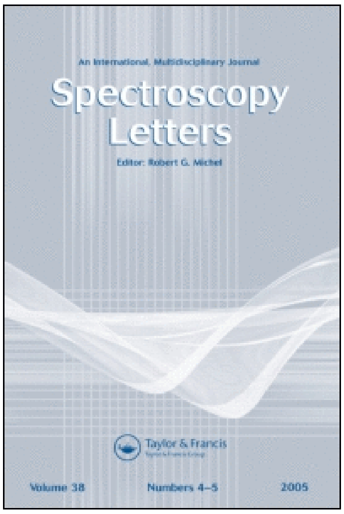

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Hydroxyl Substituent Chemical Shift (SCS) Effects in Alcohols: The ^{17}O NMR of Diols

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HYDROXYL SUBSTITUENT CHEMICAL SHIFT (SCS) EFFECTS IN ALCOHOLS: THE ^{17}O NMR OF DIOLS[†]

Keywords: ^{17}O NMR, diols, alcohols, SCS effect

by

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ABSTRACT

The ^{17}O NMR spectra for a series of saturated diols were investigated. From these studies both hydroxyl induced substituent chemical shift (SCS) effects of hydroxyl oxygen ^{17}O NMR chemical shifts were determined. In addition, linear correlations between the ^{17}O chemical shift of the hydroxyl oxygen (ROH) and the ^{13}C chemical shift for the methyl group in the corresponding hydrocarbon (RCH_3) were obtained.

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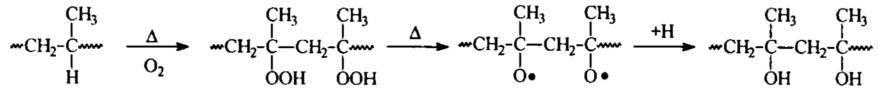
INTRODUCTION

The utility of ^{17}O NMR to probe oxidative degradation in polymer materials has recently been demonstrated in our laboratory.[1] While there continues to be extensive use of ^{17}O NMR for a variety of chemical systems, a limited number of ^{17}O NMR studies targeting polymer aging have been reported. Our ^{17}O NMR investigations have shown that significant concentrations of alcohol species are formed during the oxidative degradation of polymers.[1] The ^{17}O NMR for simple alcohols,[2] including the effects of unsaturation have been reported.[3] In addition to simple alcohols, the formation of diols or dihydroxyl compounds is possible during oxidative aging. As an example, a mechanism for diol formation during polypropylene oxidation is shown in SCHEME 1. Here diols form when adjacent hydroperoxides decompose to alkoxyl radials, and then extract hydrogens from elsewhere in the polymer, prior to any β-chain scission reactions that would instead lead to the production of ketones.

In this communication, the ^{17}O chemical shifts for a series of diols, as well as the magnitude and direction of γ, δ, ε and ζ hydroxy substituent chemical shift (SCS) effects are presented. The correlation between the ^{17}O and ^{13}C NMR chemical shifts are also discussed.

EXPERIMENTAL

All alcohols were obtained from Aldrich and used without further purification. Solution ^{17}O NMR spectra were obtained at 54.25 MHz using a Bruker AMX400 and a standard 5 mm broadband probe on neat samples. A three pulse composite pulse sequence with a 10 μs ^{17}O $\pi/2$ pulse was used to reduce acoustic ring.[4] Spectra were obtained unlocked, using ^{1}H Waltz-16 decoupling, 8K scan averages, a 19 kHz spectral width, 2K complex points, zero filling to 4K, 100 Hz line broadening and a 200 ms recycle delay. All chemical shifts were measured at 343 K to help reduce the increased line width that results from the high viscosity of the diols. All reported ^{17}O chemical shift values were referenced



SCHEME 1

externally to doubly distilled H_2O ($\delta = 0.0$ ppm), while the full width at half maximum (FWHM) line widths were obtained from spectral deconvolution. 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 data base, and correspond to ^{13}C chemical shifts at room temperature.[5]

RESULTS AND DISCUSSION

The ^{17}O NMR chemical shifts for a series of diols and related primary and secondary alcohols are listed in TABLE 1. For the primary and secondary alcohols (compounds **1,3,5,8,9,16-18**), the observed chemical shifts fall within the range previously reported for unsaturated alcohols: ranging from -3 to 10 ppm for primary (1°) alcohols, 30 to 40 ppm for secondary (2°) alcohols and from 55 to 70 ppm for tertiary (3°) alcohols. The observed ^{17}O chemical shift for the 1° and 2° alcohols in diols (compounds **2,4,6,7,10-15,19-24**) occur in a slightly larger chemical shift range with a trend for upfield (lower frequency) shifts, ranging from approximately -9 ppm to 0.3 ppm for the 1° hydroxyl oxygen in diols, and approximately 16 to 40 ppm for 2° hydroxyl in diols. This trend in hydroxyl chemical shift is most easily observed in γ substituted diols, clearly showing the effect of hydroxy substitution on the observed ^{17}O NMR chemical shift.

The observed full width at half maximum (FWHM) ^{17}O NMR line widths at 343K for the alcohols investigated are shown in TABLE 1. For the simple alcohols the FWHM ranges from 164 to 332 Hz, while the FWHM for the diols ranged from 302 to 1123 Hz. Since the line widths are governed by quadrupolar relaxation and are directly proportional to the rotational correlation time τ_c, the

TABLE 1. ^{17}O chemical shifts and line widths for diols and related alcohols at 343 K.

[a]	Compound	$\delta_{^{17}O}$ [b]	FWHM[c] (Hz)
1	$\mathrm{CH_3CH_2}\mathit{O}\mathrm{H}$	5.5	164
2	$\mathrm{H}\mathit{O}\mathrm{CH_2CH_2}\mathit{O}\mathrm{H}$	-8.5	302
3	$\mathrm{CH_3CH_2CH_2}\mathit{O}\mathrm{H}$	-0.6	218
4	$\mathrm{H}\mathit{O}\mathrm{CH_2CH_2CH_2}\mathit{O}\mathrm{H}$	-2.5	459
5	$\mathrm{CH_3CH(}\mathit{O}\mathrm{H)CH_3}$	39.4	216
6	$\mathrm{H}\mathit{O}\mathrm{CH_2CH(OH)CH_3}$ 1°	-7.7	459
7	$\mathrm{HOCH_2CH(}\mathit{O}\mathrm{H)CH_3}$ 2°	22.5	468
8	$\mathrm{CH_3CH_2CH(}\mathit{O}\mathrm{H)CH_3}$	33.5	257
9	$\mathrm{CH_3CH_2CH_2CH_2}\mathit{O}\mathrm{H}$	-0.8	274
10	$\mathrm{CH_3CH(OH)CH_2CH_2}\mathit{O}\mathrm{H}$ 1°	-0.8	634
11	$\mathrm{CH_3CH(}\mathit{O}\mathrm{H)CH_2CH_2OH}$ 2°	32.3	775
12	$\mathrm{CH_3CH_2CH(OH)CH_2}\mathit{O}\mathrm{H}$ 1°	-7.5	528
13	$\mathrm{CH_3CH_2CH(}\mathit{O}\mathrm{H)CH_2OH}$ 2°	16.3	474
14	$\mathrm{H}\mathit{O}\mathrm{CH_2CH_2CH_2CH_2}\mathit{O}\mathrm{H}$	0.2	671
15	$\mathrm{CH_3CH(}\mathit{O}\mathrm{H)CH(}\mathit{O}\mathrm{H)CH_3}$	21.9	628
16	$\mathrm{CH_3(CH_2)_3CH_2}\mathit{O}\mathrm{H}$	0.3	332
17	$\mathrm{CH_3(CH_2)_2CH(}\mathit{O}\mathrm{H)CH_3}$	33.7	307
18	$\mathrm{CH_3CH_2CH(}\mathit{O}\mathrm{H)CH_2CH_3}$	24.0	250
19	$\mathrm{CH_3(CH_2)_2CH(OH)CH_2}\mathit{O}\mathrm{H}$ 1°	-6.7	573
20	$\mathrm{CH_3(CH_2)_2CH(}\mathit{O}\mathrm{H)CH_2OH}$ 2°	16.9	603
21	$\mathrm{CH_3CH(OH)(CH_2)_2CH_2}\mathit{O}\mathrm{H}$ 1°	0.1	794
22	$\mathrm{CH_3CH(}\mathit{O}\mathrm{H)(CH_2)_2CH_2OH}$ 2°	33.9	1123
23	$\mathrm{H}\mathit{O}\mathrm{CH_2(CH_2)_3CH_2}\mathit{O}\mathrm{H}$	-0.3	748
24	$\mathrm{CH_3CH(}\mathit{O}\mathrm{H)CH_2CH(}\mathit{O}\mathrm{H)CH_3}$	31.8	901

[a] Numbering used for identification in FIG. 1.
[b] ^{17}O chemical shift referenced to external doubly distilled H_2O ($\delta = 0.0$ ppm).
[c] FWHM, full width at half maximum line width measured in Hz.

reduction of sample viscosity with increasing temperature results in narrower lines. This narrowing can be significant; for many of the diols reported in TABLE 1 the room temperature ^{17}O NMR spectra were not easily observed due to extremely broadened resonances. This line broadening resulted in the need to utilize the elevated temperature reported here (343K). The dependence of FWHM on the rotational correlation time is also apparent with the approximate linear correlation with measured compound viscosity for each class of compounds (not

TABLE 2: Hydroxyl SCS effects for primary and secondary alcohols.

	Compound	γ-SCS(OH)	δ-SCS(OH)	ε-SCS(OH)	ζ-SCS(OH)
1°	**CH_3CH_2OH**				
	$HOCH_2CH_2OH$	-13.9			
	$CH_3CH_2CH_2OH$				
	$CH_3CH(OH)CH_2OH$	-7.1			
	$HOCH_2CH_2CH_2OH$		-1.9		
	$CH_3CH_2CH_2CH_2OH$				
	$CH_3CH_2CH(OH)CH_2OH$	-6.8			
	$CH_3CH(OH)CH_2CH_2OH$		0.0		
	$HOCH_2CH_2CH_2CH_2OH$			1.0	
	$CH_3(CH_2)_3CH_2OH$				
	$CH_3(CH_2)_2CH(OH)CH_2OH$	-7.1			
	$CH_3CH(OH)(CH_2)_2CH_2OH$			-0.2	
	$HOCH_2(CH_2)_3CH_2OH$				-0.7
2°	**$CH_3CH(OH)CH_3$**				
	$HOCH_2CH(OH)CH_3$	-16.9			
	$CH_3CH(OH)CH_2CH_3$				
	$HOCH_2CH(OH)CH_2CH_3$	-17.2			
	$CH_3CH(OH)CH(OH)CH_3$	-11.6			
	$CH_3CH(OH)CH_2CH_2OH$		-1.2		
	$CH_3(CH_2)_2CH(OH)CH_3$				
	$CH_3(CH_2)_2CH(OH)CH_2OH$	-16.8			
	$CH_3CH(OH)CH_2CH(OH)CH_3$		-1.9		
	$HOCH_2(CH_2)_2CH(OH)CH_3$			0.2	

shown). The correlation is different for simple alcohols versus diols revealing that the effective correlation time is also dependent on the molecular shape, size and oxygen position.[6,7]

Substituent chemical shift (SCS) effects have also been shown to be very important in governing the ^{17}O NMR chemical shifts in alcohols.[2,3] The γ, δ, ε and ξ hydroxy SCS effects are given in TABLE 2. The hydroxyl SCS effect produced by a primary (1°) alcohol substitution is large, resulting in a -13.9 to -17.2 ppm shift, while the hydroxyl SCS effect due to a secondary (2°) alcohol substitution is smaller, producing a -6.8 to -11.6 ppm shift. In addition, the γ-SCS

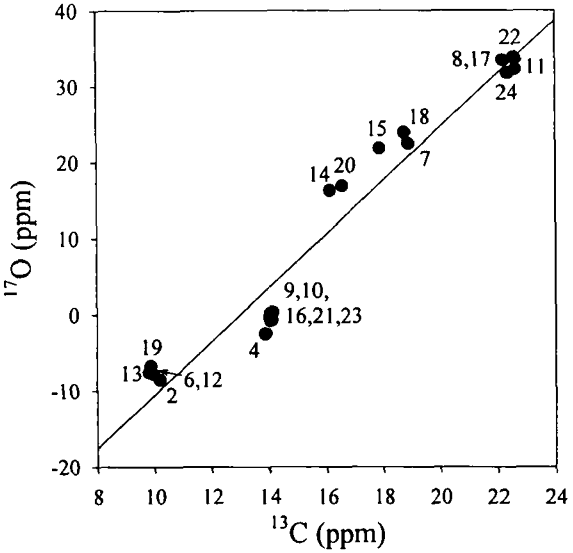


FIGURE 1: Correlation between the observed ^{17}O NMR chemical shift ($\delta_{^{17}O}$) for the hydroxyl oxygen in alcohols **1-24** (ROH) and the ^{13}C NMR chemical shift ($\delta_{^{13}C}$) for the methyl group in the corresponding alkane (RCH_3).

effect is slightly larger for the 2° alcohols (see Table 2). Similar trends are observed in ^{13}C NMR with a -5.8 ppm shift due to a 1° alcohol substitution, and a -3.3 ppm shift for a 2° substitution.[8] The hydroxy SCS effect in ^{17}O NMR is 2 to 2.5 times larger than that observed in ^{13}C NMR. Shifts due to δ, ε and ξ SCS hydroxy effects were also observed, but are significantly smaller.

^{17}O and ^{13}C Chemical Shift Correlation

The structural effects giving rise to the ^{17}O chemical shifts in these compounds can be investigated by inspection of the correlation between the ^{17}O chemical shift ($\delta_{^{17}O}$) for the hydroxyl oxygen observed for the alcohol (ROH) and the ^{13}C chemical shift ($\delta_{^{13}C}$) for the methyl group in the corresponding alkane

(RCH_3). The linear correlation for **1-24** is shown in FIGURE 1, and can be described by

$$\delta_{^{17}O} = -45.6(\pm 3) + 3.5(\pm 0.1)(\delta_{^{13}C}) \quad r = 0.975 \tag{1}$$

In previous investigations of alcohols the correlation slope was found to be slightly larger (3.7 to 3.9), compared to the 3.5 reported here,[3,9] while the intercept is also smaller than the -49.2 and -54.1 previously reported.[3,9] These differences in correlation parameters are most likely the result of using elevated temperatures for the present study (343 K) and corresponding temperature variation of the ^{17}O chemical shift. This linear correlation shows that the structural changes responsible for the ^{17}O NMR chemical shifts are the same governing the ^{13}C chemical shifts.

The development of these correlations is very important for the identification of diols using ^{17}O NMR, because the large data base and prediction mechanisms for ^{13}C chemical shifts can be directly employed in the prediction of ^{17}O NMR chemical shifts.

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