Identification of Ozonides by Oxygen-17 NMR Spectroscopy

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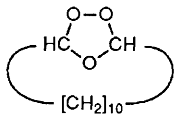
In the natural abundance ^{17}O NMR spectra of seven 1,2,4-trioxolanes (ozonides), the resonance of the peroxide and of the ether oxygens are clearly separated and allow structural identifications.

To our knowledge, ^{17}O NMR data for only one ozonide have been reported so far, *viz.* those of the ozonide of 1,2-dimethylcyclobutene.[1] We report here the natural abundance ^{17}O NMR spectra of the seven ozonides **1a**, **1b**, **2a**, **2b**, **3a**, **3b** and **4** and of the 1,2,4,5-tetroxane **5**. Table 1 gives the ^{17}O chemical shifts and linewidths of these compounds, measured at 27 °C in toluene. No concentration effects on the chemical shifts were observed within the accuracy of the measurements (±2 ppm).

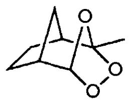
The spectrum of each ozonide showed two well resolved signals ($\Delta\delta \geqslant 160$ ppm at individual linewidths <15 ppm), which by integration could be assigned to the ether-type oxygen at low frequency and the peroxide oxygens at high frequency (relative intensity ratio 1:2). Fig. 1 shows, as an example, the ^{17}O NMR spectra of ozonide **4** and the related tetroxane **5**.

The chemical shifts of the peroxide oxygens in the ozonides were between δ 295 and 331, *i.e.* they are shifted to higher frequencies relative to those of acyclic peroxides such as di-*tert*-butyl peroxide (δ 260),[2] and they appear at the upper end of the rather large chemical shift range (*viz.* δ 232–318) given by Zagorski *et al.*[1] for a series of cyclic peroxides. The latter authors did not find a straightforward correlation between ^{17}O chemical shifts and atomic charge or ionisation potentials in peroxides. However, they suggested that conformational changes contributed to the variation in ^{17}O chemical shifts. It was confirmed, qualitatively, that the dihedral angle C–O–O–C decreases as the chemical shift increases.[1,3] Therefore, since the chemical shifts of the peroxide oxygens in the seven ozonides are very large, we can tentatively conclude that the C–O–O–C dihedral angles in these ozonides are close to 0°. The spectrum of the 1,2,4,5-tetroxane **5** showed only one signal for the peroxide oxygens, which were shielded by approx. 40 ppm relative to those in **4**, thus suggesting considerable deviation from planarity in both C–O–O–C units. Obviously, the above conclusion assumes that in the ozonides the peroxide oxygen chemical shifts are only sterically influenced by the ether oxygen, and not affected considerably by inductive effects (β deshielding). However, the chemical shift values for systems with several functional groups result from the interaction of several factors which cannot be readily accounted for at this time.[3]

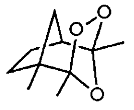
The chemical shifts of the ether oxygens in the seven ozonides were between δ 105 and 173. This means that they are shifted to high frequencies relative to dialkyl ethers (between δ −52 and 76),[2] and also relative to polycyclic ethers (*e.g.* δ 85.5 in 7-oxanorbonane).[4] Obviously, there is strong β deshielding by the peroxide oxygens, comparable to the shifts of ketals relative to ethers.[2] A deshielding of the ether oxygen in **4** by +23 ppm relative to that in **1** can be ascribed to the



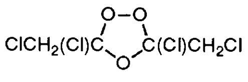
1a *cis*
1b *trans*



2a

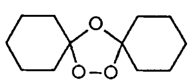


2b

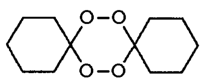


$ClCH_2(Cl)C\overset{O-O}{\underset{O}{\quad}}C(Cl)CH_2Cl$

3a *cis*
3b *trans*



4



5

Table 1 ^{17}O NMR data of seven ozonides and of a 1,2,4,5-tetroxane[a]

	Chemical shifts (δ)[b,c]	
Compound	–O–	–O–O–
1a[e]	106 (250)	306 (510)
1b[e]	106 (250)	297 (570)
2a[f]	139 (253)	310, 320[d]
2b[f]	146 (257)	329, 333[d]
3a[g]	172 (482)	327 (750)
3b[g]	162 (466)	319 (717)
4[h]	129 (450)	295 (720)
5[h]		256

[a] All compounds were obtained by ozonolysis of the corresponding alkenes on polyethylene and characterized by ^1H and ^{13}C NMR spectra as well as elemental analyses. Details will be reported elsewhere.[7–10] ^{17}O NMR spectra were recorded on a Bruker AM-360 instrument operating at 48.8 MHz. [b] In ppm relative to 1,4-dioxane used as external reference, +0.2 ppm relative to water.[5] [c] Numbers in parentheses refer to linewidths at half-height, in Hz. [d] Composite signal. [e] Ref. 7. [f] Ref. 8. [g] Ref. 9. [h] Ref. 10.

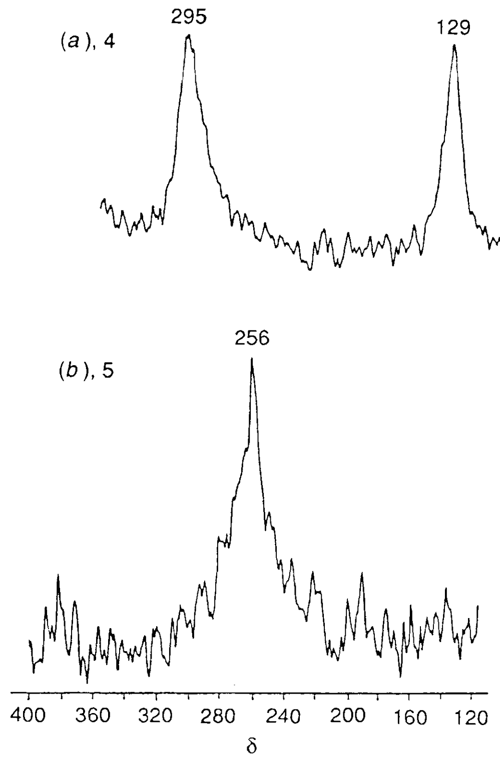


Fig. 1 ^{17}O NMR spectra of (*a*) **4** and (*b*) **5**

doubling of the β and γ effects, the former dominating the latter (up to +30 and −12 ppm, respectively, in ethers).[2] A further shift to high frequency occurred in ozonides **2**, which can be explained by the effect of steric strain. Obviously, this shift[4] fades with increasing ring size. A low frequency shift of the ether resonance in **2a** by 7 ppm relative to **2b** can be ascribed to a strong γ effect, similar to that obtained by interaction between the oxygen and the methano-bridge carbon in norbornene *exo*-oxide.[6]

It is obvious from the data reported that ^{17}O NMR spectroscopy can be recommended as an additional tool for the characterization of ozonides. Moreover, as shown by the differences in the spectra of compounds **4** and **5**, the method provides a powerful tool for the unequivocal differentiation between ozonides and 1,2,4,5-tetroxanes, the so-called 'dimeric peroxides' which are often co-products in ozonolysis reactions.[11]

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