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# A $^{13}C$, $^{17}O$, $^{29}Si$ NMR study of some silicon, germanium and tin acyloxyderivatives

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## Abstract

$^{13}C$, $^{17}O$, $^{29}Si$, $^{119}Sn$ NMR spectra of acyloxysilanes, -germanes and -stannanes $R^1R^2R^3MOCOR$ (M = Si, Ge, Sn) have been investigated. The character of substituent effects on the $^{13}C$ and $^{17}O$ chemical shifts of these compounds is almost the same for Si, Ge and Sn. $^{17}O$ and $^{119}Sn$ NMR spectra establish the predominance of the intermolecular exchange processes in acyloxystannanes.

## Introduction

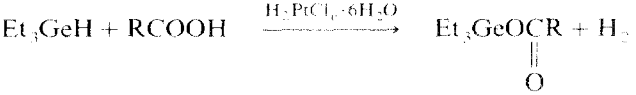
Quite an extensive bibliography on the application of $^{13}C$, $^{29}Si$ and $^{119}Sn$ NMR for the study of silicon [1–7] and tin [8–21] acyloxyderivatives has been accumulated. However, works describing the application of $^{17}O$ NMR are scarce [4,7,14,17]. In contrast to the analogous silicon and tin compounds acyloxygermanes have not been studied extensively. The present work is a part of our detailed multinuclear NMR studies of group 14 element organic derivatives, containing M–O bond (M = Si, Ge, Sn) and deals with the $^{13}C$, $^{17}O$ and $^{29}Si$ NMR investigation of acyloxysilanes, -germanes and -stannanes $R^1R^2R^3MOCOR$, where M = Si, Ge, Sn; $R^1R^2R^3 = Me_3, Et_3, MePh_2$; R = Me, Ph, $^tBu$, Pr, $CH_nCl_{3-n}$ ($n = 0$–$2$), $CF_3$.

## Experimental

NMR spectra were recorded for solutions in $CDCl_3$ at 303 K on a Bruker WM 360 spectrometer. Experimental conditions were as follows: $^{13}C$ NMR at 22.63 MHz (spectrometer Bruker WH-90/DS), complete proton decoupling, pulse width 5 μs, chemical shifts (CS) measured with accuracy ±0.07 ppm relative to internal TMS. $^{17}O$ NMR: 48.82 MHz, pulse width 40 μs, CS measured with accuracy ±0.3 ppm relative to external $H_2O$. $^{29}Si$ NMR: 71.55 MHz, complete proton decoupling, pulse width 15 μs, CS were measured with accuracy ±0.03 ppm relative to internal TMS. $^{119}Sn$ NMR: 134.29 MHz, complete proton decoupling, pulse width 11 μs, CS were measured with accuracy ±0.03 ppm relative to external tetramethyltin.

*General procedure for the synthesis of compounds*

Acyloxysilanes were obtained by dehydrocondensation of triorganylsilanes with carboxylic acids in the presence of hexachloroplatinic acid [22]. This method can be successfully applied for the synthesis of trialkylacyloxygermanes as well. Earlier it has been shown [23] that strong carboxylic acids such as trifluoroacetic acid reacted easily with triethylgermane under reflux giving the corresponding ester, while the reaction with weaker acetic acid was very slow. We have found that boiling of triethylgermane with aliphatic and aromatic acids in the presence of Speier's catalyst for 2–8 h afforded the corresponding acyloxygermanes in 58–83% yield:



$$Et_3GeH + RCOOH \xrightarrow{H_2PtCl_6 \cdot 6H_2O} Et_3GeO\underset{\underset{O}{\|}}{C}R + H_2$$

($R = Me, Pr, Ph, CH_2Cl, CHCl_2, CCl_3, CF_3$)

Physico-chemical characteristics of prepared acyloxygermanes and -silanes correspond to those given in literature [24,25]. Acyloxystannanes have been obtained in the reaction of trialkylchlorostannanes with salts of the corresponding acids.

## Results and discussion

$^{29}$Si chemical shifts (CS) of $\alpha$-substituted triethylacyloxysilanes vary within a range of 10 ppm (Table 1). The enhancement of the acceptor properties of the substituent R causes a downfield shift of the $^{29}$Si resonance signal. A linear correlation between $^{29}$Si CS and Taft constant ($\sigma^\star$) of substituent R [26] has been found:

$$\delta\,^{29}Si = 25.0 + 3.5\sigma^\star \qquad r = 0.995;\ n = 6 \qquad (1)$$

A linear correlation between $^{29}$Si CS and $pK_a$ of the corresponding acid RCOOH was observed earlier for trimethylacyloxysilanes $Me_3SiOCOR$ [1]. This holds also for triethylacyloxysilanes $Et_3SiOCOR$:

$$\delta\,^{29}Si = 35.5 - 2.1\ pK_a \qquad r = 0.996;\ n = 5 \qquad (2)$$

The eqs 1 and 2 suggest that both physical characteristics—acidity and CS—are controlled by the same factors.

$^{13}$C CS for carbonyl carbons vary within a range of 16 ppm in the compounds studied. This range of changes is comparable to that for esters and acyloxystannanes possessing similar substituents.

We have compared carbonyl $^{13}$C CS in the silicon, germanium and tin isostructural compounds $R'_3MOCOR$, M = Si, Ge, Sn (Fig. 1).

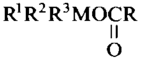
The increase in $^{13}C(C{=}O)$ CS values in the order M = Si < Ge < Sn suggest the following increase in the same order: ionic character of the M–O bond and contribution of ionic structures of the $RCOO^- MR'^+_3$ type.

The $^{17}$O NMR spectra of acyloxysilanes and -germanes display two well resolved $^{17}$O resonance signals (Table 1): one lies within the range 150–176 ppm and corresponds to etheral oxygen, the other signal is situated within the range 330–376 ppm and corresponds to carbonyl oxygen.

We have compared $^{17}$O CS in the isostructural acyloxyderivatives $R'_3MOCOR$ and MeOCOR, M = Si, Ge (Figs. 2 and 3). The effect of the substituent R on the CS of both oxygens is approximately the same for M = Si, Ge, but differs to some

Table 1

NMR data δ (ppm), $\Delta\nu_{1/2}$ (Hz) for acyloxysilanes and -germanes



$R^1R^2R^3MOC(=O)R$

| No. | R | $R^1R^2R^3$ | M | $^{17}O(C{=}O)$ |  | $^{17}O(-O-)$ |  | $\delta^{29}Si$ | $\delta^{13}C$ (RM) |  | $\delta^{13}C$ (C=O) | $\delta^{13}C$ (R) |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | δ | $\Delta\nu_{1/2}$ | Δ | $\Delta\nu_{1/2}$ |  | C-1 | C-2 |  | C-1 | C-2 |
| 1 | Me | $Me_3$ | Si | 379.0 | 320 | 177.4 | 110 | 23.1 | 0.02 | – | 172.37 | 23.09 | – |
| 2 | Me | $MePh_2$ [a] | Si | 383.8 | 310 | 174.2 | 260 | 11.6 | −1.25 | – | 171.78 | 22.96 | – |
| 3 | Me | $Et_3$ | Si | 376.5 | 300 | 167.2 | 200 | 25.0 | 5.02 | 6.71 | 171.97 | 22.80 | – |
| 4 | Me | $Et_3$ | Ge | 360.8 | 370 | 176.2 | 250 | – | 8.00 | 8.24 | 174.71 | 22.37 | – |
| 5 | Pr | $Et_3$ | Ge | 346.4 | 420 | 173.3 | 360 | – | 8.07 | 8.30 | 178.32 | 29.22 | 27.44 [b] |
| 6 | $^tBu$ | $Et_3$ | Si | 363.5 | 300 | 152.6 | 230 | 24.4 | 5.08 | 6.77 | 179.51 | 40.15 | 27.64 |
| 7 | Ph | $Et_3$ | Si | 354.6 | 450 | 150.0 | 350 | 26.3 | 5.20 | 6.92 | 166.91 | 132.32 | 130.73 [c] |
| 8 | Ph | $Et_3$ | Ge | 334.1 | 500 | 161.5 | 470 | – | 8.27 | 8.53 | 170.13 | 130.16 | 130.69 [d] |
| 9 | $CH_2Cl$ | $Et_3$ | Si | 372.3 | 480 | 159.7 | 210 | 29.1 | 4.92 | 6.61 | 167.95 | 42.52 | – |
| 10 | $CH_2Cl$ | $Et_3$ | Ge | 353.1 | 380 | 168.6 | 260 | – | 7.98 | 8.46 | 170.52 | 42.58 | – |
| 11 | $CHCl_2$ | $Et_3$ | Ge | 341.5 | 450 | 163.5 | 280 | – | 7.88 | 8.59 | 167.89 | 66.89 | – |
| 12 | $CCl_3$ | $Et_3$ | Si | 356.4 | 340 | 145.3 | 280 | 34.4 | 4.69 | 6.51 | 161.55 | 91.78 | – |
| 13 | $CCl_3$ | $Et_3$ | Ge | 333.9 | 500 | 155.9 | 320 | – | 7.85 | 8.76 | 164.60 | 92.17 | – |
| 14 | $CF_3$ | $Et_3$ | Si | 367.6 | 250 | 150.1 | 150 | 34.3 | 4.63 | 6.06 | 157.30 | 115.53 | – |
| 15 | $CF_3$ | $Et_3$ | Ge | 346.5 | 270 | 158.7 | 250 | – | 7.47 | 8.38 | 159.65 | 115.24 | – |

[a] $\delta^{13}C$(Ph): 136.43 ($C_i$); 134.19 ($C_o$); 129.05 ($C_m$); 130.74 ($C_p$). [b] $\delta^{13}C$(C-3): 10.19. [c] $\delta^{13}C_m$: 128.81; $\delta^{13}C_p$: 133.34. [d] $\delta^{13}C_m$: 128.76; $\delta^{13}C_p$: 134.32.

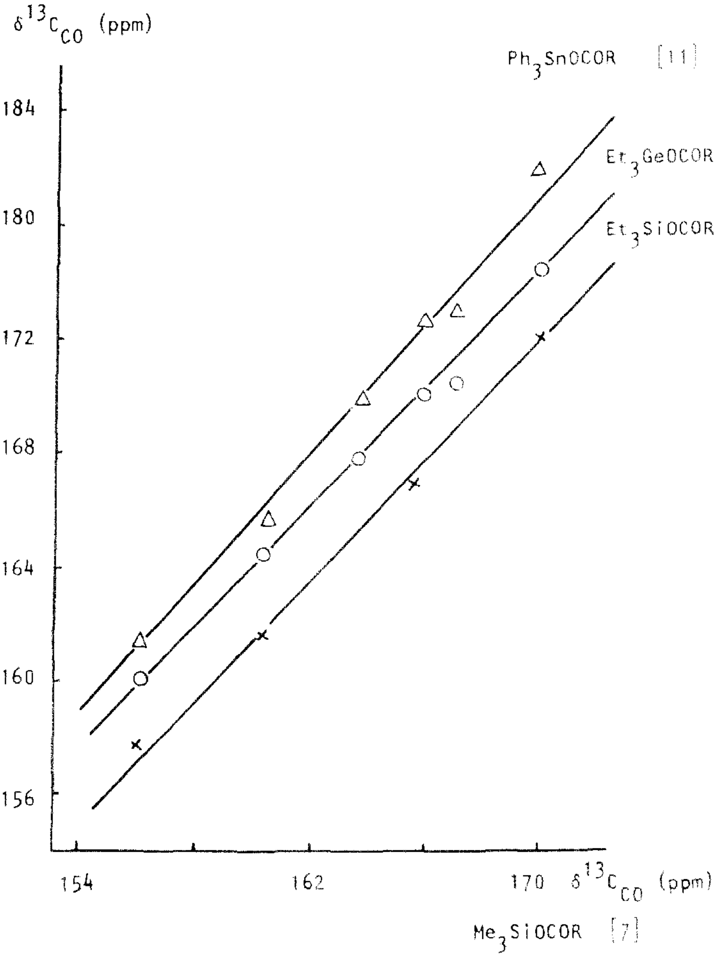


Fig. 1. The relation between carbonyl $^{13}$C CS in acyloxysilanes, -germanes and -stannanes.

extent from that in substituted methyl acetates [27]. It should be noted that our data and those of previous workers were obtained in different solvents and this could have affected the absolute CS values ($^{17}$O NMR spectra were recorded as follows: for $Et_3SiOCOR$ and $Et_3GeOCOR$ in $CDCl_3$; for $Me_3SiOCOR$ in a neat liquid [7], for MeOCOR in acetonitrile [27]). We did not find any satisfactory correlations between $^{17}$O CS and substituent R constants.

The characteristic feature of acyloxystannane $^{17}$O NMR spectra is the presence of only one signal, which is located approximately in the middle of the positions of carboxyl group $^{17}$O signals in analogous silicon and germanium compounds (Table 2). The existence of only one signal for both oxygens reflects their equivalence on the NMR time scale resulting from fast exchange processes in solution. According to [14,17] it is due to intramolecular exchange of $SnR_3$ groups between two oxygen atoms.

The comparison of differences between $^{17}$O CS for both oxygen atoms in isostructural compounds with the same set of substituents gives the following values: $\Delta = \delta(^{17}O(CO)) - \delta(^{17}O(-O-)) = 216-222$ ppm for $RCO_2CH_3$ [27], 200–217

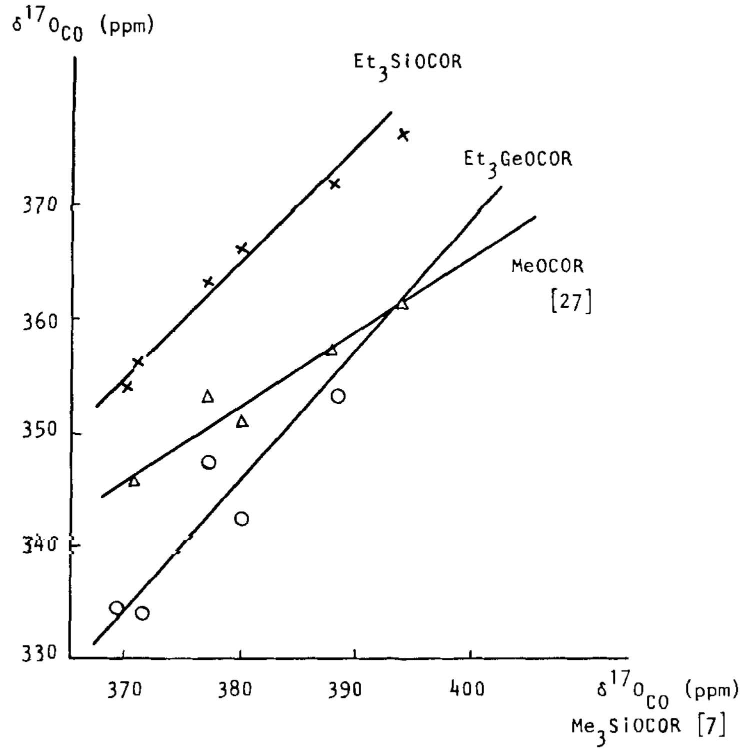
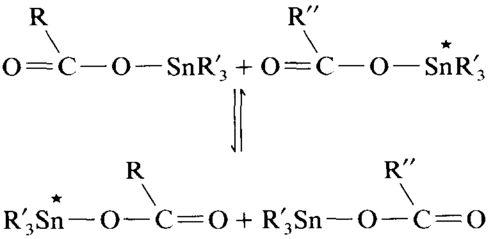


Fig. 2. The relation between carbonyl oxygen $^{17}O$ CS in acyloxyderivatives of carbon, silicon and germanium.

ppm for acyloxysilanes and 173–188 ppm for acyloxygermanes. It can be assumed that $\Delta$ value indicates the tendency of carboxyl group oxygens to equivalence, and, to some extent the rate of exchange processes in the solution. In such case the latter increases in order $M = C < Si < Ge \ll Sn$. Our results agree with those previously reported [28], where activation energy for 1,3-oxygen to oxygen rearrangement in benzoates PhCOOR were determined by means of $^{13}C$ NMR and the following sequence for the changes of this energy was obtained:

$R = CH_2Ph \gg SiMe_3 \approx SiMe_2{}^tBu > GeMe_3 > SnBu_3$

Exchange processes in solutions of tin derivatives being faster than in those of silicon and germanium analogues was also shown by the study of $^{119}Sn$ CS for some acyloxystannanes (Table 2). Only one signal has been observed in $^{119}Sn$ NMR spectra for the mixture of two tin derivatives—trimethyltin acetate $Me_3SnOCOMe$ and -cinnamate $Me_3SnOCOCH{=}CHPh$—in $CDCl_3$ (Fig. 4), confirming fast intermolecular exchange (on the NMR time scale) in solution:



$$O{=}C(R){-}O{-}SnR'_3 + O{=}C(R''){-}O{-}\overset{\star}{Sn}R'_3 \rightleftharpoons R'_3\overset{\star}{Sn}{-}O{-}C(R){=}O + R'_3Sn{-}O{-}C(R''){=}O$$

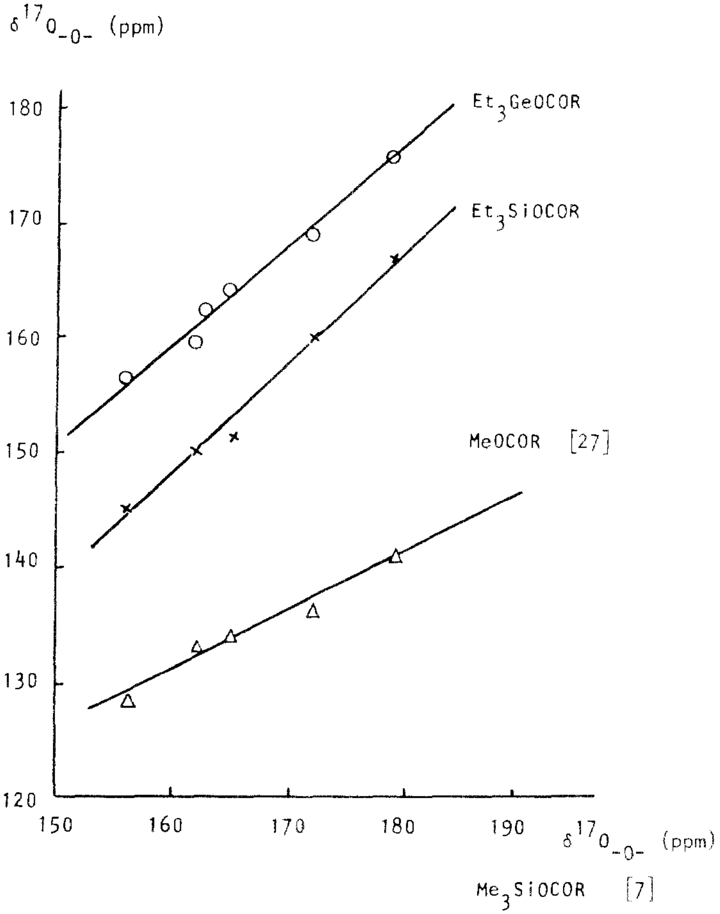


Fig. 3. The relation between etheral oxygen $^{17}O$ CS in acyloxyderivatives of carbon, silicon and germanium.

Multiple dilution of the sample by deuterochloroform reduces the rate of this exchange. As a result two $^{119}Sn$ signals, one corresponding to each acyloxystannane, can be observed at very low concentrations.

The study of the effect of the solvent on $^{17}O$ and $^{119}Sn$ CS of acyloxystannanes and -germanes also confirms the predominance of intermolecular exchange between carboxyl groups in solution (Tab. 3). The $^{119}Sn$ resonance signal is shifted to higher

Table 2

$^{17}O$ and $^{119}Sn$ NMR data $\delta$ (ppm), $\Delta\nu_{1/2}$ (Hz) for tin carboxylates $R'_3SnOCOR$

| | R′ | R | $^{17}O$ | | $\delta^{119}Sn$ |
|---|---|---|---|---|---|
| | | | $\delta$ | $\Delta\nu_{1/2}$ | |
| 1 | Me | Me | 275.2 | 200 | 129.37 |
| 2 | Me | CH=CHPh | 263.0 | 750 | 124.75 |
| 3 | Et | CH=CHPh | 254.6 | 850 | 106.90 |

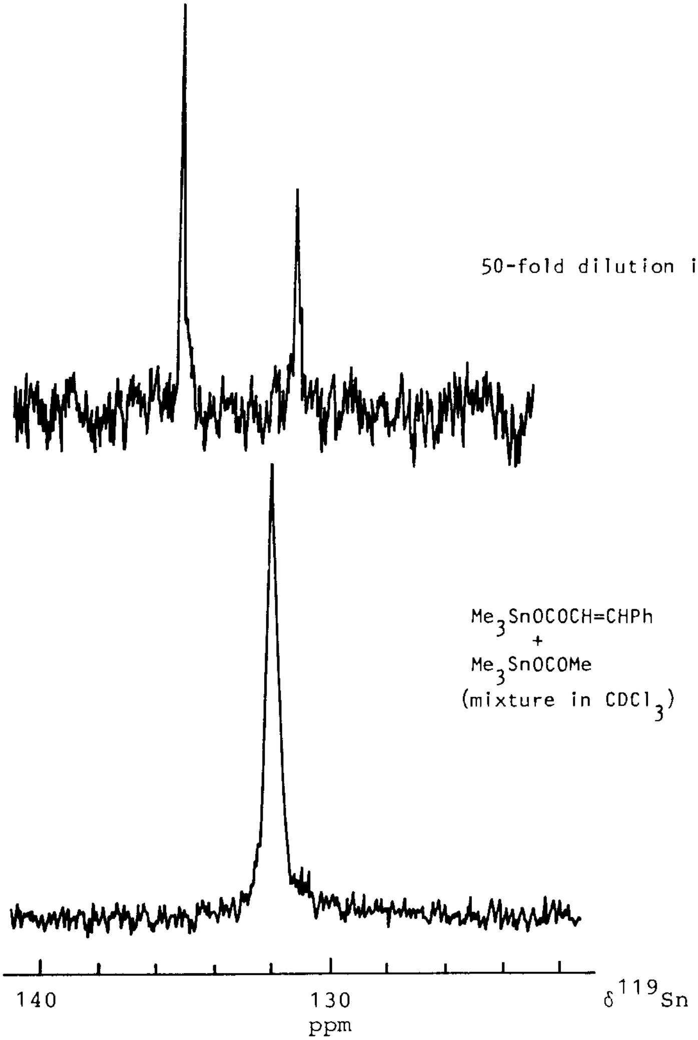


Fig. 4. $^{119}$Sn NMR spectra ($CDCl_3$, 303 K).

Table 3

Effect of solvent on the NMR parameters of tin and germanium carboxylates

| Compound | Solvent | $\delta^{17}O$ (ppm) | $\delta^{119}Sn$ (ppm) |
|---|---|---|---|
| $Me_3SnOCOMe$ | $CDCl_3$ | 275.4 | 130.2 |
| | $CDCl_3$ : pyridine | | |
| | 10 : 1 | | 58.9 |
| | 5 : 1 | 283.0 | 9.0 |
| | pyridine | 286.0 | −15.8 |
| $Et_3GeOCOCF_3$ | $CDCl_3$ | 346.5 (CO) | – |
| | | 158.7 (–O–) | – |
| | $CD_3CN$ | 360.9 (CO) | – |
| | | 176.7 (–O–) | – |
| | pyridine | 276.8 | – |

fields with increase of the amount of pyridine in the $CDCl_3$ solution. This corresponds to the increase of tin coordination number due to the complexation with pyridine. At the same time the equivalence of both oxygen atoms originates. Dissolving of trifluoroacetoxygermane in pyridine results in the coalescence of oxygen signals. This ascertains also the possibility of intermolecular exchange processes in germanium derivatives. The addition of another carboxylate or complexing agent (e.g. pyridine) shifts the equilibrium of this exchange. If the intramolecular exchange dominates, extraneous influences on the exchange equilibrium should be less pronounced.

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