

¹⁷O-ENRICHED HYDROGEN PEROXIDE AND T.BUTYL HYDROPEROXIDE :
 SYNTHESIS, CHARACTERIZATION AND SOME APPLICATIONS

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Summary : Solutions of ¹⁷O-labelled hydrogen peroxide and t.butyl hydroperoxide in water or anhydrous solvents are easily obtained, starting from labelled oxygen. These stable enriched ¹⁷O products are valuable reagents to synthesize various labelled molecules, which have been characterized by ¹⁷O-NMR spectroscopy. Chemical shifts of several O-containing groups are given.

Recent publications on ¹⁷O-NMR data on dialkylperoxides¹ and the use of ¹⁷O-enriched α-azohydroperoxides as labelling reagents², prompt us to report data obtained in our Research Center concerning the easy synthesis of ¹⁷O-enriched hydrogen peroxide and t.butyl hydroperoxide and their applications.

Labelled hydrogen peroxide 1 is prepared in three steps³ : hydrogenation, on a palladium alumina supported catalyst, of 1,2,3,4-tetrahydro-6-ethyl-anthraquinone, oxidation with 10 % ¹⁷O enriched oxygen of the crude solution, and extraction with water of the hydrogen peroxide formed. ¹⁷O-labelled t.butyl hydroperoxide 2 is obtained by careful oxidation of t.butyl magnesium chloride with ¹⁷O-enriched oxygen^{3,4}.

Both labelled peroxides are obtained in an 80 % yield based on the ¹⁷O-labelled oxygen used. They have been studied by ¹⁷O-NMR spectroscopy. The spectra obtained (Table 1) show that the chemical shifts are not solvent dependent. This is completely different from what has been observed in the case of the α-azohydroperoxides.

Table 1. ¹⁷O-NMR data for hydrogen peroxide 1 and t.butyl hydroperoxide 2 (10 % ¹⁷O)


Compd	Solvent	Conc. M	T°, C	LW (Hz) ^a		Chemical ^b shift (ppm)	
<u>1</u>	H ₂ O	1.3	65	130		180	
	dioxan	0.9	65	240		180	
	acetonitrile	1.8	65	130		180	
<u>2</u>	H ₂ O	2	r. t.	O ^x	O ^y	O ^x	O ^y
	hexane	1	r. t.	750	650	246	206
				440	330	249	206

^a Line width at half-height

^b Relative to H₂O (± 2 ppm)

These ^{17}O -labelled reagents have been used for easy in situ synthesis of various molecules and therefore for the determination of unknown ^{17}O -NMR data. Some of the molecules and results obtained are listed in Table 2.

Table 2. ^{17}O -NMR chemical shift of -O-O bridge in some peroxides

R-O-O-R' a,b	Temperature °C	LW ^c (Hz)	δ , ppm -O-O-
R=R' = 	65	800	287
R HC=O R'=H	r.t.	350	273 and 255
CH ₃ C=O "	50	400	273 " 255
C ₂ H ₅ -C=O "	60	300	280 " 266
CF ₃ -C=O "	r.t.	400	280 " 260
R=R' = CH ₃ C=O	r.t.	800	327
CF ₃ C=O	r.t.	900	319
R R'=t.butyl			
ClC=O "	r.t.	190 300	270 393
CF ₃ C=O "	"	300 600	273 372
CH ₃ C=O "	"	260 400	292 333
C ₄ H ₉ NHC=O "	"	800 1 400	273 313

^a mixture of isotopomers R-O-O-R' (81 %), R-O-O-R' = R-O-O-R' (9 %), R^{*}O-O-R' (1 %)
^{*}O = labelled oxygen

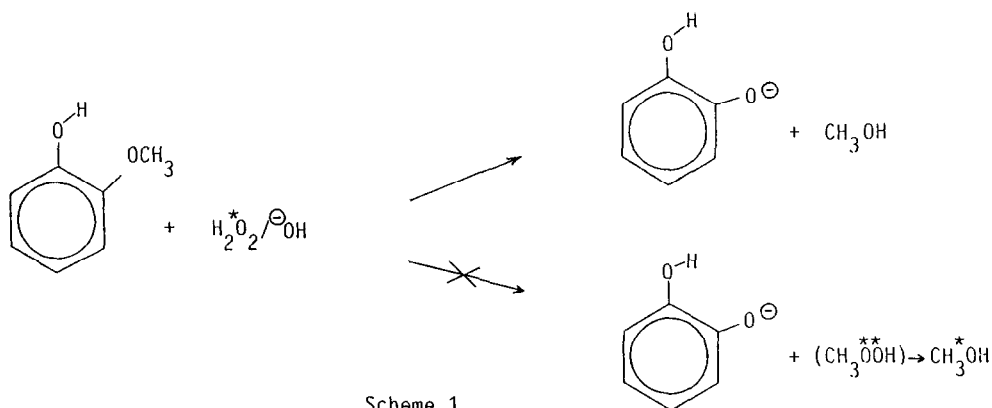
^b R=R' one signal, R≠R' two signals

- ^c Line-width at half-height

All these peroxidic reagents are useful tools to introduce ^{17}O atoms in various molecules^{5,6} and thus to elucidate reaction mechanisms or to follow the transformation of oxygenated species in vitro or in vivo.

For example in the bleaching of chemical pulps, hydrogen peroxide in alkaline medium is used to oxidize lignin polyphenolic materials.

In the lignin network, the guaiacol structure is found to undergo a demethylation reaction in these conditions. One can observe that the O-demethylation does not proceed with hydrogen peroxide, as no ^{17}O methanol can be detected (Scheme 1).



On the other hand, the acid-catalysed reaction between hydrogen peroxide and t.butanol at 80°C effectively leads to t.butyl hydroperoxide and partially to t.butyl peroxide as shown in Figure 1.

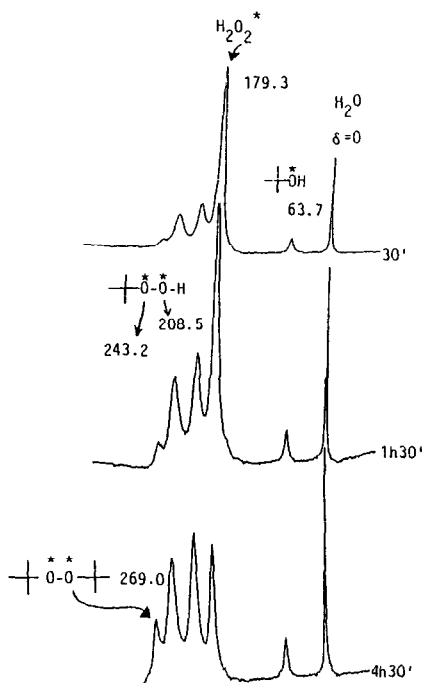


Figure 1 : ^{17}O -spectra (27.02 MHz) of the acid-catalysed reaction between hydrogen peroxide and t-butanol at 80°C .

* : labelled oxygen.

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