

The Nature of Hydrogen Bonding in Hydrotrioxides of Methyl α -Methylbenzyl Ether and α -Methylbenzyl Alcohol. Are Hydrotrioxides Self-associated in Solutions?

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^1H and ^{13}C N.m.r. spectroscopic evidence supports the hypothesis of the self-association of hydrotrioxides (**2a**) and (**2b**); inspection of molecular models of dimeric forms of these hydrotrioxides by taking into account the equilibrium geometry of methyl hydrotrioxide, calculated by the *ab initio* method at the STO 4-31G level, reveals two nearly optimal hydrogen bonding geometries in the associated hydrotrioxide species.

Although spectroscopic and other experimental evidence has been given in recent years for the existence of hydrotrioxides,¹⁻⁴ several fundamental questions regarding the structure and decomposition of these interesting species remain to be answered. We present here evidence for the existence of hydrotrioxides of methyl α -methylbenzyl ether (**2a**) and α -methylbenzyl alcohol (**2b**), and provide new insights into the structure of these polyoxides.

Ozonation of (**1a**) and (**1b**) (20 mmol, 30% w/w) with ozone-nitrogen or ozone-oxygen in ethyl acetate and [$^2\text{H}_6$]acetone at -70 to -50 °C produced the corresponding hydrotrioxides (**2a**) and (**2b**), characterized by their OOOH ^1H n.m.r. absorptions at δ 13.3 ± 0.8 ,[†] in yields of 20–40%; n.m.r. data are in Table 1.

[†] The hydrotrioxides decompose in the temperature range -35 to -10 °C in both solvents to produce oxygen, a part of which is in the singlet state ($\Delta^1\text{O}_2$) as determined with 1,3-diphenylisobenzofuran.³ The main nongaseous decomposition products of (**2a**) are acetophenone, methyl benzoate, benzoic acid, methanol, and hydrogen peroxide, while (**2b**) yields acetophenone, benzoic acid, and hydrogen peroxide (g.l.c., t.l.c., ^1H n.m.r.). In both cases, a metastable hydroperoxide(s), as yet not completely identified, was also detected in the decomposition mixture (^1H n.m.r.).

Table 1. N.m.r. data for (**2a**) and (**2b**).^a

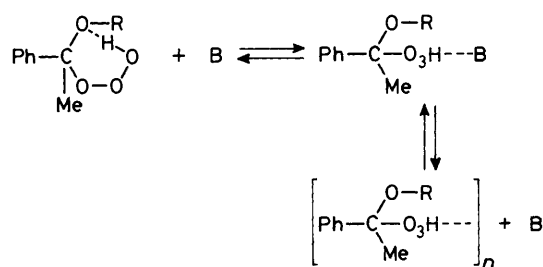
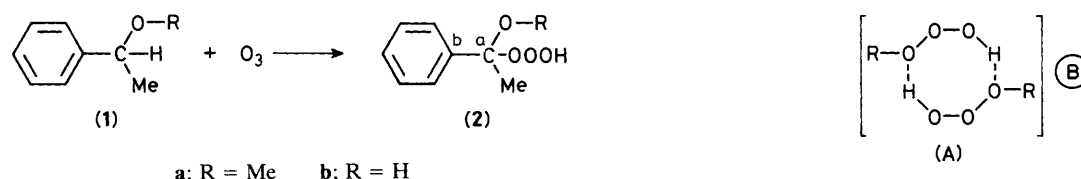
Compound	Solvent	DMA/(2)	$\delta(\text{OOH})^b$
(2a) ^c	EtOAc	—	12.90, 13.15
	EtOAc-DMA	0.7	12.96, 13.55
	EtOAc-DMA	2.1	13.17, 13.58
	EtOAc-DMA	20.0	13.66, 14.42
	(CD_3) ₂ CO	—	13.19, 13.54
(2b)	EtOAc	—	12.88, 12.91
	EtOAc-DMA	0.7	14.18
	EtOAc-DMA	2.1	14.27, 14.34
	EtOAc-DMA	20.0	14.86, 15.00
	(CD_3) ₂ CO	—	13.20, 13.23

^a N.m.r. spectra (100 MHz for ^1H) were recorded at -50 °C for 0.2–0.3 M solutions. ^b Area ratio of peaks 1 : 1.2. ^c ^{13}C in (CD_3)₂CO (values for cumyl hydrotrioxide from ref. 4b in parentheses): C^a 108.6 and 110.2 (104.3); C^b 134.3 (134.5). N.m.r. data in (CD_3)₂CO at -50 °C for α -methoxy- α -methylbenzyl hydroperoxide, the hydroperoxide analogue of (**2a**): ^1H , $\delta(\text{OOH})$ 10.83; ^{13}C , C^a 106.4; C^b 142.5. This hydroperoxide, which was believed to be too unstable for isolation, was obtained in 99.8% purity (by iodometry) by the displacement method from (1,1-dimethoxyethyl)benzene and 100% H_2O_2 in Et_2O .

Table 2. Kinetic data for (2a) and (2b).^a

Compound	Solvent	10^2k_a	10^2k_b	10^2k_{a+b}	E_a (log A_a)	E_b (log A_b)	E_{a+b} (log A_{a+b})
(2a)	EtOAc	4.35	4.58	4.43	23.5 (18.9)	19.8 (15.9)	22.7 (18.2)
(2a)	(CD ₃) ₂ CO	6.44	5.62	5.26	20.9 (16.9)	21.5 (16.6)	20.0 (16.0)
(2b)	EtOAc			6.75			16.8 (13.8)
(2b)	(CD ₃) ₂ CO			4.78			16.9 (13.3)

^a k Values ($\pm 7\%$) in s^{-1} at -20°C ; E values in kcal mol^{-1} (1 cal = 4.184 J). Kinetics were studied in the temperature range -40 to -15°C .



Scheme 1

A characteristic of the ^1H n.m.r. spectra is the appearance of two OOH absorptions. A similar feature in the n.m.r. spectra of 2-methyltetrahydrofuran² and acetal hydrotrioxides³ was originally assigned to the presence of two forms of the hydrotrioxide with OOH bonded intramolecularly to either of the lone pairs of the tetrahedral oxygen atom or to two conformational forms of the six-membered ring with R groups on the oxygen atom axial or equatorial.³ Since these hydrotrioxides were studied in a very limited number of solvents, it was difficult to test these hypotheses unambiguously. The present n.m.r. evidence is not in accord with these presumptions.

Although both OOH signals of (2a) broaden somewhat at higher temperatures, they did not coalesce even at -10°C . The addition of *N,N*-dimethylacetamide (DMA), a relatively strong oxygen acceptor base, to the solution of (2a) or (2b) in ethyl acetate caused a downfield shift of both OOH signals with no change in their relative intensities. Merging of the absorptions was not observed even in the presence of a relatively large excess of DMA.

The rate of disappearance of the two OOH absorptions was measured for (2a) in ethyl acetate and $[\text{D}_2\text{H}_6]$ acetone, and was found to obey cleanly first-order kinetics; data are in Table 2. Both absorptions disappeared with approximately the same rate.

The ratio of the intensities of the OOH absorptions for (2a) in ethyl acetate and $[\text{D}_2\text{H}_6]$ acetone, and for (2a) and (2b) in ethyl acetate-DMA, was approximately the same as found for

the relative amounts of both enantiomers in the racemic (\pm)-(1b)^{5a} and (\pm)-(1a)^{5b} used [(-):(+) = 1:1.1—1.2]. The upfield:downfield OOH absorption ratio (1:1.2) changed to 1:1.4 when (-)-(1a),^{5c} and to 1:1.7 when (-)-(1b),^{5d} both of ca. 90% enantiomeric purity,[‡] were used as precursors of the hydrotrioxides (2a) and (2b), respectively. When (+)-(1b)^{5d} of ~90% enantiomeric purity was ozonized in ethyl acetate, the intensity ratio was found to be 1:1.5. It is interesting to note that C^a of (2a) also resonates as a doublet in the ^{13}C n.m.r. spectrum (CD₃COCD₃).

All these observations led us to the conclusion that the hydrotrioxides (2a) and (2b) could potentially exist in the intramolecularly hydrogen-bonded form only in 'inert' systems,[§] and that oxygen bases, even as weak as ethyl acetate or the parent ether (1a), disrupt the chelate ring with subsequent formation of intermolecularly hydrogen-bonded associates according to Scheme 1. This type of association has already been proposed for hydroperoxides.⁶ The change in the relative intensities for OOH in the ^1H n.m.r. spectra of the hydrotrioxides (2a) and (2b), produced by the ozonation of enantiomeric starting materials, seems to support the conclusion that the n.m.r. doublets are due to the self-associated entities and not to different hydrogen-bonded species. Inspec-

[‡] The enantiomeric ratios of (\pm)-(1a) and (\pm)-(1b), as well as the optical purity of the enantiomers, were determined with the chiral shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphoro]europium(III).

[§] Low yields of (2a) (5–10%) in Freon 11/12 prevented a detailed investigation of the n.m.r. spectra of this compound in an 'inert' solvent. However, only one OOH absorption at δ 12.73 was observed in the ^1H n.m.r. spectrum of (2a) at -45°C . Below -50°C , this absorption split into two components (δ 12.6 and 12.7 at -60°C , coalescence at -55 to -50°C). The same phenomenon was observed also on adding DMA to solutions of (2a) above -40°C ; the splitting of the OOH absorption was in this case accompanied by a downfield shift of both signals. We are at present reluctant to assign the OOH absorption at δ 12.73 to the intramolecularly hydrogen bonded form of (2a), since a large excess of (1a) present in the system could potentially also cause the opening of the chelate ring with subsequent formation of the associates.

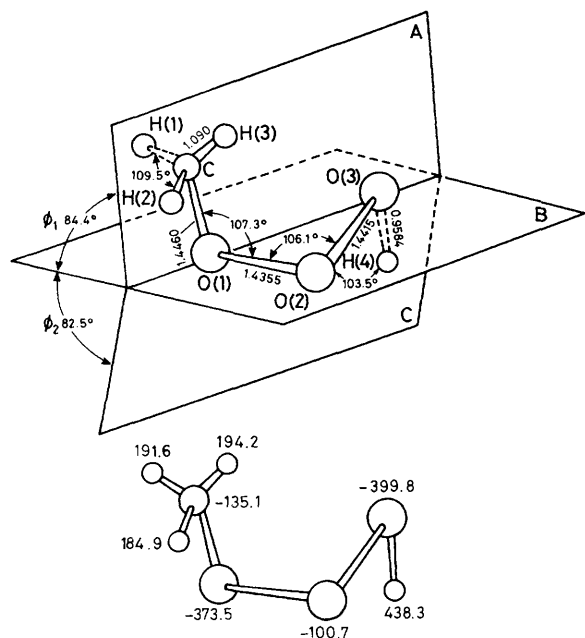


Figure 1. The equilibrium geometry and the net atomic charges ($\times 10^{-3} e$) of methyl hydrotrioxide (STO 4-31G, $E = -264.189\ 57$ a.u.). Except for the standard C–H bond length and tetrahedral angles in the methyl group, all other geometric parameters were optimized. The net atomic charge is defined as $Z - n$ (STO 4-31G), where Z is the atomic number and n is the net electronic density of an atom. H¹ is in the plane C–O¹–O²; C¹ is in the plane A; O¹, O², and O³ are in the plane B; and H⁴ is the plane C. [Figure 1 (HO₃H) in ref. 1(c) should have O² on the opposite side of the hydrogen atoms.]

tion of molecular models of dimeric forms of hydrotrioxides, taking into account the dihedral angles ϕ_1 and ϕ_2 , obtained for methyl hydrotrioxide by STO 4-31G *ab initio* calculations^{7,8} (Figure 1), reveals that two nearly optimal hydrogen-bonding geometries with O–H \cdots O bond angles only slightly distorted from the ideal value of 180° are available. Thus, these dimeric structures (A) should be substantially more stabilized than the chelated forms or the 1 : 1 hydrotrioxide–oxygen base adducts.⁹ This additional stabilization appears to be the driving force behind the formation of two distinct dimeric forms, *i.e.* ‘*cis*’ and/or ‘*trans*’ homochiral (*R*–*R*, *S*–*S*) and heterochiral (*R*–*S*, *S*–*R*) ensembles in solutions of chiral hydrotrioxides (‘anisometric’ interactions).¹⁰ These dimers are presumably solvated by the carbonyl oxygen base, which serves as a ‘chemical shift reagent’ for these systems. Some selective processes (chiral recognition and/or stereoelectronic control) in the formation of these associates are indicated. Recent evidence in support of the involvement of carbocationic intermediates in ozonation of C–H bonds in saturated compounds to produce hydrotrioxides^{4,11} implies the possibility of racemisation or inversion of enantiomeric substrates.

Implications of the observed association of hydrotrioxides on the decomposition of these compounds are apparent. The ‘pericyclic’ mechanism involving intramolecular transfer of the hydrogen atom, proposed previously for hydrotrioxides capable, at least theoretically, of existing in the chelated

form,^{2,3} cannot be operative in the solvents investigated. Rather, activation parameters for the decomposition of (2a) and (2b), which are in good agreement with those obtained for the homolytic scission of the RO–OOR bond in the decomposition of di-*t*-butyl trioxide ($E_a = 23 \pm 3$ kcal/mol, $\log A = 17 \pm 1.5$)¹² indicate homolytic processes as mechanistic pathways in these reactions. Somewhat lower values obtained in the present study [especially for (2b)] most probably reflect the importance of the induced decomposition of hydrotrioxides.^{3,4} Preliminary results of a study of decomposition of (2a) and (2b) in the presence of 2,6-di-*t*-butyl-4-methylphenol as inhibitor, *i.e.* somewhat reduced rates of decomposition and increased activation energies, although not as pronounced as reported for cumyl hydrotrioxide,⁴ support this presumption.

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References

- For reviews on ozonation of carbon–hydrogen bonds see: (a) P. S. Bailey, ‘Ozonation in Organic Chemistry,’ vol. 2, Academic Press, New York, 1982; (b) E. Keinan and H. T. Varkony, ‘The Chemistry of Peroxides,’ ed. S. Patai, Wiley, New York, 1983, ch. 19. (c) For a review on polyoxides see: B. Plesničar, ‘The Chemistry of Peroxides,’ ed. S. Patai, Wiley, New York, 1983, ch. 16.
- R. W. Murray, W. C. Lumma, Jr., and J. W.-P. Lin, *J. Am. Chem. Soc.*, **92**, 3205; F. E. Sary, D. E. Emge, and R. W. Murray, *ibid.*, 1976, **98**, 1880.
- F. Kovač and B. Plesničar, *J. Chem. Soc., Chem. Commun.*, 1978, 122; *J. Am. Chem. Soc.*, 1979, **101**, 5820.
- W. A. Pryor, N. Ohto, and D. F. Church, *J. Am. Chem. Soc.*, 1982, **104**, 5813; 1983, **105**, 3614.
- (a) A. J. Houssa and J. Kenyon, *J. Chem. Soc.*, 1930, 2260; (b) E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Am. Chem. Soc.*, 1962, **84**, 2371; (c) K. Mislow, *ibid.*, 1951, **73**, 4043; (d) E. Downer and J. Kenyon, *J. Chem. Soc.*, 1939, 1156.
- C. Walling and L. Heaton, *J. Am. Chem. Soc.*, 1965, **87**, 48. For a review see: W. H. Richardson, in ref. 1(b), ch.5.
- R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.
- These calculations represent the first reported *ab initio* studies on this molecule. For *ab initio* MO studies on hydrogen trioxide (HO₃H), and methyl hydroperoxide (CH₃OOH), see: (a) B. Plesničar, S. Kaiser, and A. Ažman, *J. Am. Chem. Soc.*, 1973, **95**, 5476; B. Plesničar, D. Kocjan, S. Murovec, and A. Ažman, *ibid.*, 1976, **98**, 3143; D. Cremer, *J. Chem. Phys.*, 1976, **98**, 3143; D. Cremer, in ref. 1(b), ch. 1; (b) R. A. Bair and W. A. Goddard III, *J. Am. Chem. Soc.*, 1982, **104**, 2719 (CH₃OOH).
- For recent reviews on hydrogen-bonding models, see: P. Schuster, G. Zundel, and C. Sandorfy, ‘The Hydrogen Bond,’ North Holland Publishing Co., Amsterdam, 1976; R. H. Stokes, *Chem. Soc. Rev.*, 1982, **11**, 257; M. Meot-Ner (Mautner), *Acc. Chem. Res.*, 1984, **17**, 186.
- K. Mislow, *Bull. Soc. Chim. Belg.*, 1977, **86**, 595; F. A. Anet, S. S. Miura, J. Siegel, and K. Mislow, *J. Am. Chem. Soc.*, 1983, **105**, 1419; A. Bauder, R. Meyer, and Hs. H. Günthard, *Mol. Phys.*, 1974, **28**, 1305; W. C. Herndon and S. P. Vincenti, *J. Am. Chem. Soc.*, 1983, **105**, 6174.
- P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, 1980, **102**, 3105.
- P. D. Bartlett and P. Günther, *J. Am. Chem. Soc.*, 1966, **88**, 3288; see also P. S. Nangia and S. W. Benson, *J. Phys. Chem.*, 1979, **83**, 1138. Thermochemical calculations show that homolytic cleavage of the CH₃O–OOH bond [$D(\text{CH}_3\text{O–OOH}) = 22.8$ kcal/mol] is 6–7 kcal/mol more favourable than CH₃OO–OH bond cleavage (1 cal = 4.184 J); J. R. Luong, *J. Chem. Ed.*, 1981, **58**, 26; S. W. Benson, ‘Thermochemical Kinetics,’ Wiley, New York, 1976.

¶ The possibility that the two OOOH absorptions might be due to the presence of two distinct 1 : 1 hydrotrioxide–oxygen base complexes appears to be unlikely, *i.e.* one would expect a much faster equilibration rate between them, at least at –10 °C, on the n.m.r. time-scale.