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Note

^{17}O NMR Investigation of Unsaturated Alcohols

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ABSTRACT: The ^{17}O NMR spectra for a series of β,γ or γ,δ unsaturated alcohols are reported. The chemical shift variation due to the introduction of the double bond in the β,γ or γ,δ position was found to be small, with the effect of β,γ unsaturation being larger than that of γ,δ unsaturation. The substituent chemical shift (SCS) effects of methyl substitution for β,γ or δ hydrogens were also determined. A linear correlation between the ^{17}O chemical shift for the alcohol (ROH) and the ^{13}C chemical shift for the methyl groups in the corresponding hydrocarbon (RCH_3) was obtained, allowing predictions of the ^{17}O chemical shift from corresponding ^{13}C data. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{17}O NMR; substituent chemical shift effects; unsaturated alcohols

INTRODUCTION

Recently, ^{17}O NMR has been shown to be a promising tool in the study of oxidative degradation in polymer systems.[1] One of the hurdles to using ^{17}O NMR for aging studies is the chemical shift assignment of degradation products. Although there is an extensive amount of literature on ^{17}O chemical shifts in organic compounds,[2] information on the ^{17}O chemical shifts of expected degradation products is limited. In particular, the ^{17}O chemical shifts for unsaturated alcohols, predicted to be one of the possible by-products of oxidative degradation in polymeric materials, have not been reported previously. We report here the ^{17}O NMR spectra of a series of β,γ and γ,δ unsaturated alcohols, and compare the effects of unsaturation and methyl SCS effects on the ^{17}O chemical shift with those in previous investigations of saturated alcohols.[3–9]

EXPERIMENTAL

Alcohols were obtained from Aldrich and used without further purification. But-2-ene-1,4-diol (**1**) was 95% *cis*, but-2-en-1-ol (**2**) a mixture of isomers, pent-2-en-1-ol (**4**) 95% *cis* and pent-3-en-2-ol (**6**) predominantly *trans*.

Solution ^{17}O NMR spectra were obtained on neat samples at 54.25 MHz using a Bruker AMX400 instrument and a standard 5 mm broadband probe. Spectra were obtained unlocked, using a 10 μs $\pi/2$ ^{17}O pulse, Waltz ^{1}H decoupling, 8 K scan averages, a 19 kHz spectral width, 2K complex points, zero-filling to 4 K, 50 Hz line broadening and a 200 ms recycle delay. All chemical shifts were measured at 298 K unless otherwise noted. Chemical shifts and linewidths reported in Table 1 were obtained from deconvoluting the experimental spectra. The ^{17}O chemical shift values were referenced externally to doubly distilled H_2O ($\delta = 0.0$ ppm), and were found to be reproducible to within ± 0.5 ppm. The ^{13}C chemical shifts of the corresponding hydrocarbons used for correlation of $\delta_{^{17}O}$ and $\delta_{^{13}C}$ were obtained from the Aldrich Chemical NMR spectral database.[10]

RESULTS AND DISCUSSION

The ^{17}O chemical shifts for a series unsaturated alcohols containing either a β,γ or γ,δ double bond are listed in Table 1. The observed ^{17}O chemical shifts for these unsaturated alcohols fall approximately within the ^{17}O chemical shift ranges reported previously for saturated alcohols,[7] ranging from -3 to 10 ppm for primary (1°) alcohols, from 30 to 40 ppm for secondary (2°) alcohols and from 55 to 70 ppm for tertiary (3°) alcohols. These distinct ranges allow for easy classification of alcohol products produced during oxidative degradation. The observed full width at half-maximum (FWHM) ^{17}O linewidths for the unsaturated alcohols are *ca* 400–600 Hz, and *ca* 500–800 Hz for the corresponding saturated alcohols (with the notable exception of the diols). Unfortunately, these large linewidths (*ca* 10 ppm) make the identification of different alcohol species in complex mixtures by ^{17}O NMR very difficult. For quadrupolar relaxation, the linewidth is directly proportional to the rotational correlation time τ_c,[11,12] with narrower linewidths being observed with increase in sample temperature. For ^{17}O NMR investigations of aged material at elevated temperature, variations in the chemical shift and the possibility of additional chemical reactions would need to be considered.

The changes in the ^{17}O chemical shifts, $\Delta\delta_{^{17}O}$, due to β,γ unsaturation for alcohols (ROH) are given in Table 1. The effect of introducing the double bond in these

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Table 1. ^{17}O NMR chemical shifts and linewidths for β,γ and γ,δ unsaturated alcohols

Type	No.	Compound	$\delta_{^{17}O}$ (ppm)	FWHM (Hz)[b]	$\delta_{^{17}O}$ (ppm)[c] (saturated)	FWHM (Hz)[b]	$\Delta\delta_{^{17}O}$[d]
β,γ							
1°	**1**	$HOCH_2CH{=}CHCH_2OH$	2.7	1000	−0.3	3029	+3.0
1°	**2**	$CH_3CH{=}CHCH_2OH$	3.3	566	0.0	522	+3.3
1°	**3**	$(CH_3)_2C{=}CHCH_2OH$	3.6	520	−2.3	777	+5.9
1°	**4**	$CH_3CH_2CH{=}CHCH_2OH$	2.0	529	0.7	601	+1.3
2°	**5**	$CH_2{=}CHCH(CH_3)OH$	32.3	413	34.2	547	−1.9
2°	**6**	$CH_3CH{=}CHCH(CH_3)OH$	37.1	551	34.3	773	+2.8
2°	**7**	$CH_2{=}CHCH(OH)CH_2CH_3$	27.2	610	25.7	679	+1.5
3°	**8**	$CH_2{=}CHC(CH_3)_2OH$	57.6	556	58.2	806	−0.6
γ,δ							
1°	**9**	$CH_2{=}CHCH_2CH_2OH$	0.4	444	0.0	522	−0.4
1°	**10**	$CH_2{=}CHCH(CH_3)CH_2OH$	−3.1	613	−6.0	644	−2.9
2°	**11**	$CH_2{=}CHCH_2CH(CH_3)OH$	35.0	585	32.9	803	+2.1

[a] ^{17}O chemical shift of neat alcohol referenced to external doubly distilled H_2O ($\delta = 0.0$ ppm), error *ca* ±0.5 ppm.
[b] Full width at half-maximum (FWHM) linewidth obtained from deconvolution.
[c] ^{17}O chemical shift of corresponding saturated alcohol, error *ca* ±0.5 ppm.
[d] $\Delta\delta$ = chemical shift of unsaturated alcohol minus chemical shift of saturated alcohol.

alcohols is small, ranging from −1.9 to 5.9 ppm. The magnitude of the $\Delta\delta_{^{17}O}$ shift is similar to that observed in β,γ unsaturated vinyl ethers,[6] but smaller than the large $\Delta\delta_{^{17}O}$ observed for α,β unsaturated ethers ($\Delta\delta \approx 40$–80 ppm).[3] The $\Delta\delta_{^{17}O}$ shift for unsaturated alcohols is larger than the $\Delta\delta_{^{13}C}$ shifts observed in the methyl resonance of corresponding alkanes and alkenes (RCH_3).[4] A small $\Delta\delta_{^{17}O}$ is produced for γ,δ unsaturation (Table 1).

Substituent-induced chemical shift (SCS) effects have also been shown to be very important in governing the ^{17}O NMR chemical shifts in both alcohols and ethers.[4,9] Methyl-induced β,γ and δ SCS effects for unsaturated alcohols are given in Table 2. The first β-methyl substitution produces a shift to higher frequency of *ca* 32–34 ppm, with subsequent β-methyl substitution reducing the SCS effect to *ca* 25 ppm, similar to that observed for aliphatic alcohols.[4] Methyl-induced β-SCS effects are also seen for ^{13}C NMR, but the SCS effect on ^{17}O chemical shifts are approximately 3.5–4 times larger.

A comparison between the structural effects of these different alkyl substitutions on the ^{17}O shielding in the OH group of alcohols and their effect on the ^{13}C shielding of an attached methyl group can be made by inspection of the correlation between the $\delta_{^{17}O}$ observed for the saturated and unsaturated alcohols **1–11** (ROH) and the methyl $\delta_{^{13}C}$ for the corresponding alkenes and alkanes (RCH_3). Excellent correlation was observed for the β,γ and γ,δ unsaturated alcohols [Fig. 1(a)], and can be described by the linear relationship

$$\delta_{^{17}O} = -48.7(\pm 2) + 3.7(\pm 0.1)(\delta_{^{13}C}) \qquad r = 0.993 \tag{1}$$

and for saturated alcohols [Fig. 1(b)] by

$$\delta_{^{17}O} = -54.1(\pm 3) + 3.9(\pm 0.1)(\delta_{^{13}C}) \qquad r = 0.983 \tag{2}$$

Within experimental error, the correlation slopes are the same, with the difference in intercept being attributed to the chemical shift differences due to unsatu-

Table 2. β,γ,δ-SCS(CH_3) effects in ^{17}O NMR of unsaturated alcohols

Compound	$\delta_{^{17}O}$ (ppm)	β-SCS(CH_3)	γ-SCS(CH_3)	δ-SCS(CH_3)
$CH_2{=}CHCH_2OH$	−1.6[a]			
$CH_2{=}CHCH(CH_3)OH$	32.3	33.9		
$CH_2{=}CHC(CH_3)_2OH$	57.6	25.3		
$CH_2{=}CHCH(CH_2CH_3)OH$	27.2		−5.1	
$CH_3CH{=}CHCH(CH_3)OH$	37.1			+4.8
$CH_2{=}CHCH_2CH_2OH$	0.4	—	—	
$CH_2{=}CHCH_2CH(CH_3)OH$	35.0	34.6		
$CH_2{=}CHCH(CH_3)CH_2OH$	−3.1		−3.5	
$CH_3CH{=}CHCH_2OH$	3.3			
$CH_3CH{=}CHCH(CH_3)OH$	37.1	33.8		
$(CH_3)_2C{=}CHCH_2OH$	3.6			+0.3

[a] ^{17}O shift obtained from Ref. 9.

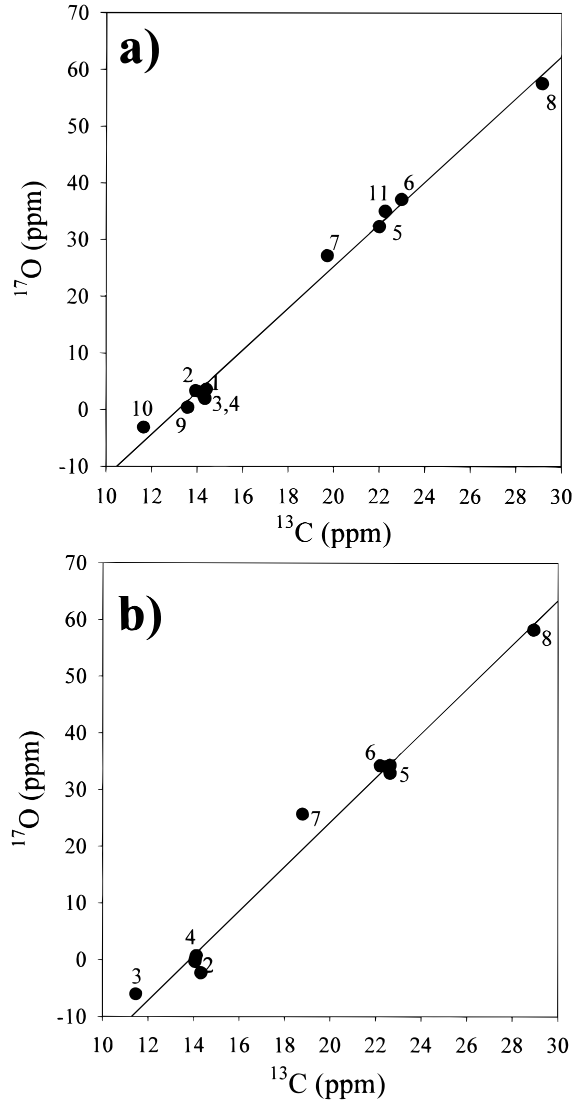

Figure 1. Correlation between the ^{17}O chemical shift for hydroxyl oxygen for the alcohols **1–11** (ROH) and the ^{13}C chemical shift for the methyl carbon in the corresponding alkene and alkane (RCH$_3$) for both (a) unsaturated and (b) saturated alcohol systems. The ^{17}O chemical shifts are given in Table 1.

ration ($\Delta\delta_{^{17}\mathrm{O}}$). These correlations compare well with that reported previously for a series of simple alcohols (slope = 3.83, intercept −49.2, $r = 0.979$).[9] This relationship between $\delta_{^{17}\mathrm{O}}$ and $\delta_{^{13}\mathrm{C}}$ suggests that the introduction of β,γ and γ,δ double bonds does not greatly perturbed the structural components, but has a small influence on the ^{17}O chemical shifts. Because there is such a large knowledge base of ^{13}C chemical shifts, the establishment of these correlations between $\delta_{^{17}\mathrm{O}}$ and $\delta_{^{13}\mathrm{C}}$ provides an important tool for identification of alcohols using ^{17}O NMR.

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