derivatives do not correspond, however, to the strong electron-donating effect of the $(\text{CH}_3)_3\text{GeCH}_2$ -group which was established by Bott and coworkers²⁰ for carboxylic acids and for germyl-substituted benzenes, but resembles rather the behaviour of the H_3GeCH_2 -group in methoxymethylgermane²¹. The increased relative basicity of (trimethylgermylmethoxy)-trimethylsilane can be explained, therefore by the electron-donating effect of the $(\text{CH}_3)_3\text{GeCH}_2$ -group, which is exhibited only on polarisation of the group by electrophilic hydrogen of phenol approaching the oxygen of the germane.

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