

**^{17}O , ^{13}C , AND ^{29}Si NMR SPECTRA OF SOME ACYLOXY-
AND DIACETOXY-SILANES AND ACETOXYGERMANES**

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The ^{17}O , ^{13}C and ^{29}Si NMR spectra of $(\text{CH}_3)_3\text{SiOC(O)R}$, $\text{CH}_3(\text{XCH}_2)\text{Si}(\text{OC(O)CH}_3)_2$, and $\text{R}_3\text{GeOC(O)CH}_3$ compounds are reported. In the ^{17}O NMR spectra at 350 K the only signal is observed with the two latter series, but two well-resolved signals are displayed with the $(\text{CH}_3)_3\text{SiOC(O)R}$ compounds. The equivalence of both oxygen atoms in carboxyl group on the NMR time scale is discussed from the viewpoint of a possible coordination of the oxygen atoms to the IVB group element of the periodic system.

^{17}O NMR spectra of organic esters of carboxylic acids always show two, mostly well-resolved signals which belong to magnetically nonequivalent oxygen atoms of the $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{R}$ groups¹⁻³. We have recently found⁴ that ^{17}O NMR spectra of $\text{R}_2\text{Sn}(\text{OC(O)R})_2$ and $\text{R}_3\text{SnOC(O)R}$ compounds at $T \geq 330$ K give only one signal with the chemical shift $\delta(^{17}\text{O})$ being displayed roughly between those for both oxygens in organic esters, which corresponds to an "identity" of both oxygens of OC(O)R group on the NMR time scale. The possible implications of this finding relating to a coordination of the both oxygens to tin resulting in the formation of an asymmetric chelate bonding were discussed in our previous papers^{4,5}.

This contribution presents the study of ^{17}O , ^{13}C , and ^{29}Si NMR spectra of $(\text{CH}_3)_3\text{SiOC(O)R}$, $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, (\text{CH}_3)_2\text{CH}, \text{CH}_3\text{COCH}_2\text{CH}_2, \text{C}_6\text{H}_5\text{CH}_2, \text{C}_6\text{H}_5, \text{ClCH}_2, \text{Cl}_2\text{CH}, \text{Cl}_3\text{C}, \text{F}_3\text{C}, \text{NCCH}_2, \text{CH}_3\text{OCH}_2, (\text{CH}_3)_3\text{SiCH}_2$, and $(\text{CH}_3)_3\text{SiOCH}_2$, compounds (I), along with $\text{CH}_3(\text{XCH}_2)\text{Si}(\text{OC(O)CH}_3)_2$ ($\text{X} = \text{H}, \text{Cl}, \text{CH}_3\text{C(O)O}$) (II) and $\text{R}_3\text{GeOC(O)CH}_3$ ($\text{R} = 1-\text{C}_4\text{H}_9, \text{C}_6\text{H}_5$) (III) compounds undertaken with the aim of experimental verification of equivalence of the ^{17}O NMR signals of carboxyl oxygen atoms and, possibly, confirmation of the hypothesis of coordination of other central IVB group atoms with both carboxyl oxygen atoms.

EXPERIMENTAL

The preparation of the model compounds used for the NMR spectra measurement has been described previously (series *I* and *II* in refs^{6,7} and series *III* in refs^{8,9}). The identity, purity and their structure were checked by elemental analysis and through their ¹H, ¹³C, and ²⁹Si NMR spectra.

¹⁷O, ¹³C, and ²⁹Si NMR spectra were recorded on a JNM-FX 100 (JEOL) instrument equipped with a multinuclear probe at 13.505 MHz, 25.047 MHz, and 19.788 MHz, respectively. If not shown otherwise all the compounds except *III* with R = C₆H₅ (measured as saturated solution in C²HCl₃ at 330 K) were measured as neat liquids in 10 mm NMR tubes at 350 K. As a lock substance and a standard ($\delta = 0$) for chemical shift measurement $\delta(^{17}\text{O})$ deuterium oxide in a coaxial capillary was used. (²H)₅-Nitrobenzene in the coaxial capillary served for the same purpose with the compound *I* (R = CCl₃), measured at 420 K. Its chemical shift $\delta(^{17}\text{O})$ 579 ppm was determined at 370 K with neat liquid using coaxial capillary filled with deuterium oxide. Hexamethyldisiloxane was used as external standard ($\delta = 0$) for $\delta(^{29}\text{Si})$ and $\delta(^{13}\text{C})$ measurement (tetramethylsilane cannot be used for this purpose due to high temperatures employed) and 6.5 ppm (ref.¹⁰) and 1.0 ppm, respectively, were added to convert the chemical shifts to internal tetramethylsilane. Methyl group in butyl substituent of *III* with R = 1-C₄H₉ was ascribed to have $\delta(^{13}\text{C}) = 13.50$ ppm, the $\delta(^{13}\text{C})$ values of *III* with R = C₆H₅ were referenced to C²HCl₃ signal ($\delta(^{13}\text{C}) = 77.00$ ppm). The following parameters were used for the measurement of ¹⁷O NMR spectra: spectral width 10 000 Hz, 1 K (zero filling to 8 K), 90° pulse, pulse repetition 60 ms, proton-noise decoupling, 25–50 Hz exponential broadening factor to the FID prior to Fourier transformation. ¹³C and ²⁹Si NMR spectra were recorded by a standard way at digital resolution 1.22 Hz/point (that is 0.06 ppm/point and 0.05 ppm/point, respectively).

RESULTS AND DISCUSSION

The ²⁹Si, ¹⁷O, and ¹³C chemical shifts of studied compounds are gathered in Tables I–III. Chemical shifts $\delta(^{13}\text{C})$ were assigned either on the basis of multiplicity in proton-coupled spectrum, or after the comparison with ¹³C NMR spectra of similar model compounds. ²⁹Si NMR spectra of all the compounds but *I* with R = (CH₃)₃SiCH₂ and R = (CH₃)₃SiOCH₂ exhibit, disregarding the standard, only one signal. The signals in ²⁹Si NMR spectra of two compounds containing two nonequivalent silicon atoms were assigned on the basis of the comparison of $\delta(^{29}\text{Si})$ chemical shifts of similar compounds. For such a comparison following pairs were considered: 1) *I*, R = (CH₃)₃SiCH₂ and (CH₃)₃SiCH₂COOC₂H₅ ($\delta(^{29}\text{Si}) = 2.87$, referred to tetramethylsilane^{10,11}) and 2) *I*, R = (CH₃)₃SiOCH₂ and *I*, R = CH₃OCH₂. The ²⁹Si NMR spectra of the series *I* had already been reported^{6,12} under different experimental conditions and in various solvents. All herein studied compounds were measured under the same experimental conditions and it must be stated that distinct differences were observed as compared with the data published earlier.

The characteristic feature of ¹⁷O NMR spectra of the series *I* measured at 350 K (neat liquids) is, similarly as in the case of organic esters, the occurrence of two well resolved ¹⁷O NMR signals. Typical ¹⁷O NMR spectrum of these compounds is given

TABLE I
Chemical shifts $\delta(^{29}\text{Si})$, $\delta(^{17}\text{O})$, and $\delta(^{13}\text{C})$ of $(\text{CH}_3)_3\text{SiOC}(\text{O})\text{R}$ compounds

R	$\delta(^{29}\text{Si})$ ppm	$\delta(^{17}\text{O})$, ppm ($w_{1/2}$, Hz)		$\delta(^{13}\text{C})$, ppm		
		C=O	C—O	COO	$(\text{CH}_3)_3\text{Si}$	R
H	24.6	396(50)	182(35)	159.7	-1.2	
CH_3	21.7	394(85)	179(40)	169.4	-1.2	21.4
CH_3CH_2	21.8	385(120)	174(75)	173.1	-1.1	28.4 (CH_2); 8.4 (CH_3)
$(\text{CH}_3)_2\text{CH}$	21.9	381(135)	169(75)	175.6	-1.0	34.7 (CH); 18.3 (CH_3)
$\text{CH}_3\text{COCH}_2\text{CH}_2$	22.7	384 ^a (300)	175(210)	172.1	-0.8	204.6 (CO); 37.7 (COCH_2); 29.5 (CH_2COO); 28.8 (CH_3)
$\text{C}_6\text{H}_5\text{CH}_2$	23.2	389(245)	176(155)	170.6	-0.8	42.5 (CH_2); 134.4 (i); 128.0 (o)
C_6H_5	23.6	370(400)	163(200)	165.5	-0.8	128.8 (m); 126.4 (p)
ClCH_2	26.6	388(180)	172(105)	166.4	-0.9	131.5 (i); 127.8 (o); 129.7 (m); 132.1 (p)
Cl_2CH	30.3	380(195)	165(115)	163.3	-0.9	41.7
Cl_3C	32.8	371(255)	156(135)	160.1	-0.9	65.6
Cl_3C^b		375(135)	156(95)			91.3
F_3C	32.8	377(100)	162(60)	155.8 ^c	-2.5	114.3 ^d
NCCH_2	28.2	387(340)	180(200)	163.3	-0.9	113.7 (CN); 25.7 (CH_2)
$(\text{CH}_3)_3\text{SiCH}_2$	20.5 ^e	383(195)	180(100)	171.3	-0.9	28.2 (CH_2); -1.9 ($(\text{CH}_3)_3\text{SiCH}_2$)
$(\text{CH}_3)_3\text{SiOCH}_2$	23.8 ^f	384(430)	166 ^g (200)	170.9	-0.9	61.5 (CH_2); -0.9 ($(\text{CH}_3)_3\text{SiO}$)
CH_3OCH_2	23.9	382(210)	167 ^h (140)	169.6	-1.0	69.9 (CH_2); 58.0 (CH_3)

^a $\delta(^{17}\text{O})$ (CH_3CO) = 566 ppm, $w_{1/2}$ = 210 Hz; ^b 420 K, referenced to external (²H)₅-nitrobenzene ($\delta(^{17}\text{O})$ = 579 ppm); ^c $^2 J(^{19}\text{F}^{13}\text{C})$ = 42.7 Hz; ^d $^1 J(^{19}\text{F}^{13}\text{C})$ = 285.6 Hz; ^e $\delta(^{29}\text{Si})$ ($(\text{CH}_3)_3\text{SiCH}_2$) = 2.4 ppm; ^f $\delta(^{29}\text{Si})$ ($(\text{CH}_3)_3\text{SiOCH}_2$) = 19.2 ppm; ^g signal for SiOCH_2 was not observed; ^h $\delta(^{17}\text{O})$ (CH_3OCH_2) = -24 ppm, $w_{1/2}$ = 170 Hz.

TABLE II
Chemical shifts $\delta(^{29}\text{Si})$, $\delta(^{17}\text{O})$, and $\delta(^{13}\text{C})$ of $\text{CH}_3(\text{XCH}_2)_2\text{Si}(\text{OC}(\text{O})\text{CH}_3)_2$ compounds

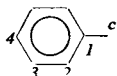
X	$\delta(^{29}\text{Si})$ ppm	$\delta(^{17}\text{O})$, ppm ($w_{1/2}$, Hz)			$\delta(^{13}\text{C})$, ppm			
		C=O	C—O	COO	CH_3COO	$(\text{CH}_3)_3\text{Si}$	XCH_2Si	
H^a	3.4	393(620)	187(500)	169.3	21.3	—2.3	—2.3	
H^b		270 ^c (700)	270 ^c (700)					
Cl^a	—9.7	285 ^c (730)	285 ^c (730)	169.5	21.4	—5.2	26.4	
Cl^d		287 ^c (480)	287 ^c (480)					
Cl^e		285 ^c (1600)	285 ^c (1600)					
$\text{CH}_3\text{C}(\text{O})\text{O}^a, f$	—15.8	284 ^c (550)	284 ^c (550)	169.3	21.4	—3.1	54.8	
$\text{CH}_3\text{C}(\text{O})\text{O}^d, g$		287 ^c (450)	287 ^c (450)					

^a 350 K; ^b 400 K, referenced to external neat (²H)₅-nitrobenzene; ^c one common signal; ^d 370 K; ^e 330 K; ^f X: $\delta(\text{CH}_3\text{COO}) = 18.9$, $\delta(\text{CH}_3\text{COO}) = 172.5$, $\delta(\text{C}=\text{O}) = 354$, $w_{1/2} = 340$ Hz, $\delta(\text{C}-\text{O}) = 151$, $w_{1/2} = 300$ Hz; ^g X: $\delta(\text{C}=\text{O}) = 358$, $w_{1/2} = 300$ Hz, $\delta(\text{C}-\text{O}) = 150$, $w_{1/2} = 260$ Hz.

in Fig. 1. Table I compiles chemical shifts $\delta(^{17}\text{O})$ and signal half-widths $w_{1/2}$. In agreement with the reference¹³ the signals shifted to higher field were ascribed to oxygen atoms of C—O—Si(CH₃)₃ moiety. The compounds were also, in part, measured at lower temperature (300 K) at which the signal half-widths increased 1.5 to 2 times. This makes exact determination of $\delta(^{17}\text{O})$ chemical shifts more difficult. ¹⁷O NMR spectrum of *I*, R = CCl₃ was also recorded at higher temperature (420 K). Also at this temperature we observed two signals which do not alter their positions with regard to those measured at 350 K, but experience a decrease in $w_{1/2}$ values (Tab. I). Chemical shifts $\delta(^{17}\text{O})$ C=O of the series *I* are, compared to analogous organic esters RC(O)OC(CH₃)₃ (R = CH₃, C₂H₅, (CH₃)₂CH, C₆H₅) (ref.²) shifted downfield by 24–29 ppm $\delta(^{17}\text{O})$ C=O for (CH₃)₂CHC(O)OC(CH₃)₃ (ref.²) should be 352.5 as it turns out from $\Delta\delta(^{17}\text{O})$ introduced in ref.², while $\delta(^{17}\text{O})$ COSi(CH₃)₃ are shifted by 26–36 ppm upfield. Both the oxygen signals with RC(O)OSi(CH₃)₃ compounds (*I*) appear to be shifted downfield with regard to analogous RC(O)OCH₃ (R = H, CH₃, C₂H₅, (CH₃)₂CH) (ref.²) compounds (the $\delta(^{17}\text{O})$ C=O by 34 to 37 ppm and $\delta(^{17}\text{O})$ COSi(CH₃)₃ by 44–55 ppm). No simple correlations were found between parameters of ¹⁷O, ¹³C, and ²⁹Si NMR spectra.

¹⁷O NMR spectrum of *II*, X = H at 350 K shows two signals, but only one signal is observed at 400 K. It is located about between both the signals at 350 K (Table II). Compound *II*, X = Cl shows one signal in a broad temperature range (Table II, Fig. 2), the presence of two, very broad signals being apparent only at 300 K. The attempt to obtain two well resolved signals with further temperature decrease failed and the disappearance of the signal at 275 K is probably due to an increase of the signals half width as a consequence of an increase of solution viscosity. ¹⁷O NMR spectrum of compound *II*, X = CH₃COO is shown in Fig. 3. It consists of one ¹⁷O signal for all oxygen atoms of Si(O(O)CCH₃)₂ groups and two ¹⁷O signals for CH₃C(O)O group (Table II). The occurrence of the only signal for both oxygen

TABLE III
Chemical shifts $\delta(^{17}\text{O})$ and $\delta(^{13}\text{C})$ of R₃GeOC(O)CH₃ compounds

R	$\delta(^{17}\text{O})$, ppm ($w_{1/2}$, Hz)	$\delta(^{13}\text{C})$, ppm					
		COO	CH ₃ COO	C(1)	C(2)	C(3)	C(4)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^a$	277 ^b (750)	171.2	21.4	16.0	26.1	26.1	13.5
	~290 ^{b,d} (1200)	173.4	21.9	133.7	134.7	128.3	130.1

^a Neat liquid, 350 K; ^b one common signal of both oxygens in carboxylic group; ^c saturated solution in C²HCl₃, 330 K; ^d weak signal.

atoms of SiOC(O)CH_3 groups reflect their equivalency on the NMR time scale resulting from their fast exchange as depicted below

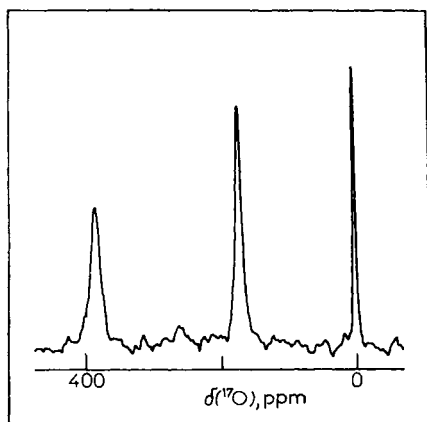
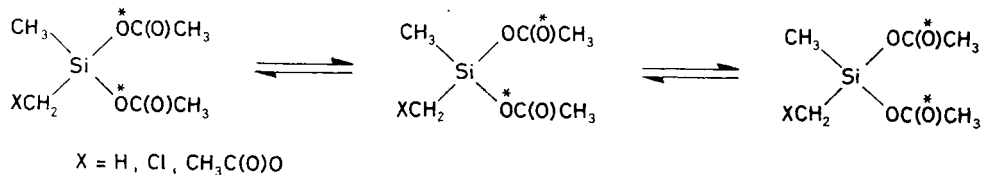


FIG. 1
 ^{17}O NMR spectrum of $\text{ClCH}_2\text{C(O)OSi}(\text{CH}_3)_3$ (neat liquid, external standard $^2\text{H}_2\text{O}$) at 350 K

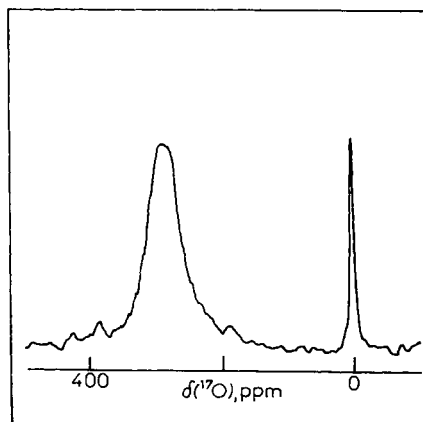
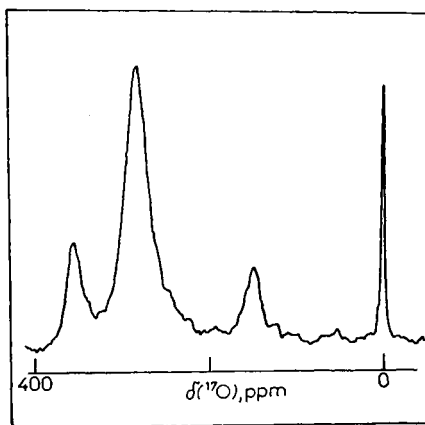
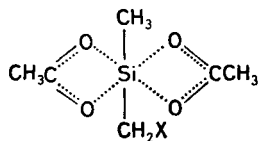


FIG. 2
 ^{17}O NMR spectrum of $\text{ClCH}_2(\text{CH}_3)\text{Si}(\text{OC(O)CH}_3)_2$ (neat liquid, external standard $^2\text{H}_2\text{O}$) at 350 K

FIG. 3
 ^{17}O NMR spectrum of $\text{CH}_3(\text{CH}_3\text{C(O)OCH}_2)\text{Si}(\text{OC(O)CH}_3)_2$ (neat liquid, external standard $^2\text{H}_2\text{O}$) at 350 K



In the sense of the conclusions (refs^{4,5}) concerning the coordination of both the oxygen atoms of the SnOC(O)CH_3 group, it is possible to express the equivalence of the two oxygen atoms in compounds *II* by the formula *IV*



IV

Bonding interaction of both oxygen^{4,5} atoms seems to support this assumption of chelate structure for *II*, $\text{X} = \text{Cl}$, $\text{CH}_3\text{C(O)O}$, and also, perhaps for *II*, $\text{X} = \text{H}$. A strong coordination bonding leading to an increase of the silicon coordination number from 4 to 6 should, however, result in a pronounced upfield shift of $\delta(^{29}\text{Si})$ (ref.¹⁴). Despite that this chemical shift for compounds *II* compared to compounds *I*, or that for *II*, $\text{X} = \text{Cl}$, $\text{CH}_3\text{C(O)O}$ compared to *II*, $\text{X} = \text{H}$ are really shifted in this way, the differences are to be preferentially explained by the substitution of CH_3 moiety with more polar $\text{CH}_3\text{C(O)O}$ or Cl substituents. Weak coordination bonding to silicon cannot be, however, utterly ruled out. In any case the chelate structure is to be assumed labile and highly asymmetric.

In summary then, the ^{17}O NMR signals coalescence was observed with $\text{R}_2\text{M(OC(O)R)}_2$ ($\text{M} = \text{Sn, Si}$) and $\text{R}_3\text{MOC(O)R}$ ($\text{M} = \text{Sn}$) compounds^{4,5}. The ^{17}O and ^{13}C NMR spectra of the series $\text{R}_3\text{GeOC(O)CH}_3$ (*III*, $\text{R} = 1\text{-C}_4\text{H}_9, \text{C}_6\text{H}_5$) (Table III) recorded in order to build more general picture of the bonding nature within acyloxysubstituted organometallic compounds of the IVB group show that the only signal in ^{17}O NMR spectra of these compounds is observed, which implies that compounds *III* are more alike to organotin than organosilicon compounds. Thus from the results presented in this paper it appears that the probability of the both oxygen atoms equivalency in ^{17}O NMR spectra of acyloxy compounds of IVB elements increases in the order $\text{C} \ll \text{Si} < \text{Ge} \leq \text{Sn}$, with increasing number of polar acyloxy groups attached to the IVB atoms and with increasing electron-withdrawing ability of their substituents ($\text{CH}_3 < \text{ClCH}_2 \approx \text{CH}_3\text{C(O)OCH}_2$).

The above structural changes lead also to an increase in electron-acceptor ability of the IVB atom, which makes our hypothesis⁴ on bidentate nature of carboxylic group in some carboxylic derivatives of IVB group elements and on a weak chelate structure of these compounds reasonable. The fact that the signals coalescence occurs at rather high temperatures is consonant most of all with higher probability of fast exchange on the NMR time scale, but is not contradictory to generally known increase of chelate stability with increasing temperature (chelate effect)¹⁵.

REFERENCES

1. Delseth C., Thi Thanh-Tam Nguyen, Kintzinger J. P.: *Helv. Chim. Acta* **63**, 498 (1980).
2. Orsini F., Severini Ricca G.: *Org. Magn. Reson.* **22**, 653 (1984).
3. Balakrishnan P., Baumstark A. L., Boykin D. W.: *Org. Magn. Reson.* **22**, 753 (1984).
4. Lyčka A., Holeček J.: *J. Organometal. Chem.* **294**, 179 (1985).
5. Holeček J., Handljiř K., Lyčka A., Chattopadhyay T. K., Majee B., Kumar A. K.: *This Journal* **51**, 1100 (1986).
6. Pola J., Jakoubková M., Papoušková Z., Chvalovský V.: *This Journal* **42**, 1540 (1977).
7. Pola J., Jakoubková M., Chvalovský V.: *This Journal* **39**, 1169 (1974).
8. Anderson H. H.: *J. Am. Chem. Soc.* **73**, 5800 (1951).
9. Srivastava T. N., Tandon S. K.: *Z. Anorg. Allgem. Chem.* **353**, 87 (1967).
10. Marsmann H. in the book: *NMR Basic Principles and Progress* (P. Diehl, E. Fluck, R. Kosfeld, Eds) Vol. 17, p. 152. Springer, Berlin 1981.
11. Scholl R. L., Maciel G. E., Musker W. K.: *J. Am. Chem. Soc.* **94**, 6376 (1972).
12. Mc Farlane W., Seaby J. M.: *J. Chem. Soc., Perkin Trans. 2* **1972**, 1561.
13. Kintzinger J. P. in the book: *NMR Basic Principles and Progress* (P. Diehl, E. Fluck, R. Kosfeld, Eds), Vol. 17, p.1. Springer, Berlin 1981.
14. Ref. 10, p. 229–231.
15. Spike C. G., Parry R. W.: *J. Am. Chem. Soc.* **75**, 2726 (1953).

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