51. Oxygen-17 and Carbon-13 Nuclear Magnetic Resonance. Chemical Shifts of Unsaturated Carbonyl Compounds and Acyl Derivatives

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Summary

The ^{17}O and ^{13}C chemical shifts (δ) of 14 α,β-unsaturated aldehydes and ketones and 33 acyl derivatives RXC=O (X=Cl, OH, OMe, OEt, NH_2 and R=H or alkyl) have been measured. In the unsaturated carbonyl series, a correlation exists between δ ^{17}O and the π electron density at the β-carbon atom. From this correlation, an δ ^{17}O of 530 ppm was extrapolated for the loss of one electron at the oxygen atom. In the acyl series, the δ ^{17}O were also sensitive to changes in the polarity of the carbon-oxygen bond. A partial correlation between ^{17}O-NMR. chemical shifts and the nuclear quadrupole coupling constants exists for aldehydes, ketones, esters and amides but not for acyl chlorides.

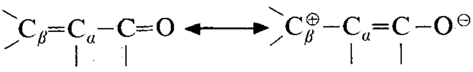
Introduction. - The oxygen-17 chemical shifts (δ ^{17}O) of saturated carbonyl compounds previously studied [1] are sensitive to modifications of the electronic density on the oxygen atom through changes in the carbon-oxygen π bond polarity. To verify the validity of this relation in a more diversified series of compounds, we now explore the δ ^{17}O of unsaturated carbonyl compounds and acyl derivatives.

The paramagnetic contribution, σ_p, to the total screening constant, σ, is the predominant term in ^{17}O nuclear shieldings [1-4]. Our results will be discussed in terms of this contribution:

$$\sigma_p = \text{cst.} \cdot \Delta E^{-1} \cdot \langle r^{-3} \rangle_{2p} \cdot \Sigma Q_{AB}$$

where ΔE represents the 'mean excitation energy', $\langle r^{-3} \rangle_{2p}$ the mean inverse cube radius for the $2p$ orbitals and ΣQ_{AB} is related to electronic charges and bond orders [5].

The comparison between an oxygen atom of a saturated carbonyl compound and that of a conjugated system requires the consideration of two mutually antagonistic effects arising from the mesomerism **A**↔**B**:



A **B**

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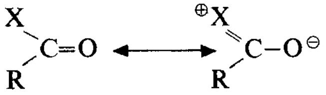
- An increase of the charge density at the oxygen atom implies an expansion of the *2p* orbitals and thereby a reduction of σ_p and an ^{17}O shielding;
- An increase of the maximum wavelength for n→ π* transition $\lambda_{max}^{n \to \pi^*}$ (*i.e.* a decrease of the excitation energy for the lowest electronic transition) leads to an increase of σ_p and hence to an ^{17}O deshielding.

Accordingly, prediction of $\delta\,^{17}O$ for unsaturated carbonyl compounds appears somewhat fortuitous. However, information can be obtained from ^{13}C-NMR. data since the electrons gained by the oxygen atom have been lost by the C_β carbon atom [6].

For acyl derivatives, ^{17}O shieldings should also be sensitive to changes in the polarity of the carbon-oxygen bonds, and as before, the mesomerism **A'**↔ **B'** must be considered:



A' **B'**

The variation in oxygen-17 quadrupole coupling constant (QCC.) of acyl derivatives is related to the variation in the electronic density on this atom [7]. If the same parameter is predominant for the ^{17}O shieldings, a correlation between $\delta\,^{17}O$ and the QCC. should appear.

Results and discussion. - *A. Unsaturated carbonyl compounds.* The $\delta\,^{17}O$ and $\delta\,^{13}C$ together with ^{17}O linewidths measured for 14 α,β-unsaturated aldehydes and ketones are collected in *Table 1.* For the alicyclic compounds, the π electron deficiencies at the carbon β to the carbonyl group, Z_β^π, were calculated following the treatment of *Levin et al.* [6] *(Table 1).* It is apparent that within the series of the four methyl ketones, the ^{17}O nucleus is found to be shielded when the Z_β^π electron deficiency increases; the same is true for the comparison between the two aldehydes. The assumption that these electrons are transferred to the oxygen atom allows the extrapolation that the gain of one *2p* electron on this atom will generate a ^{17}O shielding of -530 ± 70 ppm. The gain of one *2p* electron on a carbon atom generates a ^{13}C shielding of approximatively -240 ppm [6]. The ratio $530/240 = 2.2$ is comparable to the value calculated using the theory of *Pople & Karplus* applied to the comparison between $\delta\,^{17}O$ of aliphatic ethers and $\delta\,^{13}C$ of the corresponding carbon atom in analogous alkanes [4].

On comparing the $\delta\,^{17}O$ of saturated aliphatic aldehydes with those of the analogous methyl ketones, a difference of $\beta^\pi = -24$ ppm was found [1]. Similarly, a value of $\beta^\pi = -18$ ppm was found on comparing acrolein to methyl vinyl ketone *(Table 1).* However, acetophenone is only slightly shielded with respect to benzaldehyde since the β^π shielding effect is more or less compensated by the loss of coplanarity between the carbonyl group and the aromatic ring. As measured previously by *Sardella & Stothers* [8] for 2-methyl- and 2,6-dimethylacetophenone, further decrease in the conjugation deshields the oxygen nucleus. In the hydroxybenzaldehyde series, the comparison between salicylaldehyde and 4-hydroxybenzaldehyde shows that there is a contribution of an intramolecular hydrogen bond to the high field resonance of the salicylaldehyde carbonyl oxygen. Indeed, hydrogen bonds involving this type of oxygen atom are known to induce a shielding [8] [9].

Table 1. *δ ^{17}O and δ ^{13}C, ^{17}O linewidths ($\Delta\nu_{h/2}$), π electron deficiencies at the β carbon atom (Z^{π}_{β}) for α,β-unsaturated carbonyl compounds*

Compound	$\delta^{17}O$	$\Delta\nu_{h/2}$	$\delta^{13}C$				$\Delta\delta^{17}O$[a])	Z^{π}_{β}
			C=O	C_{α}	C_{β}	C_{γ}		
acrolein	579.0	26	194.2	138.8	137.6		− 0.5	0.134
crotonaldehyde	563.0	50	193.4	134.9	153.7	18.5	− 26.0	0.164
methyl vinyl ketone	561.0	60	197.5	Me 25.7			3.5	0.091
				Vin. 137.1	128.0			
ethyl vinyl ketone	543.5	120	200.1	Et 32.8	8.0		− 3.5	0.084
				Vin. 136.8	127.2			
methyl 1-propenyl ketone	553.0	160	197.0	Me 26.6			− 10.0	0.102
				Pr 133.2	142.7	18.0		
4-methyl-3-penten-2-one	549.5	220	197.7	Me 31.4			18.5	0.114
				i-Bu 124.5	154.3	27.4		
						20.5		
methyl isopropenyl ketone	565.0	220	199.3	Me 25.4			8.0	0.083
				i-Pr 145.2	125.2			
					17.3			
benzaldehyde	569.0	115	191.5	135.4	129.3	128.6		
acetophenone	562.0	170	196.9	Me 25.7				
				Ph 137.0	127.8	128.1		
salicylaldehyde	502.0	130	196.5	120.6	161.3	133.5		
	78.0(OH)	130(OH)			117.1	136.6		
3-hydroxybenzaldehyde	532.5	200	192.7	122.6	137.8	156.7		
	68.0(OH)	130(OH)			121.9	115.0		
4-hydroxybenzaldehyde	517.0	250	191.6	129.2	115.9	132.3		
	82.0(OH)	250(OH)						
furfural	524.0	200	177.8	153.4	121.3	112.8		
	234.5(-O-)	140(-O-)				148.3		
methyl furyl ketone	521.0	220	186.4	Me 25.9				
	240.0(-O-)	150(-O-)		Fu 153.2	117.4	112.4		
						146.8		

[a]) $\Delta\delta^{17}O$ is the chemical shift difference between an unsaturated carbonyl compound and its saturated homolog [1]. Negative sign corresponds to a shielding.

B. Acyl derivatives. The δ ^{17}O and δ ^{13}C together with ^{17}O linewidths measured for 33 acyl derivatives RXCO where X = Cl, OH, OMe, OEt, NH_2 and R = H or alkyl are collected in *Table 2.* In addition, the values δ $^{17}O = 490$ ppm and $\Delta\nu_{h/2} = 30$ Hz are measured for phosgene. These results are in agreement with previous measurements [2] [10-14] and suggest the following. a) The **carbon** chemical shifts vary only slightly with changes of R or X: δ $^{13}C = 175 \pm 15$ ppm. This is due to the fact that in the mesomerism $\mathbf{A}' \leftrightarrow \mathbf{B}'$ the carbon atom does not change its π bond order. The paramagnetic contribution σ_p to the screening constant of **A'** and **B'** are therefore identical. *Maciel* has shown [12] that in these compounds, the parameter which correlates best with the $\delta^{13}C$ variations is the inductive effect of X.

Table 2. $\delta^{17}O$ and $\delta^{13}C$, ^{17}O *linewidths* ($\Delta\nu_{h/2}$) *for acyl compounds* $RXC=O$

R	Cl			OH			OMe[a]				
	$\delta^{13}C$	$\delta^{17}O$	$\Delta\nu_{h/2}$	$\delta^{13}C$	$\delta^{17}O$	$\Delta\nu_{h/2}$	$\delta^{13}C$	$\delta^{17}O$	$\Delta\nu_{h/2}$	$\delta^{17}OR$	$\Delta\nu^{OR}_{h/2}$
H				167.3	253.5	120	161.6	359	30	137.5	70
Me	170.1	502.5	30	178.1	250.5	175	171	357	50	134	60
Et	174.4	495	55	181.5	244	175	174.4	350	74	130	85
i-Pr	177.6	493.5	57	184.1	242	165	176.9	346.5	90	127	90
t-Bu	179.8	496.5	62	185.8	240	130[b]	178.1	347.5	100	124	125
Pr	173.2	498	75	180.6	246.5	140[c]	173.5	353	95	132	95
i-Bu	172.4	501	100	180.0	248.5	155[c]	172.8	355	125	132.5	145
*neo*Pen	171.0	504.5	95	179.2	253.5	145[c]	171.9	361	140	137.5	150

	OEt[a]					NH_2		
	$\delta^{13}C$	$\delta^{17}O$	$\delta\nu_{h/2}$	$\delta^{17}OR$	$\Delta\nu^{OR}_{h/2}$	$\delta^{13}C$[e]	$\delta^{17}O$[e]	$\Delta\nu_{h/2}$
H	161.0	360.5	43	109	78	167.3	310	39[f]
Me	170.3	359.5	80	165	85	177.8	313.5	130[f]
Et	173.8	351.5	95	161	105	181.7	308	190[f]
i-Pr	176.4	346	135	158.5	140	185.1	306	110[g]
t-Bu	177.8	348	135	152	135	186.8	314.5	80[h]

[a] For esters: δ ^{17}OR and $\Delta\nu^{OR}_{h/2}$ are the chemical shifts and the linewidths of the methoxy and ethoxy oxygen atoms.

[b] At 40°. [c] At 60°.

[d] For ^{13}C measurements, the amides are dissolved in D_2O/H_2O/dioxane, δ ^{13}C are measured relative to dioxane (67.4 ppm) and are reported to TMS (0.0 ppm).

[e] δ ^{17}O are measured relative to internal 3M nitromethane (602.5 ppm) and are reported to H_2O (0.0 ppm).

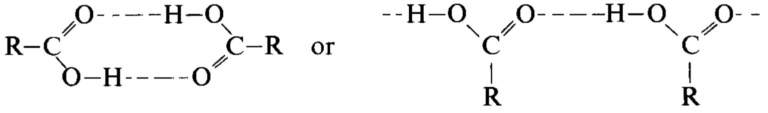
[f] At 90°.

[g] At 120° (sealed tube).

[h] At 130° (sealed tube).

b) The **oxygen** chemical shifts vary strongly with changes of X: δ $^{17}O \simeq 500$ ppm for X=Cl; 350 ppm for X=OR; 310 ppm for $X=NH_2$. All these chemical shifts are smaller than those of aldehydes and ketones [1]. This can be explained by the preponderance of the mesomeric form **B′** in RXCO compared to the equivalent form in RR′CO. The substitution of hydrogen atoms by methyl groups in acyl derivatives introduces smaller β^{π} and γ^{π} shieldings than in aldehydes and ketones [1], an observation also in agreement with a reduced π bond order in C=O bonds of esters and amides. Conversely, the methoxy oxygen in methyl acetate (δ $^{17}O = 134$ ppm) is more deshielded than that in methoxy-2-propene (δ $^{17}O = 62.5$ ppm [15]); this confirms the increased sp^2 character of the former.

In the acids, fast proton exchange in dimers or polymers such as:



leads to the equivalence of the two oxygen atoms and only a single line is observed; this line is found at the mid-point between the 2 ester lines (δ $^{17}O = 240$ ppm).

Table 3. *Quadrupole coupling constants (QCC.), net charges on the oxygen (Z_O), wavelengths of maximum absorption for $n \to \pi^*$ transitions ($\lambda_{max}^{n\to\pi^*}$) and δ ^{17}O for acyl derivatives*

Compounds	QCC.a) MHz	Z_Oa) e	$\lambda_{max}^{n\to\pi^*}$b) nm	$\delta^{17}O$c) ppm
aldehydes, ketones	10.8	0.83	295-275	570-600
esters	9.5	0.92	205	350
amides	9.4	0.94	210	310
acyl chlorides	8.6	1.02	235	500

a) Values from [7]. b) Average values [16]. c) Average values from *Table 3.*

Cheng & Brown [7] have recently measured the quadrupole coupling constant of several compounds containing carbonyl groups. From these results they calculated the net charge on the oxygen atom, Z_O, using a simple *Townes & Dailey* model. Typical data are listed in *Table 3*. From these Z_O values and from the shift value of – 530 ppm for the gain of one electron on the oxygen, one would predict shieldings of approximatively –50 to –60 ppm for esters and amides, and about –100 ppm for acyl chlorides, relative to aldehydes and ketones. The experimental values are quite different, showing this approach to be oversimplified. On the other hand, in previous work [2], the δ ^{17}O in acyl derivatives have been exclusively attributed to the variation of the mean excitation energy term through changes in $\lambda_{max}^{n\to\pi^*}$, but this assumption is also oversimplified (see *Table 3*). Even if the effect of increasing charge on the oxygen atom and that of decreasing $\lambda_{max}^{n\to\pi^*}$ for the carbonyl group were combined, one cannot arrive at a satisfactory explanation of all the results.

Correlations between electronic charges and chemical shifts are very attractive but the examples studied here show that this approach has serious limitations. One of the most severe difficulties is to decide whether the variations of the mean excitation energy term are negligible or not.

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Experimental Part

Apart from methyl isopropenyl ketone (donated by Prof. *M. Schlosser*, Lausanne University), the unsaturated carbonyl compounds and acyl derivatives were obtained from *Fluka* A.G., Buchs, Switzerland, and purified by distillation before measurements.

Natural-abundance ^{17}O-NMR. spectra were recorded on a *Bruker* HX90 spectrometer using the conditions reported [1] (12.2 MHz, F.T. mode, spectrum width: 12 KHz, 8K data points, proton lock signals). Unless specified otherwise, the compounds were examined as pure liquids at RT. The δ ^{17}O are measured and reported relative to external ^{17}O-enriched (0.1 at%)-acid-water (δ ^{17}O = 0.0 ppm, accuracy: ± 1 ppm). The ^{17}O linewidths at half-height, $\Delta\nu_{h/2}$ in Hz, are corrected from the broadening due to exponential multiplications of the FID signals.

The ^{13}C-NMR. spectra were recorded on a *Bruker* WP60DS spectrometer at 15.08 MHz. The δ ^{13}C were measured in $CDCl_3/CCl_4$/TMS 5:4:1 (v/v) at a concentration of 1:2 (v/v solute/solvent) and reported relative to internal TMS (δ ^{13}C = 0.0 ppm, accuracy: ±0.2 ppm).

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