November, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (11), 3391—3396 (1979) 3391

Oxygen-17 Nuclear Magnetic Resonance. III.[1] Oxygen Atoms with a Coordination Number of Two

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(Received May 23, 1979)

Fourier transform ^{17}O NMR spectra have been measured for a number of alcohols, ethers, acetals, formates, acetates, and esters of inorganic acids in natural abundance at 10.8 MHz. The ^{17}O chemical shifts which cover a range as large as several hundred ppm are primarily governed by the sum of electronegativity of the first atoms or groups attached to the central oxygen. The downfield shift due to β-methyl groups in alcohols and ethers is in parallel with decrease in their ionization potentials, demonstrating the importance of the paramagnetic screening term in the ^{17}O shifts of these compounds. Diamagnetic shift due to γ-carbons and -oxygens has also been disclosed.

The first observation of ^{17}O nuclear magnetic resonance signals was reported as early as in 1951.[2] Chemical shifts of more than one hundred organic compounds of relatively small molecular weight were documented by Christ *et al.* in 1961.[3] Wider applications of the ^{17}O NMR technique have since been hampered both by a low natural abundance (0.037%) and by an appreciable electric quadrupole moment ($Q=-2.6\times10^{-26}\,cm^2$) which effects line broadening of the ^{17}O isotope. Recent advances in FT-NMR instrumentation together with rf units with a frequency synthesizer and probe heads with a tunable preamplifier have made observation of ^{17}O NMR routinely available on samples with ^{17}O isotope in natural abundance.[4] In view of an important role of oxygen-containing functions in chemistry, establishment of a useful ^{17}O NMR shifts *vs.* structure correlation is indispensable. We wish to report here the ^{17}O NMR shifts of a variety of alcohols, ethers, acetals, formates, acetates, and esters of inorganic acids, and review a number of empirical rules governing the shift data of these compounds as well as the literature values[4] for some typical compounds with dicoordinated oxygen functions.

Results and Discussion

A General Trend in ^{17}O Shifts. The ^{17}O NMR shift data of dicoordinated oxygen functions are given in Table 1. Firstly we note that the ^{17}O shifts have a wide range of several hundred ppm. This is quite large in reference to 10 and 200 ppm of the ^1H and ^{13}C shift ranges, respectively, of ordinary organic compounds and will give the impression that ^{17}O NMR spectra can be most informative as a structural probe. Strictly speaking, however, we have also to take into account of the wide ^{17}O NMR line-width unprecedented in ^1H and ^{13}C NMR. The amount of information derivable from chemical shift is approximately given by the shift range (Δ) divided by the spectral line width ($\Delta_{1/2}$). When the ^1H, ^{13}C, and ^{17}O NMR are compared, Δ can be taken as 0.8, 4, and 8 kHz for example and $\Delta_{1/2}$ may be typically 1, 1, and 100 Hz, respectively. Therefore, the capacity of information derivable from chemical shift data of ^1H, ^{13}C, and ^{17}O NMR spectroscopies would be ($\Delta/\Delta_{1/2}=$) 800, 4000, and 80, respectively. The widest shift range observed for the ^{17}O NMR should not necessarily be overemphasized.

It may be noted in the second place that the water molecule has the oxygen atom which resonates at one of the highest field region,[5] and the resonance for the central oxygen atom of ozone appears at the extreme downfield. Other data on the oxygens attached to various kinds of elements are scattered in between. Changes in the oxygen-17 chemical shift appear to be due primarily to alterations in the electron density at oxygen caused by changes in the electronegativity of α-atoms attached to the central oxygen atom. As illustrated by an approximately linear correlation in Fig. 1, downfield shift is produced as more electronegative atoms are introduced. The line has a slope of about 270 ppm/electronegativity unit which is about six times as steep as those obtained by similar plots of the ^{13}C shifts *vs.* the electronegativity of the adjacent hetero atoms.[6] We point out that, whereas the diamagnetic electric current which is directly affected by the electronegativity of ligands plays a major role in controlling the chemical shifts of ^1H, the ^{13}C and ^{17}O NMR shifts are governed by the paramagnetic screening and decrease of shielding with the increasing electronegativity of the substituents may be provided by increase in the mean inverse cube of the 2p electron radius $\langle r^{-3}\rangle_{oxygen}$ and the orbital term Q_{AA} (*vide infra*).[7]

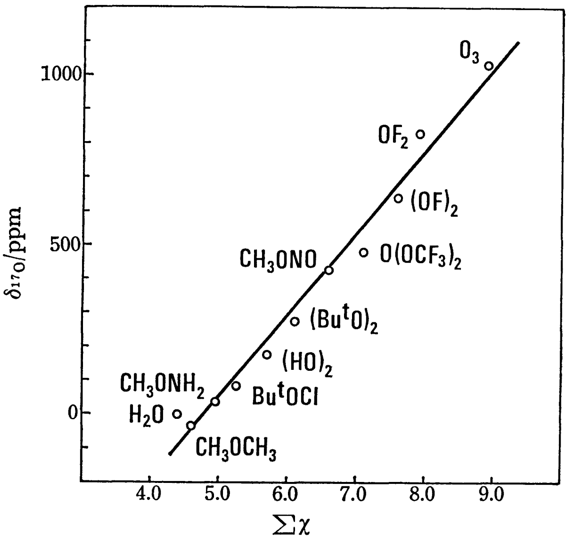


Fig. 1. Plots of ^{17}O NMR shifts *vs.* the sum of the electronegativities for dicoordinated oxygen compounds. Electronegativities (which are group values where relevant) are from Ref. 20.

TABLE 1. ^{17}O CHEMICAL SHIFTS (ppm DOWNFIELD FROM WATER) OF DICOORDINATED OXYGEN COMPOUNDS

	$\delta_{^{17}O}$	$\Delta_{1/2}$ [c] Hz	Solvent	Temp °C
Alcohols and phenols				
Methaol	−38	60	neat	amb
1-Butanol	−3	172	CCl_4 (1:1)[a]	70
1-Butanol	−1	168	neat	62
3-Methyl-1-butanol	−2	244	neat	75
Benzyl alcohol	4		CCl_4 (1:1)	70
Citronellol	5		CCl_4 (1:1)	80
Ethanol	8	128	neat	amb
2-Pentanol	30		CCl_4 (1:1)	70
2-Butanol	36	160	CCl_4 (1:1)	70
Cyclohexanol	36		CCl_4 (1:1)	70
2-Propanol	39	280	neat	amb
2-Methyl-2-butanol	55	200	CCl_4 (1:1)	70
2,3-Dimethyl-2-butanol	55	200	CCl_4 (1:1)	70
α-Terpineol	55		CCl_4 (1:1)	70
t-Butyl alcohol	63	180	CCl_4 (1:1)	68
t-Butyl alcohol	68		neat	amb
Phenol	79		C_6H_6 (1:2)	76
o-Nitrophenol	87		C_6H_6 (1:2)	76
Hydrogen peroxide	174		30% aq.	amb
Ethers				
Ethylene oxide	−49		neat	amb
Dimethyl ether	−42		$CDCl_3$ (1:1)	−40
Oxetane	−12	48	neat	amb
Tetrahydropyran	10		$CDCl_3$ (1:1)	amb
Oxepane	14	80	neat	amb
Diethyl ether	16		neat	amb
Tetrahydrofuran	18		neat	amb
Tetrahydrofuran	18		$CDCl_3$ (1:1)	amb
Anisole	50	180	neat	amb
Diisopropyl ether	64		neat	amb
7-Oxanorbornane	86		$CDCl_3$ (1:1)	amb
Di-*t*-butyl ether	88	140	CCl_4 (1:1)	amb
Di-*t*-butyl ether	90		neat	amb
1,2-Dimethoxyethane	−23		neat	amb
Diethylene glycol dimethyl ether	−27 (center) −3 (end)		neat	70
1,4-Dioxane	0	85	$CDCl_3$ (1:1)	amb
15-Crown-5	0		DMF	128
Furan	240		neat	amb
Furfural	237		neat	amb
Trimethyloxonium tetrafluoroborate	−29	180	CH_3NO_2	amb
Diethyl ether–BF_3	31		neat	amb
Hexamethyldisiloxane	43		neat	amb
Acetals and orthoestes				
Dimethoxymethane	10	60	neat	amb
1,3-Dioxolane	34		$CDCl_3$ (1:1)	amb
1,3-Dioxane	37		$CDCl_3$ (1:1)	amb
1,3-Dioxane	38		neat	amb
Bis(methoxymethyl) ether	65 (center) 10 (end)	100 100	neat	amb
1,3,5-Trioxane	65		$CDCl_3$	amb
(2*H*-)1,3-Benzodioxole	82		$CDCl_3$	amb
Trimethyl orthoformate	30		neat	amb
2,8,9-Trioxaadamantane	67	200	$CDCl_3$	amb

Table 1. (Continued)

	$\delta_{^{17}\mathrm{O}}$	$\Delta_{1/2}$/Hz	Solvent	Temp/°C
1,4,6,9-Tetraoxaspiro[4.4]nonane	75		neat	amb
Esters				
Methyl formate	143 (364)[b]		neat	amb
Ethyl formate	173 (364)		neat	amb
Isopropyl formate	200 (364)		neat	amb
t-Butyl formate	212 (380)		neat	amb
Methyl acetate	148 (355)		neat	amb
Ethyl acetate	169 (363)		neat	amb
Isopropyl acetate	196 (363)		neat	amb
t-Butyl acetate	207 (375)		neat	amb
Methyl acrylate	132 (345)		neat	amb
Diethyl oxalate	166 (359)		neat	amb
γ-Butyrolactone	176 (335)		neat	amb
Diethyl carbonate	123 (242)		neat	amb
Trimethyl phosphite	44 ($J_{\mathrm{O-P}}=183$ Hz)		neat	amb
Trimethyl phosphate	65 ($J_{\mathrm{O-P}}=164$ Hz) (19)		$CDCl_3$	amb
2,8,9-Trioxa-1-phospaadamantane	82		CD_2Cl_2	amb
Methyl nitrite	420 (790)[18]			
Propyl nitrite	455 (803)[3]			
Isopentyl nitrite	467 (819)		$CDCl_3$ (1:1)	amb
t-Butyl nitrite	513 (838)[3]			
Dimethyl sulfate	142 (101)		$CDCl_3$ (1:1)	amb
Others				
O-Methylhydroxylamine	35[3]			
t-Butyl hypochlorite	79			
Di-*t*-butyl peroxide	276 269[3]			
$(CF_3O)_2O$	479 (center)[19] 321 (end)			
FOOF	647[19]			
F_2O	830[19]			
Ozone	1032 (center)[19] 1598 (end)			

a) An approximate ratio in volume. b) Shift values in parentheses are for doubly bonded oxygens. c) No window function was applied for the measurement except for alcohols where a sensitivity enhancement parameter was set at −0.02 s throughout.

Simple Alcohols and Ethers. Shifts to lower field in the ^{17}O resonance are observed as the α-carbon is substituted with alkyl groups. Primary, secondary, and tertiary alcohols, for example, have their characteristic shift ranges: −3—10 (except for −38 ppm of methanol), 30—40 and 55—70 ppm downfield relative to water, respectively. We have so far met no exception to the above rule on the ^{17}O shifts brought about by the alkyl substitution. The presence of diamagnetic γ-effect is suggested by a slightly high field shift of 1-butanol and 2,3-dimethyl-2-butanol as compared to ethanol and *t*-butyl alcohol, respectively. An example which would violate the above shift ranges could be found in sterically congested alcohols. Changes in chemical shifts are steeper in ethers than in alcohols and esters.

The findings have two facets of importance. One is as a new method for differentiating among primary, secondary, and tertiary structures of unknown alcohols, ethers and esters. The method appears quite unique and useful, but let us point out that there is a certain limitation to the practical application of this rule to the structural elucidation of complex organic molecules. Since the oxygen-17 nucleus ($I=5/2$) has electric quadrupole moment and the line width of resonance signals is directly proportional to correlation time τ_c for the overall rotation of the molecules which in turn is correlated to solution viscosity η, a fairly fluid sample solution must be employed. When isotropic molecular tumbling is rapid on the NMR time scale, the line width $(1/T_1)$ determined by quadrupole relaxation is given by Eq. 1, where q and η stand for the electric field gradient and the asymmetry parameter at the nuclear site. The Stokes-Einstein-Debye equation (Eq. 2) relates τ_c to temperature T. The measurement at elevated solution temperature is thus preferred. A

$$\frac{1}{T_1}=\frac{3}{125}\left(1+\frac{\eta}{3}\right)\left(\frac{e^2Qq}{h}\right)^2\tau_c \qquad (1)$$

$$\tau_c=\frac{4\pi\eta a^3}{3kT} \qquad (2)$$

sample of relatively large molecular weight ($M>150$) for which a solution of considerably high concentration may be required by the sensitivity of the present instrument often tends to be hard to measure because of line-broadening. The limitation could be avoided in principle by the use of a spectrometer with higher magnetic field and/or isotopically enriched samples.

The other is on the origin of the observed ordering of chemical shifts. There are ample examples which show that electron density at the oxygen atom increases as we go from methanol *via* ethanol and 2-propanol to *t*-butyl alcohol. The polar substituent, constants σ^* for the methyl, ethyl, isopropyl, and *t*-butyl groups are 0 (by definition), -0.1, -0.19, and -0.3, respectively. The observed shifts in Table 1 show that ^{17}O screening decreases on going from methanol to *t*-butyl alcohol, and is not compatible with the electron density at oxygen dominating the ^{17}O shifts as was the case in the previous section.

According to the Pople-Karplus theory on paramagnetic screening,[7] the screening constant of atom A bound to other atom B is given by Eq. 3. The Q's are orbital terms related to charge density on atom

$$\sigma_p^A=-\frac{e^2\hbar^2\langle r^{-3}\rangle}{2m^2c^2(\Delta E)}\left[Q_{AA}+\sum_{B\neq A}(Q_{AB})\right] \qquad (3)$$

A and bond order between A and B, and ΔE is a mean or effective excitation energy. If the diamagnetic screening or the $\langle r^{-3}\rangle$ and Q_{AA} terms in the paramagnetic screening were the determining factor, tertiary alcohols and ethers which have highest electron density at oxygen should have given the highest field shifts in the ^{17}O resonance. Resonance can move downfield as the lowest-energy electronic transition is shifted to longer wavelength. The n→π* transition has been shown to be crucial to the shift differences in the ^{17}O NMR of carbonyl compounds.[8] In the present case of aliphatic alcohols and ethers, the excited states to be mixed with the ground state by an external magnetic field is either the n→σ* or Rydberg states.[9] Since the corresponding transition appears in the vacuum ultraviolet region and is not unambiguously characterized, let us take the adiabatic ionization potentials of these compounds as a measure of ΔE. A reasonably smooth correlation is found in the ^{17}O chemical shifts *vs.* the inverse of the ionization potentials plots both for alcohols and ethers as shown in Fig. 2.

Whereas there is no strict meaning in the apparent linearity of the plots, the correlation appears to demonstrate that the energy levels of the oxygen n-electrons are more sensitive to the structural changes in the alkyl groups than the terminating orbital levels of oxygen and that ΔE gets smaller on going from the methyl through ethyl and isopropyl to *t*-butyl groups. The paramagnetic contribution to the total screening constant is concluded to be important in simple alcohols and ethers.

Simple cyclic ethers present no anomaly in that

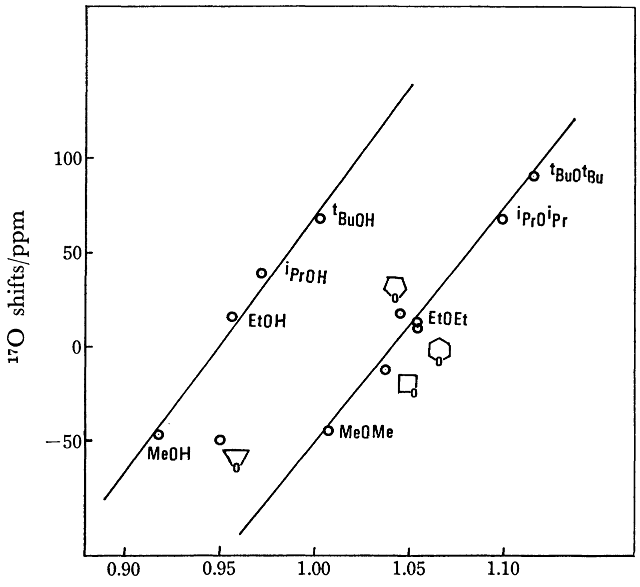


Fig. 2. Plots of ^{17}O chemical shifts *vs.* the inverse of adiabatic ionization potentials (from Ref. 11) of alcohols and ethers.

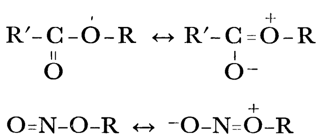
their ^{17}O shifts *vs.* $1/IP$ plots conform to a line given by acyclic ethers. Oxiranes form a conspicuous exception to this trend. Just as the well-known case of the ^1H and ^{13}C shielding of three membered rings, the ^{17}O resonance of oxiranes shows a marked shielding effect. The diamagnetic shielding is, however, not as strong as it should be expected from the ^{17}O shifts *vs.* $1/IP$ plots for other ethers. These anomalies of oxiranes will be discussed separately in the forthcoming paper in view of the importance of the epoxide functions in many fields of chemistry.

Acetals and Orthoesters. When the β-methylene group in methyl propyl ether (δ −18)[10] is replaced by oxygen to make dimethoxymethane (δ 10), downfield shift by 28 ppm is obtained. The downfield shift of a similar amount (Δδ 27 ppm) is observed on going from tetrahydropyran (δ 10) to 1,3-dioxane (δ 37). An approximate additivity appears to hold for this downfield shift due to introduction of the β-oxygen atoms. A shift by 56 ppm on going from dipropyl ether (δ 7)[10] to bis(methoxymethyl) ether (δ 65) is just twice as large as 28 ppm. The ^{17}O resonances for 1,3,5-trioxane and 2,8,9-trioxaadamantane appear at 54 and 56 ppm downfield of tetrahydropyran, respectively.

γ-Effects. Effects of the γ-carbon atom on the ^{17}O NMR shifts have been pointed out;[10] replacement of β-hydrogens in ethyl methyl ether with the methyl groups produces a stepwise highfield shift by 6, 1.5, and 2.5 ppm. Now, replacement of the γ-carbon atom in butyl methyl ether (δ −18)[10] by oxygen to give 1,2-dimethoxyethane accompanies 5 ppm upfield shift. Similar upfield shifts are observed also in diethylene glycol dimethyl ether (6.5 ppm from dibutyl ether (δ 3.5)) and *p*-dioxane (11 ppm from tetrahydropyran).

The observed diamagnetic shifts of 6 and 12 ppm of ethylene glycol and 2-chloroethanol, respectively, relative to 1-propanol (δ 0) may be additional examples of γ-effect due to a hetero atom.

Esters. The effect of alkyl groups on ^{17}O shifts of the ethereal oxygen of esters is similar to that in alcohols and ethers but is less pronounced. The shift differences between two extreme alkyl groups, namely, the methyl and *t*-butyl derivatives, are 130 and 106 in ethers and alcohols, respectively, and only 93, 70, and 60 ppm in nitrites, formates, and acetates, respectively. The results may be a manifestation of resonance interaction as depiced in Eq. 4 serving as a buffer of the electronic effect of alkyl groups R. Contribution of the zwitterionic canonical structure in each resonance hybrid will be in the order: acetates>formates>nitrites.



$$\mathrm{R'{-}\underset{\underset{O}{\|}}{C}{-}O{-}R \leftrightarrow R'{-}\underset{\underset{O^-}{|}}{C}{=}\overset{+}{O}{-}R} \qquad (4)$$

$$\mathrm{O{=}N{-}O{-}R \leftrightarrow {}^-O{-}N{=}\overset{+}{O}{-}R}$$

We conclude that, in spite of some difficulties inherent in natural-abundance ^{17}O NMR measurements, this new technique has a number of merits worth the effort. Firstly, the technical difficulties are partly compensated by the short spin-lattice relaxation times of the quadrupolar ^{17}O which enable us to accumulate a large number of transients in a given time. Often a spectrum with good S/N ratios is obtained within a time period shorter than that necessary for measuring ^{13}C NMR signals due to quaternary carbons of relatively long T_1 and with almost no NOE effect. Secondly, we have pointed out that ^{17}O NMR spectra are highly informative as a structural probe. Shift ranges as large as 1000 ppm for dicoordinated oxygens are governed by the paramagnetic screening and can be interpreted in terms of empirical rules basically similar to the familiar ones employed in ^{13}C NMR spectroscopy.

Experimental

Spectral Measurements. The measurements were made with the ^{17}O nuclei in natural abundance (0.037 %) on a Varian FT-80A spectrometer at 10.782 MHz. For a 8000 Hz spectral width, 320 data points in the time-domain spectra were used, the Fourier number being kept at 16384. The number of transients accumulated with a 90° pulse and an acquisition time of 0.02 s was in the range 10^4—10^5 to get spectra of reasonable S/N ratios. When a longer acquisition time (AT) of 0.1 s was employed, the number of data points (DP) increased to 1600 according to equation $DP = 2AT \cdot SW$ (SW is a spectral width). The measurement under these conditions was found to be worse with respect to the S/N of spectra, not only because it required the accumulation time five times as long as the previous one to get the same sum of the number of transients, but also because it sampled mostly noise signals after the free induction signals practically decayed at $5T_1(<0.02\ \mathrm{s})$. The ^{17}O shifts and half-band-widths did not differ at all from those obtained under the standard conditions. Since quadrupole relaxation of ^{17}O nuclei is rapid, the use of long delay times between the end of each rf pulse and the beginning of data collection is not in principle necessary. However, some baseline distortions in transformed frequency-domain signals often resulted due to incomplete spectrometer recovery following rf pulse, when too short delay times were employed.[12] This was more pronounced in ^{17}O NMR, as the rf frequency was lower than those of ^1H and ^{13}C spectroscopy. Alpha delay was usually set at 800—1000 μs.

Chemical shifts were measured as frequency shifts from the rf synthesizer frequency (8.532000 MHz) and expressed in ppm relative to the oxygen of water which resonated at 10.78321 MHz when measured in a capillary tube placed concentrically within a sample tube of 10 mm o.d. Chemical shifts are accurate to ±1 ppm. The sample temperature was at 34—36 °C unless otherwise stated in Table 1. The half-band-widths of alcohols and ethers were 60—280 Hz under these conditions.

Materials. The following compounds were prepared according to the literature and their purity was confirmed by VPC and/or spectral data: di-*t*-butyl ether,[13] trimethyloxonium tetrafluoroborate,[14] bis(methoxymethyl) ether,[15] 2,8,9-trioxaadamantane,[16] and 2,8,9-trioxa-1-phosphaadamantane.[17] The samples of (2*H*-)1,3-benzodioxole and 1,4,6,9-tetraoxaspiro[4.4]-nonane were kindly supplied by Prof. Dr. S. Smoliński of Jagellonian University, Kraków, Poland. Pure samples from commercial sources were used otherwise.

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