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^{17}O NUCLEAR MAGNETIC RESONANCE: MUTUAL EFFECT BETWEEN TWO β OXYGEN ATOMS AND α,β-DOUBLE BOND EFFECT ON ^{17}O CHEMICAL SHIFT

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Abstract—Natural abundance ^{17}O NMR spectra of acetals, ketals and 1,3-dioxolane derivatives have been measured. The mutual effect between oxygen atoms on ^{17}O chemical shift is studied. The variations are tentatively explained in terms of changes in the conformation of the compounds. The ^{17}O chemical shifts of unsaturated ethers were also studied. The ^{17}O deshielding is found to be related to the β carbon shielding.

INTRODUCTION

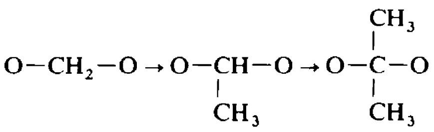
The application of fourier transform (FT) techniques to ^{17}O NMR has notably increased the accuracy of signal measurements.[1] The influence of small changes in molecular structure on the oxygen-17 chemical shift of several functional groups has been recently reported.[2-4] The substitution of a hydrogen by a methyl group at various positions in cyclohexanones,[5] other carbonyl compounds,[6] ethers[7] and alcohols[8] induces ^{17}O chemical shift perturbations which have been interpreted in terms of the substituent chemical shifts, a concept widely used in ^{13}C NMR.[9] By contrast, the effect on ^{17}O chemical shifts of other substituents has not received any attention other than the pioneering work of Dahn *et al.*[10] In our paper, an attempt at calculating the mutual effect between oxygen atoms on ^{17}O chemical shift will be described. The effect of a carbon-carbon double bond in unsaturated ethers was also examined.

RESULTS AND DISCUSSIONS

1,3-*Dioxolane derivatives, ketals and orthoesters*

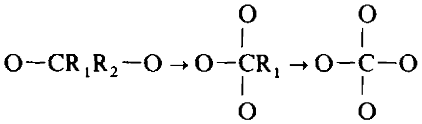
The ^{17}O chemical shifts measured for 1,3-dioxolane, two of its methyl derivatives and twelve ketals and orthoesters of general formula $(CH_3)_mCH_n(OR)_{4-m-n}$ where R = methyl or ethyl, are listed in Table 1. Together with δ ^{17}O data for ethers, these results allow one to study the effect on the oxygen-17 chemical shifts of the substitution of a hydrogen, at a position β to the oxygen atom, by an alkoxy group. The mutual effect between the oxygens can be examined by varying:

(a) The nature of the carbon atom separating them,



$$O{-}CH_2{-}O \rightarrow O{-}\underset{CH_3}{\underset{|}{C}}H{-}O \rightarrow O{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}O$$

(b) The number of the oxygen atoms at the β position,



$$O{-}CR_1R_2{-}O \rightarrow O{-}\overset{O}{\overset{|}{\underset{O}{\underset{|}{C}}}}R_1 \rightarrow O{-}\overset{O}{\overset{|}{\underset{O}{\underset{|}{C}}}}{-}O$$

β_0^C *effect*. The β_0^C effect is defined as the δ ^{17}O chemical shift variation produced by substitution of the β hydrogen by a methyl group. In our case, this effect is the difference of δ ^{17}O in the series $(CH_3)_mCH_n(OR)_{4-m-n}$ when R changes from a methyl group to an ethyl group. A mean value of 31 ± 2 ppm for β_0^C is observed (see Table 1), the same as has been found for ethers.[7]

β_0^0 *effect—Variation with alkyl substitution on the β carbon*. The β_0^0 effect is defined in the following substitutions (R = methyl or ethyl),

$$ROCH_3 \rightarrow ROCH_2OH$$
$$ROCH_2CH_3 \rightarrow ROCH(OH)CH_3$$
$$ROCH(CH_3)_2 \rightarrow ROC(OH)(CH_3)_2$$

In case of the substitution by a methoxy (or ethoxy) group instead of a hydroxy group, some corrections must be taken into consideration to evaluate the magnitude of the β_0^0 effect. These corrections correspond to γ_0^C and δ_0^C effects for which the following values have been established in the ether series:[7] $\gamma_0^C = -5$ ppm; $\delta_0^C = 0 \rightarrow 2$ ppm (the value of 1 ppm is used for the latter). The results are collected in Table 1. A mean characteristic value of β_0^0, depending on the nature (secondary, tertiary or quaternary) of the carbon between oxygens is found. Thus,

$$\beta_0^0 = \begin{cases} 60.5\,\text{ppm for a secondary carbon,} \\ 45.5\,\text{ppm for a tertiary carbon,} \\ 26.5\,\text{ppm for a quaternary carbon.} \end{cases}$$

We shall attempt to explain this diminution of the β_0^0 effect in terms of conformations. When the C–O bonds are *gauche* or *trans*, there are none, one or two parallel lone pairs and this should influence differently β_0^0 (see

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Table 1. ^{17}O chemical shift of acetals, ketals, orthoesters and 1,3-dioxo dervatives; Calculations of β_0^C and β_0^0 effects

No	Compounds	$\delta^{17}O$ reference ether (±1ppm)	$\delta^{17}O^a$ (±1ppm)	β_0^C effect (±2ppm)	β_0^0 effect (±2ppm)
1	$CH_2(OCH_3)_2$	CH_3OCH_3 (-52.5)	3.0		60.5
2	$CH(OCH_3)_3$		24.0		26.0
3	$C(OCH_3)_4$		22.0		3.0
4	$CH_2(OCH_2CH_3)_2$	$CH_3OCH_2CH_3$ (-22.5)	34.0	31.0	60.5
5	$CH(OCH_2CH_3)_3$		53.0	29.0	23.0
6	$C(OCH_2CH_3)_4$		56.5	34.5	7.5
7	$CH_3CH(OCH_3)_2$		18.0		45.5
8	$CH_3C(OCH_3)_3$		30.5		17.5
9	$CH_3CH(OCH_2CH_3)_2$	$CH_3CH_2OCH_2CH_3$ (6.5)	48.0	30.0	45.5
10	$CH_3C(OCH_2CH_3)_3$		58.5	28.0	14.5
11	$(CH_3)_2C(OCH_3)_2$	$(CH_3)_2CHOCH_3$ (-2.0)	19.5		26.5
12	$(CH_3)_2C(OCH_2CH_3)_2$	$(CH_3)_2CHOCH_2CH_3$ (28.0)	52.0	32.5	28.0
13	1,3-dioxolane		33.5		
14	2-Me-1,3-dioxolane		53.0		
15	2,2-Me,Me-1,3-dioxolane		61.0		

a: pure liquid at 25°C, in ppm relative to water; a positive sign corresponds to downfield shift.

Fig. 2). The term parallel is used in this paper as a convenient geometric description without implying the real electron distribution. The distribution of conformers can be calculated, taking into account the statistical weight of each possible conformation together with the number and the magnitude of the following interactions:

(a) The 1,4 attraction between an oxygen lone pair and a proton, the corresponding energy $\Delta H_0 = -0.8$ kcal/mole;[13]

(b) The 1,4 repulsion between two hydrogens, in this case $\Delta H_0 = 1.2$ kcal/mole.[14] The results are reported in Table 2. They show that the g ± g ± conformation is strongly dominant for the three compounds. Electron diffraction of dimethoxy-methane in the vapour phase[15] confirmed the predominance of the conformer g ± g ±. Since our calculations of conformational population are very sensitive to energy values, the population of conformers cannot be calculated with an accuracy which would allow the

Table 2. Conformational population (%) of dimethoxyalkanes

	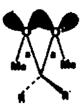		
Dimethoxymethane (R=R'=H)	2.2%	33.7%	64.0%
1,1-Dimethoxyethane (R=H; R'=Me)	0.4%	23.0%	76.7%
2,2-Dimethoxypropane (R=R'=Me)	0.06%	6.6%	93.3%

Table 3. ^{17}O and ^{13}C chemical shifts of some unsaturated ethers

No	Unsaturated ethers	$\delta^{17}O$ (±2.0ppm)	$\delta^{13}C$ (±0.1ppm)[b]					$\Delta\delta^{17}O$[c]
				C_α	C_β	C_γ	Others	
1	Ethylvinylether	77.5	Et	63.4	14.6			71.0
			Vinyl	152.0	86.2			
2	Methylisopropenylether	62.5	Me	54.6				64.5
			isoPropenyl	150.9	80.7 20.7			
3	Ethylpropenylether	60.0	Et(cis) (trans)	64.5 67.4	14.9 15.4			58.0
			Pr(cis) (trans)	98.1 101.0	147.0 145.6	9.2 12.6		
4	Anisole	44.0	Me	54.9				
			Phenyl	160.0	114.1	129.6	120.8	
5	Phenetole	68.0	Et	63.1	14.8			
			Phenyl	159.3	114.6	129.4	120.6	
6	Diphenylether	101.5[a]	Phenyl	157.4	129.7	123.1	118.9	
7	Dibenzofuran	158.0[a]	Phenyl	156.2	124.2 126.9	122.5 120.5	111.6	
8	1,4-Dibenzopyran	100.0[a]	Pyran			27.8		
			Phenyl	152.0	128.8 120.4	122.9 127.6	116.4	
9	Furan	228.5		142.7	109.6			214.5
10	α-Furaldehyde	234.5	Furan	153.4	121.3	112.8	143.8	
			CHO		177.8			
11	2-Acetylfuran	240.0	Furan	146.8 153.2	112.4 117.4			
			Acetyl		186.4	25.9		
12	2,3-Dihydro-γ-pyran	53.5		144.7 65.8	100.4 23.2	19.9		48.5
13	Allylethylether	1.5	Allyl	71.6	135.4	116.4		-0.5
			Et	65.7	15.2			
14	Diallylether	-5.5		71.0	135.1	116.4		2.0
15	2,5-Dihydrofuran	-7.0		75.5	126.9			
16	2,5-Dimethoxy-2,5-dihydrofuran	26.5		107.2 108.7	131.5 131.9		53.8($O\underline{C}H_3$)	
17	Methylisopentenylether	-22.5	Me	57.5				
			isoPentenyl	69.0	121.5	136.5	25.7; 17.9	7.0

a : value measured at 353°K,

b : $\delta^{13}C$ are recorded with respect to internal standard TMS and $\delta^{17}O$ to internal reference CH_3NO_2 but reported to H_2O (positive value corresponds to downfield shifts);

c : $\Delta\delta^{17}O$ is chemical shift difference between the unsaturated ethers and their saturated analogs [7].

exact determination of the β_0^0 values for each conformer. Nevertheless, the overall results agree with a mean value of β_0^0 becoming more important when the population of the aa and ag± conformers increases. The ^{17}O NMR measurements on 1,3-dioxolane and its 2 methyl derivatives also showed the influence of the relative orientations of the oxygen lone pairs on oxygen-17 chemical shifts (Table 1). The $\delta\,^{17}$O difference between tetrahydrofuran (14 ppm) and diethylether (6.5 ppm) shows that the formation of a five membered ring causes only a small deshielding effect ($\Delta\delta = 7.5$ ppm). If one compares 1,3-dioxolane (33.5 ppm) with dimethoxymethane (3 ppm), 2-methyl-1,3-dioxolane (53 ppm) with 1,1-dimethoxyethane (18 ppm) and 2,2-dimethyl-1,3-dioxolane (61 ppm) with dimethoxypropane (19.5 ppm), the following cyclization shifts appear: 30.5; 35 and 41.5 ppm. Cyclization constrains the lone pairs of oxygen to be more or less parallel. As dimethoxypropane has the smallest β_0^0, it is expected to experience the largest cyclization shift. The influence of the lone pairs orientation on the value of β_0^0 is in line with the β carbon deshielding effect interpreted in terms of H_0-C_0, $C_\beta-H_\beta$ orientation in the fragment $H_0-C_0-C_\alpha-C_\beta-H_\beta$.[16] According to this interpretation an appreciable attenuation for the successive β_0^0 effects should be expected.

β_0^0 effect –Variation with the number of alkoxy substituents. The magnitude of the β_0^0 effect, according to the number of hydroxy substituents can be determined as before by comparing the $\delta\,^{17}$O of the series $R'_nC(OR)_{4-n}$ with those of compounds $R'_{n+1}C(OR)_{4-n-1}$, taking into account the corrective terms γ_0^C and δ_0^C. The results are collected in Table 1. They can be recapitulated as follows:

1. The first hydroxy substituent induces the β_0^0 effects which have been discussed in the preceding paragraph: $\beta_0^0 = 60.5$, 45.5 and 26.5 ppm depending on whether a secondary, tertiary and quaternary carbon C_α separates the oxygens
2. The second hydroxy substituent induces the smallest effects, with a mean value of $\beta_0^0 = 20$ and 11 ppm respectively for tertiary and quaternary C_α.
3. The third hydroxy substituent has no effect.

Unsaturated ethers: double bond effect on oxygen-17 chemical shift

The presence of a double bond in an unsaturated ether is expected to cause appreciable changes in electron density in the system and thereby influences the ^{17}O chemical shift. A recent ^{17}O NMR study[7] showed that the $\delta\,^{17}$O in the saturated ethers is governed by the mean excitation energy ΔE, assuming the Karplus & Pople paramagnetic term:[17]

$$\sigma_{\text{para}} \simeq (\Delta E)^{-1}\langle r^{-3}\rangle_{2p}\Sigma Q.$$

The ^{17}O chemical shifts of 17 unsaturated ethers are collected in Table 3. Taking into consideration the polarized forms, one observes that a double

$$C{=}C{-}O{-}C \leftrightarrow \overset{\ominus}{C}{-}C{=}\overset{\oplus}{O}{-}C$$

bond in an α,β position relative to the oxygen atom strongly deshields the $\delta\,^{17}$O as expected from the $(\Delta E)^{-1}$ increase and from the electronic charge decrease at the oxygen centre. Following the treatment given previously for unsaturated carbonyl compounds,[18] the ^{17}O deshielding of $C_\beta{=}C_\alpha{-}O{-}C$ with respect to $C{-}C{-}O{-}C$ is related to the C shielding of $C_\beta{=}C_\alpha{-}O{-}C$ compared to $C{-}C{-}O{-}C$.[19] The proportionality factor of 2.5 ± 0.1 is about the same as is found for the unsaturated carbonyl compounds.

In the case of allylic ethers, only slight deshielding is observed relative to aliphatic compounds as the double bond is too far from oxygen to produce any appreciable effect.

CONCLUSION

The ^{17}O chemical shifts discussed here clearly show that, according to the type of the molecule, either the average energy term or the electronic charge is the dominant factor determining the chemical shift value. For the carbonyl compounds,[19] unsaturated carbonyl compounds[18] and unsaturated ethers, electric charge effects arising from bond polarization are dominant. For other aliphatic compounds, ΔE effects are more important.

EXPERIMENTAL

Chemical shift measurements. Natural abundance ^{17}O NMR of pure liquids were obtained on a Bruker HX-90 spectrometer operating in the FT mode at 12.2 MHz (SW = 12 kHz, 8K data points, 298°K unless specifications). 2M--Nitromethane was chosen as the internal chemical shift reference.[7] Natural abundance ^{13}C NMR spectra were recorded using a 3M-solution in a mixture $CDCl_3/CCl_4$ (50/50), on a Bruker WP-60 operating in FT mode at 15.08 MHz (SW = 3.75 kHz, 8K data points, 298°K).

Chemicals. 2,2-diethoxypropane was prepared according to ref. 11; 2-methyl dioxolane and 2,2-dimethyl dioxolane were prepared as described by Organikum.[12] The other compounds investigated were commercial products.

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