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OXYGEN-17 NMR CHEMICAL SHIFTS OF ALCOHOLS, ETHERS AND ESTERS

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The ^{17}O NMR chemical shifts of alcohols, ethers and esters have been determined in natural abundance at 10.8 MHz. As the alkyl groups are changed, shielding of oxygen atoms decreases in the order: primary < secondary < tertiary. The downfield shifts which nicely parallel the lowering of the ionization potentials of alcohols and ethers demonstrate the importance of the paramagnetic screening term in the ^{17}O shifts of these compounds.

An innovative use of ^{17}O NMR in structural studies of oxygen-containing compounds has been the recent topic of great interest.[1] A wide shift range of ca. 800 ppm which the ^{17}O chemical shifts of ordinary compounds cover promises a very informative spectroscopic method rivalling ^{1}H and ^{13}C NMR.[2] As part of our exploratory survey of ^{17}O NMR spectroscopy as a structural probe, we have measured the ^{17}O shifts of a series of alcohols, ethers, formates and acetates and found a useful and intriguing shift vs. structure correlation.[3]

The measurements were made with the ^{17}O in natural abundance (0.037 %) on a Varian FT-80A spectrometer at 10.8 MHz. For 8000 Hz spectral width, 328 data points were available. The number of transients was in the range $10^4 - 10^6$ with the aquisition time of 0.02 s. Internal lock was effected by using deuterium oxide or acetone-d_6 sealed in a capillary tube. All the chemical shifts were referenced to the ^{17}O resonance of these deuterated solvents. The half-band-widths of alcohols were 80–200 Hz and those of ethers were 70–80 Hz.

A number of interesting trends can be found in the shift data collected in Table 1. Firstly, we note that the oxygen resonance is shifted to lower field as the alkyl groups are changed from the primary via secondary to tertiary ones. Primary, secondary and tertiary alcohols, for example, have their characteristic shift ranges: -2–10 (except for -38 of methanol), 30–40 and 55–70 ppm downfield relative to water, respectively. The change in chemical shifts is steeper in ethers than in alcohols and esters. We have so far met no exception to the above rule on the ^{17}O shifts brought about by the alkyl substitution.

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

Table 1. ^{17}O chemical shifts (ppm downfield from water) of alcohols, ethers and esters.

	shift[a]	solvent	temp/°C		shift[a]	solvent	temp/°C
Alcohols							
methanol	-38	neat	amb[b]	cyclohexanol	36	CCl_4(1:1)	70
1-butanol	-3	CCl_4(1:1)	70	2-propanol	39	neat	amb
1-butanol	-1	neat	62				
benzyl alcohol	4	CCl_4(1:1)	70	2-methyl-2-butanol	55	CCl_4(1:1)	70
citronellol	5	CCl_4(1:1)	80				
ethanol	8	neat	amb	2,3-dimethyl-2-butanol	55	CCl_4(1:1)	70
				α-terpineol	55	CCl_4(1:1)	70
2-pentanol	30	CCl_4(1:1)	70	t-butyl alcohol	63	CCl_4(1:1)	68
2-butanol	36	CCl_4(1:1)	70	t-butyl alcohol	68	neat	amb
Ethers							
dimethyl ether	-42	$CDCl_3$	-40	diisopropyl ether	64	neat	amb
diethyl ether	16	neat	amb	di-t-butyl ether	90	neat	amb
				di-t-butyl ether	88	CCl_4(1:1)	amb
Esters							
methyl formate	143 (364)[c]	neat	amb	methyl acetate	148 (355)[c]	neat	amb
ethyl formate	173 (364)	neat	amb	ethyl acetate	169 (363)	neat	amb
isopropyl formate	200 (364)	neat	amb	isopropyl acetate	196 (363)	neat	amb
t-butyl formate	212 (380)	neat	amb	t-butyl acetate	207 (375)	neat	amb

a) accurate to ± 2 ppm. b) 34–36 °C. c) shifts for the carbonyl oxygens.

the oxygen-17 (I = 5/2) has nuclear 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,[4] a fairly fluid sample solution has to be employed. Thus a sample of relatively large molecules (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 compounds.

The other is on the origin of the observed odering 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 Taft's σ* values are a typical measure of the electron-donating ability of alkyl groups. 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 diamagnetic term dominating the ^{17}O shifts. The diamagnetic screening should have placed tertiary alcohols and ethers which have highest electron density at

the oxygen to resonate at the highest applied magnetic field. According to the Pople's theory on paramagnetic screening, nuclear shielding is inversely proportional to a mean or effective excitation energy ΔE. Resonance moves downfield as the lowest-energy electronic absorption moves to longer wavelength. The $n \rightarrow \pi^*$ transition has been shown to be crucial to the shift differences in ^{17}O NMR of carbonyl compounds.[5] In the present case of aliphatic alcohols and ethers, excited states to be mixed with the ground state by an external magnetic field is either the $n \rightarrow \sigma^*$ or Rydberg states.[6] Since the corresponding transition appears in the vacuum ultraviolet region and is not unambiguously characterized, let us take adiabatic ionization potentials of these compounds as a measure of ΔE.[7] A reasonably smooth correlation is found in the chemical shift vs. ionization potentials plots both for alcohols and ethers as shown in Figure 1.

Whereas there is no meaning in the apparent linearity of the plots, the correlation appears to demonstrate that the HOMO levels of the oxygen n-electrons are more sensitive to the structural changes in the alkyl groups than the

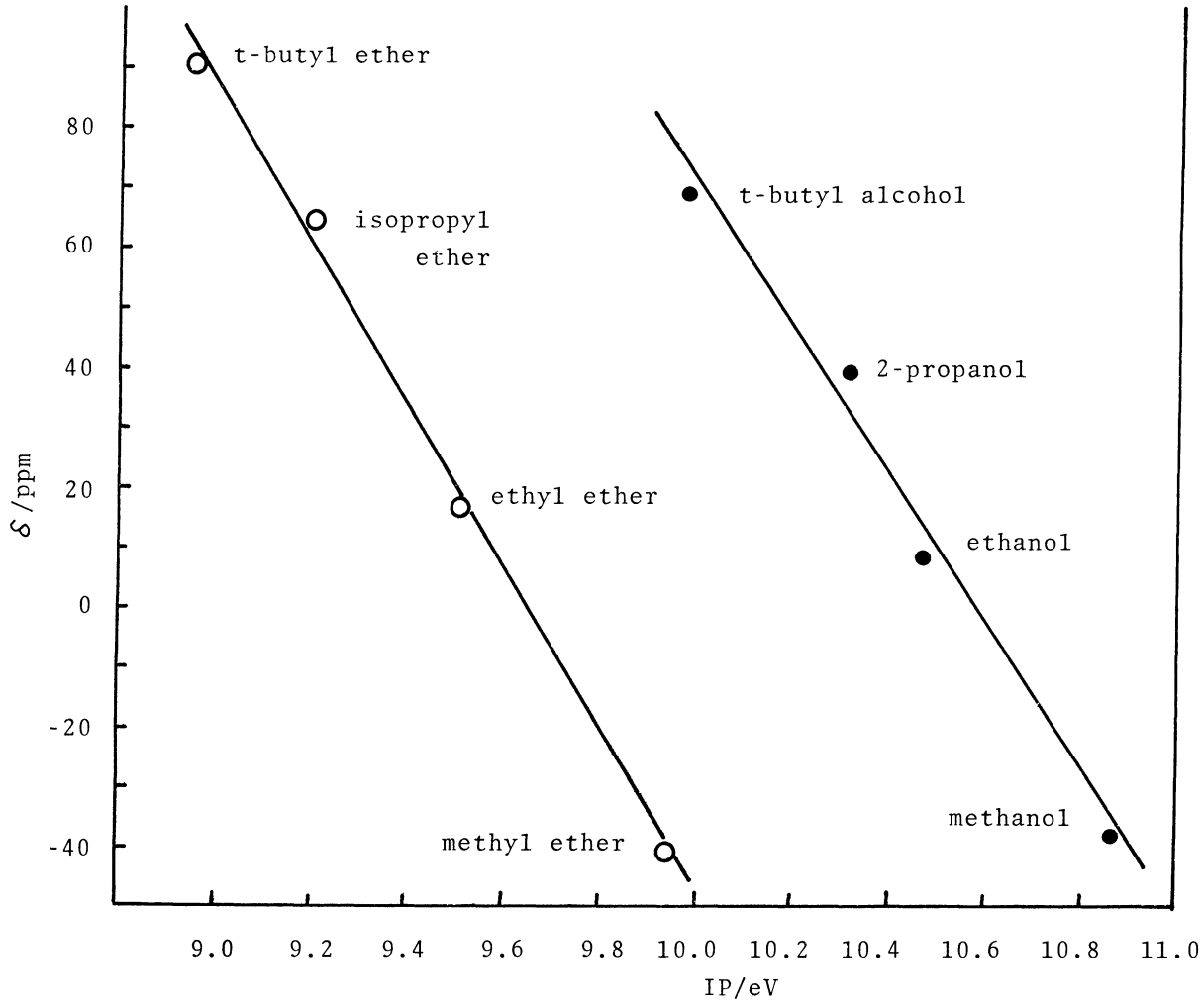

Figure 1. Plots of ^{17}O chemical shifts vs. adiabatic ionization potentials (from ref. 7) of alcohols and ethers.

terminating MO levels and that ΔE gets smaller on going from the methyl to the t-butyl group. The paramagnetic contribution to the total screening constant is concluded to be important in simple alcohols and ethers.

Another point of interest in the data of Table 1 is that the effect of alkyl groups on the ethereal oxygen of esters is less pronounced; the shift differences between the methyl and t-butyl derivatives for example are 106 and 130 in alcohols and ethers, and 70 and 60 in formates and acetates, respectively. The results are a manifestation of resonance interaction $R'-\underset{\underset{O}{\|}}{C}-O-R \longleftrightarrow R'-\underset{\underset{O^-}{|}}{C}=O^+-R$ serving as a buffer of the electronic effect of R.

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2) The amount of information derivable from chemical shifts is approximately given by the shift range (Δ) divided by the spectral line width ($\Delta_{1/2}$). When ^{1}H, ^{13}C and ^{17}O NMR are compared, we note that Δ is 0.8, 4 and 8 kHz for example and $\Delta_{1/2}$ is typically 1, 1 and 100 Hz, respectively. Therefore the capacity of information from chemical shifts of ^{1}H, ^{13}C and ^{17}O is 800, 4000 and 80. The widest shift range of ^{17}O NMR should not be overemphasized.

3) Some of the ^{17}O shift data on alcohols, ethers and esters are already reported (H. A. Christ, P. Diehl, H. R. Schneider, and H. Dahn, Helv. Chim. Acta, 44, 865 (1961)). Our data agree nicely with those in the literature.

4) When isotropic molecular tumbling is rapid on the NMR time scale, the line width determined by quadrupole relaxation is given by Eq. 1. The Stokes-Einstein-Debye equation (Eq. 2) relates τ_c to temperature T and solution viscosity η.

$$\frac{1}{T_1} = \frac{3}{125}\left(1 + \frac{\eta^2}{3}\right)\left(\frac{e^2Qq}{\hbar}\right)^2\tau_c \quad (1) \qquad \tau_c = \frac{4\pi\eta a^3}{3kT} \quad (2)$$

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