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REVIEW

^{17}O NMR Spectroscopy in the Study of Group 14 Organometallic Compounds

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A study of Group 14 organometallic compounds using ^{17}O NMR spectroscopy carried out at the Latvian Institute of Organic Synthesis has been reviewed. The main areas of ^{17}O NMR application—studies of electronic effects, conformational analysis and coordinative interactions—have been characterized.

Keywords: Oxygen-containing organometallics, organosilicon, organogermanium, organotin ^{17}O NMR

INTRODUCTION

Characteristics of the oxygen magnetic isotope ^{17}O present a combination of properties highly unfavourable for magnetic resonance studies: low natural abundance (0.037%), high spin ($I = 5/2$) and electric quadrupole moment.[1] Predominance of the quadrupolar relaxation mechanism results in considerable line broadening, complicating the observation of ^{17}O resonances due to some loss of the signal in the preacquisition period and acoustic ringing, especially in spectrometers with low working frequency.

These features explain the scarcity of data on ^{17}O NMR for organometallic compounds. Historically, the first ^{17}O NMR spectra for some Group 14 organometallic compounds were recorded in 1961.[2] Systematic studies in this field started in the 1980s but the method was applied mainly to organosilicon compounds.

This report characterizes ^{17}O NMR spectroscopic studies on organosilicon, organogermanium and organotin compounds carried out at the Latvian Institute of Organic Synthesis in Riga, Latvia.

The compounds studied can be divided in two main groups. The first group comprises compounds with the oxygen atom attached directly to silicon, germanium or tin, as in alkoxy,[3-5] aroxy,[6] siloxy,[7-9] acyloxy derivatives,[10] silocanes[11] and atranes.[12] The second group embraces compounds without direct M–O bonds, e.g. Group 14 elements containing furan derivatives[13-15] and benzoates.[16]

^{17}O NMR has been applied in three main directions: to study electronic effects, conformational analysis and coordinative interactions of these compounds.

ELECTRONIC EFFECTS

The ^{17}O chemical shifts (CS) of alkoxy and siloxy derivatives of silicon and germanium compounds fall in the range from −30 ppm (Et_3SiOMe[3]) to 70 ppm [for $(ClMe_2Si)_2O$].[7]

The half-width of ^{17}O resonance signals ($\Delta\nu_{1/2}$) ranges from 110 Hz ($Me_3SiOCH_2CF_3$) to 680 Hz for $Si(OC_5H_{11})_4$. Usually $\Delta\nu_{1/2}$ of ^{17}O resonances are 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 at higher temperature and lower solution viscosity.[1, 17] An approximate relationship between the molecule size and $\Delta\nu_{1/2}$ for the compounds studied was observed: an increased molecular radius implies a greater linewidth of ^{17}O resonance.

At the same time, $\Delta\nu_{1/2}$ is considerably smaller for siloxanes than for ethers[18] and alkoxysilanes, regardless of the fact that the former are more bulky. We assume that the ^{17}O resonance signals in siloxanes are narrower due to the rise in symmetry of the molecules caused by increase of the bond angle magnitude, ∠Si—O–Si, as compared with ∠Si—O—C or ∠C–O—C in alkoxysilanes and ethers, respectively.

We failed to obtain statistically significant correlations between ^{17}O CS and substituent constants, indirectly characterizing the charge variations for the whole data array, while in the limited

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series of compounds linear correlations do exist. Generally, the influence of a silicon substituent on the ^{17}O CS is smaller or even opposite to that of an oxygen substituent, as shown in Eqns [1] and [2]:

$$\delta^{17}\mathrm{O}\,[\mathrm{Me_2RSiOEt}] = 14.7 + 3.6\,\sigma^*_\mathrm{R} + 8.1\,E_\mathrm{S} \qquad [1]$$

$(r = 0.93, n = 6)$
$\mathrm{R} = \mathrm{Me, Et, Pr, Bu, ClCH_2, Ph}$

$$\delta^{17}\mathrm{O}\,[\mathrm{Me_3SiOCH_2R}] = 11.5 - 8.6\sigma^*_\mathrm{R} - 0.6\,E_\mathrm{S} \qquad [2]$$

$(r = 0.98, n = 6)$
$\mathrm{R} = \mathrm{Me, Pr, CH{=}CH_2, C{\equiv}CH, CH_2OMe, CF_3}$

This may be due to the different conductivity of electronic effects along the Si—O bond, confirmed also by ^{29}Si and ^{13}C NMR.

Linear correlations exist between ^{17}O CS in isostructural silicon and germanium compounds, indicating a similar sensitivity of ^{17}O shifts to the influence of a substituent at oxygen: (eqns [3] and [4]).

$$\delta^{17}\mathrm{O}\,[\mathrm{Ge(OR)_4}] = 0.6 + 1.1\delta^{17}\mathrm{O}\,[\mathrm{Si(OR)_4}] \qquad [3]$$

$(r = 0.96; n = 7)$
$\mathrm{R} = \mathrm{Me, Et, Pr, i\text{-}Pr, i\text{-}Bu, CH_2CH{=}CH_2, CH_2CF_3}$

$$\delta^{17}\mathrm{O}[\mathrm{Cl}_{4-m}\mathrm{Ge(OR)}_m] = 0.9 + 1.3\delta\,^{17}\mathrm{O}[\mathrm{Cl}_{4-m}\,\mathrm{Si(OR)}_m] \qquad [4]$$

$(r = 0.99; n = 8)$
$\mathrm{R} = \mathrm{Pr, CH_2CH{=}CH_2}, m = 1\text{–}4.$

There has been a considerable discussion in the literature as to whether so-called $(p\text{–}d)_\pi$ back-bonding occurs in the M—O bond (M = Si, Ge). ^{17}O NMR has proved to be a suitable experimental tool to clarify some points in this discussion.

A linear relationship has been found[19] to exist between the ^{17}O CS for methyl ethers (MeOR) and the OH stretching frequencies [ν(OH)] of the corresponding saturated alcohols, ROH (Eqn [5]):

$$\delta(^{17}\mathrm{O}) = 6413.7 - 1.7705\nu\,(\mathrm{OH}) \qquad [5]$$

$(r = 0.987; n = 11)$
$\mathrm{R} = \mathrm{Et, Pr, i\text{-}Pr, Bu, i\text{-}Bu, s\text{-}Bu, t\text{-}Bu, Me_3CCH_2, Me_2CHCH_2CHC_3, Me_3CCH_2CH_2}$

We have found that a similar correlation exists also between ^{17}O CS in the alkoxysilanes $\mathrm{Et_3SiOR}$ (Eq [6]) and in $\mathrm{MePh_2SiOR}$ (Eq [7]) and the OH stretching frequencies of the corresponding alcohols, ROH:[20]

$$\delta(^{17}\mathrm{O}) = 3718(\pm 21) - 3.2(\pm 0.6)\nu(\mathrm{OH}) \qquad [6]$$

$(r = 0.97; n = 6)$
$\mathrm{R} = \mathrm{Me, Et, Pr, i\text{-}Pr, Bu, s\text{-}Bu}$

$$\delta(^{17}\mathrm{O}) = 3722(\pm 21) - 3.2(\pm 0.6)\nu(\mathrm{OH}) \qquad [7]$$

$(r = 0.97; n = 6)$
$\mathrm{R} = \mathrm{Me, Et, Pr, i\text{-}Pr, Bu, s\text{-}Bu}$

As follows from Eqns [5]–[7], ^{17}O CS in alkoxysilanes are more sensitive to the effects of substituents at the oxygen atom than in ethers. This may be due to partial π-bonding in the Si—O fragment of alkoxysilanes.

The characteristic feature of all the Si—O and Ge—O bond-containing compounds $\mathrm{R'_{4-n}M(OR)}_n$, M = Si, Ge is a sagging pattern of the dependence of $\delta\,^{17}$O on n (Fig. 1), regardless of the nature of substituents R and R′. At the same time our CNDO/2 calculations[3] show a gradual increase in the negative charge at the oxygen atom with the growth of the number of the alkoxy groups (Fig. 2). ^{17}O CS should move downfield with increasing n, as was shown earlier by Fliszar for carbon analogues.[21]

These experimental curves could be explained if we assume that the position of ^{17}O resonances in the alkoxy derivatives is dominated by the π-electron density at the oxygen nuclei and, consequently, by the π-charge as well as by partial double bonding between the oxygen and silicon atoms, which is represented by the term Q_AB in the equation for paramagnetic shielding contribution (Eqn [8]):

$$\sigma_\mathrm{p} \cong (\Delta E)^{-1}\langle r^{-3}\rangle_\mathrm{2p} \sum Q_\mathrm{AB} \qquad [8]$$

where ΔE is the mean excitation energy and $\langle r^{-3}\rangle_\mathrm{2p}$ is the inverse cube of the radius of the $2p$ orbital. Q_AB is defined in terms of charge density elements and the bond-order matrix.

Enhanced $(p\text{–}d)_\pi$ bonding between the oxygen and silicon atoms decreases the π-electron charge on the oxygen atom and increases the order of the Si—O bond (and consequently the 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 $(p\text{–}d)_\pi$ interaction declines with an increasing number of alkoxy substituents, thereby leading to an increase in the partial π-charge on the ^{17}O nucleus. By analogy with

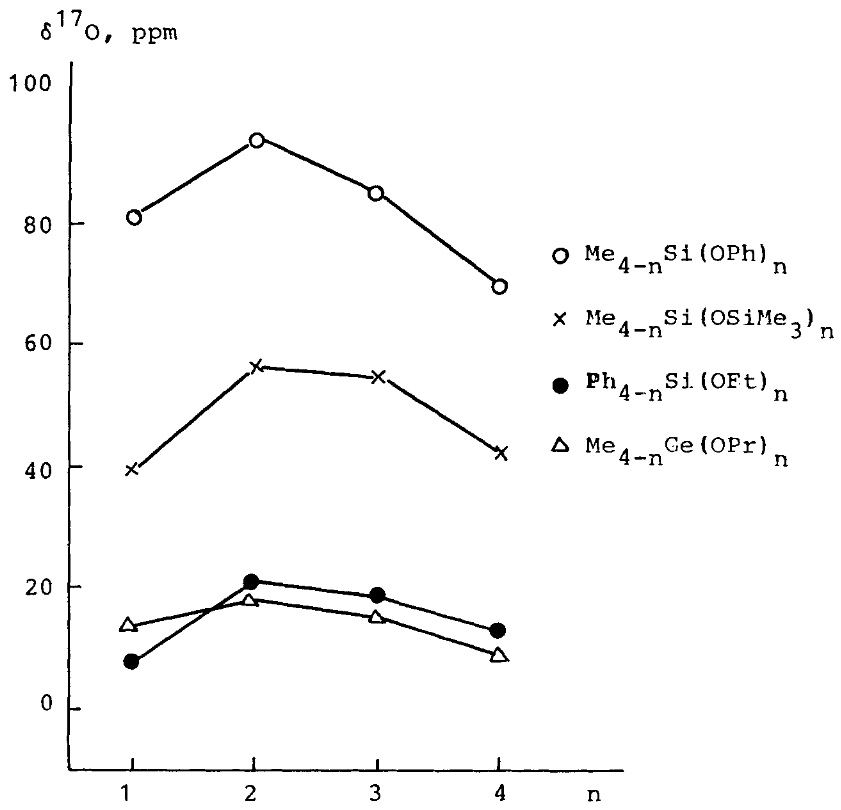


Figure 1 The dependence of ^{17}O CS on the number of oxygen containing substituents.

systems containing a double-bonded oxygen atom, an increasing π-charge accounts for the observed upfield shift of ^{17}O resonance signals.

All the above holds true also for alkoxygermanes but the extent of back-bonding is smaller in the Ge—O bond as compared with the Si—O bond.

The only exception for the sagging pattern of the dependence of δ^{17}O on n is the case when a molecule contains a chlorine atom as a substituent at the silicon and germanium (Fig. 3), i.e. in compounds where the possibility of overlapping in the M—O bond is negligible.

In trimethyl(aroxy)silanes $Me_3SiOC_6H_4R$, the ^{17}O CS are well correlated with the Taft constants of the substituent (Eqn [9]). The inductive drawing-in of the electrons from the oxygen leads to the contraction of the 2π-orbitals. The subsequent increase in the radial term of the shielding constant reduces the shielding. Consequently, the changes in ^{17}O CS of aroxysilanes as well as in anisoles are governed by the changes in the radial term of the shielding constant.

$$\delta^{17}O = 55.5 + 27.8\sigma^{*}_{C_6H_4R} \qquad [9]$$
$$(r = 0.99;\ n = 5)$$
$$R = F, Cl, Br, I, NO_2$$

A comparison of three series of the following aromatic compounds and the ratio of coefficients ρ/ρ', supports the earlier proposed participation of oxygen atoms of aroxysilanes both in the interaction with Si atoms and in $(p\text{-}\pi)_\pi$ conjugation with the aromatic ring (Eqns [10]–[12]).

$$Me_3SiOC_6H_4R\colon\ \delta^{17}O = 82.3 + 27.8\,\sigma^{0}_{R} + 9.5\,\sigma_{I}$$
$$\rho/\rho' = 2.9\ (r = 0.95;\ n = 8) \qquad [10]$$
$$R = Me,\ i\text{-}Pr,\ H,\ F,\ Cl,\ Br,\ I,\ NO_2$$

$$MeOC_6H_4R\ [22]\colon\ \rho/\rho' = 1.8\ (r = 0.98;\ n = 10) \qquad [11]$$

$$CH_2{=}CHOC_6H_4R\ [22]\colon\ \rho/\rho' = 2.8\ (r = 0.93;\ n = 6) \qquad [12]$$

In the substituted furans XC_4H_3O, a relationship has been found between ^{17}O CS and the Swain–Lupton constants of substituents, indicating that the resonance effects dominate over the substituent influence[14] (Eqn [13]).

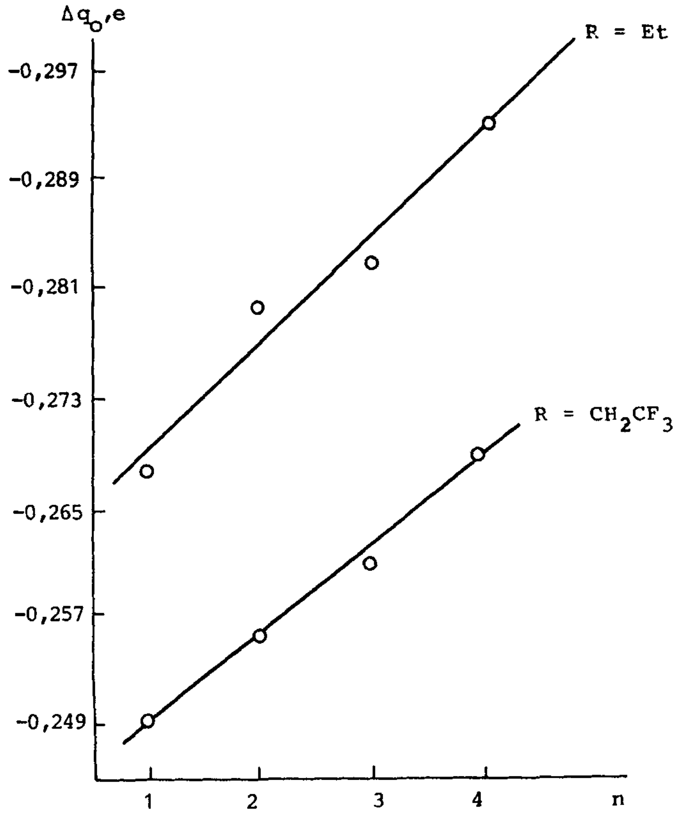


Figure 2 Variation of charge on oxygen atom in alkoxysilanes Me$_{4-n}$Si(OR)$_n$

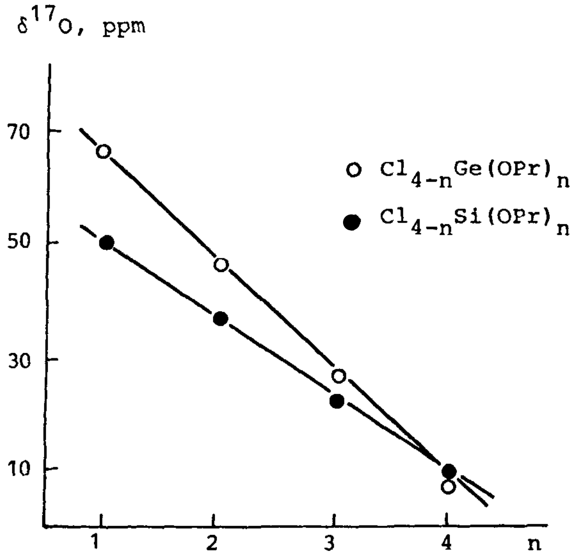
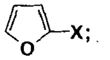


Figure 3 The dependence of ^{17}O CS on the number of alkoxy groups in chloroalkoxysilanes and -germanes

$\delta^{17}O = 238.63 + 4.78F - 30.04R$ ($r = 0.985$; $n = 9$)


X; X = NO_2, CN, CHO, COOMe, Br, H, Me, t-Bu, Me_3Si [13]

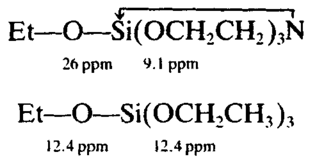
At the same time the inductive and resonance effects act in opposite directions. Our CNDO/2 calculations have revealed a linear dependence of ^{17}O CS on the magnitude of the π-charge on the oxygen atom (Eqn [14]):

$$\delta^{17}O = -2146 + 1337\, q\pi(O) \quad (r = 0.952;\ n = 9) \qquad [14]$$

X is as defined under Eqn [13].

STRUCTURAL ANALYSIS

Comparison of the ^{17}O CS in silatranes[12] and triethoxysilanes[3] reveals a negligible effect of cyclization and transannular bond formation on the ^{17}O CS of the equatorial oxygen atoms. In contrast, a considerable low-field shift (~13 ppm) has been observed for the axial oxygen atom in 1-ethoxysilatrane:



$$\mathrm{Et{-}O{-}\overset{\curvearrowleft}{Si}(OCH_2CH_2)_3N}$$

26 ppm 9.1 ppm

$$\mathrm{Et{-}O{-}Si(OCH_2CH_3)_3}$$

12.4 ppm 12.4 ppm

^{17}O CS in cyclic siloxanes are practically independent of the ring size.[7] This has been explained by the opposing action of the factors governing the values of the ^{17}O CS, thus making them balanced. However, this equilibrium is shifted in the case of cyclosiloxazanes, as indicated by the tendency of ^{17}O resonances to move to higher fields with decreasing ring size.[7]

^{17}O CS in siloxanes are more sensitive to the variation of substituents at the Si atoms than ^{29}Si CS (Table 1). This makes ^{17}O NMR attractive for the analysis of siloxane mixtures.

The application of ^{17}O NMR to conformational analysis has been demonstrated in the case of silocanes (1,3-dioxa-5-aza-2-silacyclooctanes).[11] the ^{17}O NMR signal of the derivatives existing in the crown conformation is shifted downfield by 7–10 ppm relative to the derivatives existing predominantly in conformations belonging to the boat–chair family. This shift is assumed to be due to an anomeric effect in silocanes.

The ^{17}O NMR spectrum of 4,8-dimethylsilocane displays two signals at 47.8 ppm and 57.8 ppm, corresponding to the *RR* and *RS* diastereomers, respectively. This supports the suggested conformational dependence of ^{17}O CS, as the conformational equilibrium for the *RS* diastereomer is completely shifted towards the crown conformation.

There is the particular possibility of the application of ^{17}O NMR to the study of tautomeric equilibrium in solution. ^{17}O NMR spectra of monoacyloxysilanes and germanes display two well resolved ^{17}O resonance signals.[10] One lies in the region of 150–176 ppm and corresponds to the ether oxygen; the other signal is situated in the range 330–376 ppm and corresponds to the carbonyl oxygen. But only one signal appears in the ^{17}O spectra of diacyloxysilanes in the intermediate position (270–287 ppm).[23] This reflects the equivalence of both oxygens in the NMR timescale resulting from their fast exchange.

Table 1 Dependence of CS on substituents at the Si atom in siloxanes

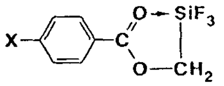
	δ^{17}O (ppm)	δ^{29}Si (ppm)
$(Me_3Si)_2O$	39.0	6.5
$(Me_2ClSi)_2O$	70.0	6.9
$(Me_2HSi)_2O$	22.9	−5.0

The characteristic feature of the acyloxystannane ^{17}O NMR spectrum is also the presence of only one signal, located approximately in the middle of the positions of carboxyl group ^{17}O signals in the analogous silicon and germanium compounds.[10] The existence of only one signal for both oxygens again reflects their equivalence in the NMR timescale resulting from fast exchange processes in solution. With the help of ^{119}Sn NMR we have ascertained the predominance of an intermolecular exchange mechanism in this case.

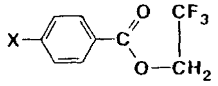
COORDINATIVE INTERACTION

It was shown that involvement of an ether oxygen atom in coordination does not cause any significant variation in ^{17}O CS.[24]

In contrast to ether oxygen atoms, carbonyl oxygen CS are more sensitive to coordinative interactions. Thus we have studied ^{17}O CS for two series of *para*-substituted benzoic acid esters—trifluorosilylmethyl (**I**) and the corresponding carbon analogues (**II**). The sensitivity of the ^{17}O CS to the substituent effects in silicon compounds is more pronounced, thus suggesting the influence of an additional effect. This effect could be charge transfer from the carbonyl oxygen to silicon, which varies with the substituent X in the aromatic ring. An increase in acceptor properties reduces the degree of the transmission. This assumption has been affirmed by IR spectroscopy and dipole moment data for these compounds[25] (Eqns [15], [16]).



I



II

$$\textbf{I}: \delta^{17}O_{CO} = 277.3 + 28.0\sigma_p \qquad [15]$$
$(r = 0.97; n = 7)$

$$\textbf{II}: \delta^{17}O_{CO} = 337.9 + 17.1\delta_p \qquad [16]$$
$(r = 0.94; n = 7)$

X = OMe, Me, H, F,Cl, Br, NO_2

The transition from **I** to **II** causes marked downfield shifts of the carbonyl oxygen ^{17}O resonance. The magnitude of the shift varies from 47 to 65 ppm and may be partially due to the steric effects in the bent form.

Thus it has been proved that NMR spectroscopy of the quadrupole nucleus ^{17}O may be quite successfully applied for solving various problems of Group 14 organometallic chemistry and we are convinced that the information gained from the ^{17}O NMR spectra outweighs the experimental difficulties of obtaining the data.

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