J. Am. Chem. Soc. 1988, 110, 214-222

Chemistry of Hydrotrioxides.[1] Preparation, Characterization, and Thermal Decomposition of Hydrotrioxides of Alkyl α-Methylbenzyl Ethers and α-Methylbenzyl Alcohol. Attempted Spin Trapping of Trioxyl Radicals[†]

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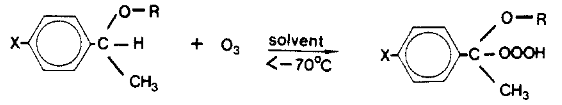
Abstract: The characterization of hydrotrioxides, produced by the low-temperature ozonation of methyl α-methylbenzyl and ethyl α-methylbenzyl ethers and α-methylbenzyl alcohol, is reported. The NMR spectroscopic evidence, i.e., the appearance of two OOOH absorptions at ca. δ 13 downfield from Me_4Si, was interpreted in terms of the existence of two distinct self-associated dimeric and/or intramolecularly hydrogen-bonded hydrotrioxide species. The products of and the kinetic and activation parameters for the decomposition of hydrotrioxides **4–6** in various solvents are reported. The effect of solvents and radical inhibitors on the decomposition is relatively small. Electron-withdrawing groups in **4** and **5** accelerate decomposition while electron-donating groups retard it. The Hammett ρ values (for **4**) range from 0.7 ± 0.1 in ethyl acetate to 1.4 ± 0.2 in acetone. Although nonradical ("pericyclic") decomposition pathways cannot be completely ruled out, the evidence obtained strongly indicates the involvement of homolytic processes in the decomposition of hydrotrioxides under investigation, with the scission of the RO–OOH bond and subsequent cage disproportionation of the cage radical pair (the Benson mechanism) being most probably the main decomposition pathway. Possible contributions of the concerted two-bond homolysis in and an S_H2 type chain decomposition of the hydrotrioxides to the overall decomposition mechanism(s) are also discussed. Attempts to trap the alkyltrioxyl radicals, presumably formed in the induced decomposition of hydrotrioxides, were unsuccessful. The ESR characteristics of methyl α-methoxybenzylperoxyl radical spin adduct of methyl-*N*-durylnitrone (MDN), formed by adding the spin trap to the deozonized solutions of **4a** in ethyl acetate at low temperatures and also generated independently by the alkoxyl radical induced decomposition of hydroperoxide (**7**) in the presence of MDN, are reported for the first time.

The reaction of ozone with saturated organic compounds has been studied extensively in recent years.[2] Spectroscopic and other experimental evidence for the existence of hydrotrioxides in these reactions has already been given.[1-4] Nevertheless, several questions of fundamental importance regarding the structure and decomposition of these important intermediates remain to be elucidated.[3]

In the present paper we report the results of a low-temperature ozonation of racemic and enantiomeric alkyl α-methylbenzyl ethers (**1**, **2**) and α-methylbenzyl alcohol (**3**).[1,5] NMR spectroscopic evidence for hydrotrioxides **4–6** formed in these reactions has been given, and an attempt has been made to elucidate the nature of hydrogen bonding in these polyoxides. We also present here kinetic and activation parameters for the decomposition of hydrotrioxides under investigation in the absence and presence of radical inhibitors and the results of a study of the effect of substituents on the rate of decomposition. Results of attempts to trap alkyltrioxyl radicals, presumably formed in the induced decomposition of hydrotrioxides, by using the ESR spectroscopic technique known as spin trapping are also presented.

Results and Discussion

NMR Spectra. Ozonation of **1–3** (20 mmol, 30% (w/w)) with ozone–nitrogen or ozone–oxygen mixtures in ethyl acetate, acetone, or diethyl ether at −70 °C produced the corresponding hydrotrioxides **4–6**, characterized by their ^1H NMR OOOH absorption at δ 13 ± 0.8 downfield from Me_4Si, in yields of 10–40%.[1b]



(1) $R = CH_3$
(2) $R = C_2H_5$
(3) $R = H$

a, $X = H$
b, $X = CH_3$
c, $X = OCH_3$
d, $X = F$
e, $X = Cl$
f, $X = Br$

(4) $R = CH_3$
(5) $R = C_2H_5$
(6) $R = H$

As in the case of acetal hydrotrioxides,[1a] a characteristic feature of the ^1H NMR spectra of these intermediates is the appearance of two OOOH absorptions. Figures 1 and 2 show the OOOH region of the ^1H NMR spectra of **4a** and **6a** in ethyl acetate, acetone-d_6, and diethyl ether, respectively. Although both OOOH absorptions broaden somewhat at higher temperatures, they did not coalesce even at −10 °C. The two OOOH absorptions disappeared with approximately the same rate (see discussion below). The addition of *N*,*N*-dimethylacetamide (DMAA), a relatively strong oxygen acceptor base, to the solution of **4a** or **6a** in ethyl acetate caused a downfield shift of both OOOH absorptions with no appreciable change in their relative intensities. Merging of the absorptions was not observed even in the presence of a relatively large excess of DMAA. Figure 3 shows the response of the OOOH absorption shifts to various amounts of DMAA added to **4a** in ethyl acetate. It is evident from Figure 3 that the OOOH

[†] Dedicated to the memory of Professor Andrej Ažman.

[1] For the previous paper in this series, see: (a) Kovač, F.; Plesničar, B. *J. Am. Chem. Soc.* **1979**, *101*, 2677. (b) For a preliminary account of a part of the present work, see: Plesničar, B.; Kovač, F. *Abstracts of Papers*, 186th National Meeting of the American Chemical Society, Washington, DC; American Chemical Society: Washington, DC, 1983; ORGN 225. Plesničar, B.; Kovač, F.; Hodoščėk, M.; Koller, J. *J. Chem. Soc., Chem. Commun.* **1985**, 515. (c) Abstracted in part from: Kovač, F. Ph.D. Dissertation, Edvard Kardelj University, 1985.

[2] Bailey, P. S. *Ozonation in Organic Chemistry*; Academic: New York, 1982; Vol. II.

[3] Plesničar, B. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 16.

[4] (a) Stary, F. E.; Emge, D. E.; Murray, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 1880. (b) Pryor, W. A.; Ohto, N.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 3614. (c) Pryor, W. A.; Prier, D. G.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 2883. (d) Rakhmankulov, D. L.; Kuramshin, E. M.; Zlotskii, S. S. *Usp. Khim.* **1985**, *54*, 923. (e) Zarth, M.; de Meijere, A. *Chem. Ber.* **1985**, *118*, 2429. (f) Corey, E. J.; Mehrotra, M. M.; Khan, A. *J. Am. Chem. Soc.* **1986**, *108*, 2472. (g) Posner, G. H.; Wetzberg, M.; Nelson, W. M.; Murr, B. L.; Seliger, H. H. *J. Am. Chem. Soc.* **1987**, *109*, 278.

[5] For recent leading references on ozonation of ethers, see: (a) Erickson, R. E.; Hansen, R. T.; Harkins, J. *J. Am. Chem. Soc.* **1968**, *90*, 6777. (b) Bailey, P. S.; Lerdal, D. A. *J. Am. Chem. Soc.* **1978**, *100*, 5820. (c) Giamalva, D. H.; Church, D. F.; Pryor, W. A. *J. Am. Chem. Soc.* **1986**, *108*, 7678.

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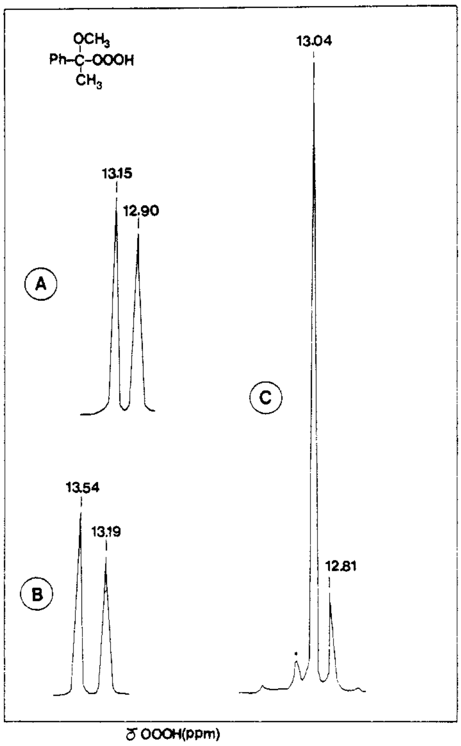


Figure 1. Segments of ^{1}H NMR (100 MHz) spectra of **4a** at −60 °C: (A) in ethyl acetate; (B) in acetone-d_6; (C) in diethyl ether. The absorption marked with an asterisk is due to the presence of small amounts of a hydrotrioxide derived from the solvent after prolonged ozonation. This hydrotrioxide decomposes faster than **4a**.

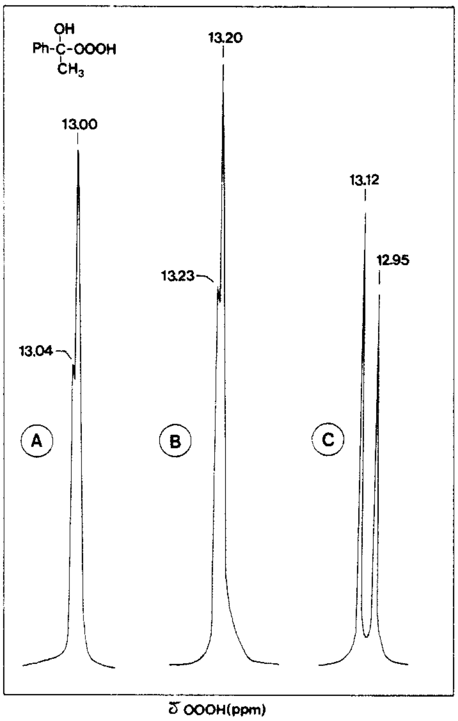


Figure 2. Segments of ^{1}H NMR (100 MHz) spectra of **6a** at −60 °C: (A) in ethyl acetate; (B) in acetone-d_6; (C) in diethyl ether.

absorption nonequivalence increases with an increase in DMAA concentration. Maximum nonequivalence was observed at DMAA/RO$_3$H ratios between 5–7. After that little increase was observed. The magnitude of the Δδ was enhanced somewhat with a decrease in temperature.

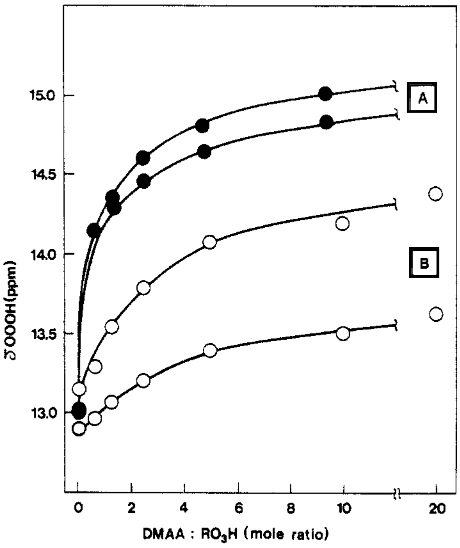


Figure 3. Plots of the chemical shifts of the OOOH absorptions (at −60 °C) as a function of added DMAA to solutions of (A) **6a** and (B) **4a** in ethyl acetate, respectively.

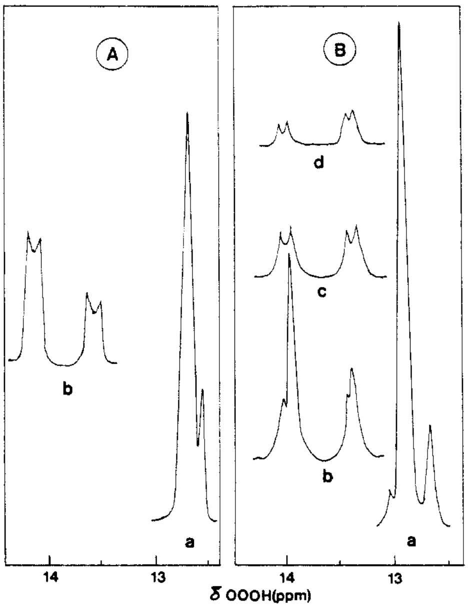
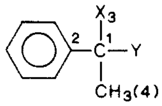


Figure 4. Segments of ^{1}H NMR (60 MHz) spectra of **4a** at −60 °C: (A) in Freon 11/12 (a) before the addition of DMAA and (b) 2 min after the addition of DMAA (molar ratio, DMAA:RO$_3$H = (3–5):1); (B) in diethyl ether (a) before the addition of DMAA and (b) 1 min, (c) 4 min, and (d) 8 min after the addition of DMAA (molar ratio, DMAA:RO$_3$H = (3–5):1).

The ^{1}H NMR spectra of **4a–f** and **5a–f** in diethyl ether represent a special case. Although two OOOH absorptions were also observed for these hydrotrioxides, the observed relative intensities of both OOOH absorptions changed from approximately 1:1 in ethyl acetate and acetone-d_6 to 1:8 ± 2 (upfield:downfield) in diethyl ether. The downfield (stronger) absorption disappeared somewhat faster than the upfield one. The possibility that the less intense upfield absorption might be due to the presence of small amounts of hydrotrioxide, derived from the solvent, was rejected. Control experiments showed that negligible amounts of a hydrotrioxide species (see Figure 1) were formed in the low-temperature (−70 °C) ozonation of diethyl ether. Also, the addition of DMAA to solutions of **4a** in this solvent caused a downfield shift of both OOOH absorptions together with a change of their relative intensities. It is interesting to note that these absorptions were additionally split into two components soon after the addition of DMAA to solutions of **4a** in diethyl ether (Figure 4).

Only one OOOH absorption at δ 12.7 ppm was observed in the ^{1}H NMR spectrum of **4a** in Freon 11/12 at −40 °C. Below −50 °C this absorption split into two components (Δδ = 0.13, −70 °C;

Table I. ^1H and ^{13}C NMR Chemical Shifts (δ) of Methyl α-Methylbenzyl Ether and α-Methylbenzyl Alcohol and Their Hydroperoxide and Hydrotrioxide Derivatives (0.15–0.25 M)[a]



			^1H NMR			^{13}C NMR			
X	Y	solvent	CH_3	(C–X)	C–Y	C(1)	C(2)	C(3)	C(4)
OCH_3	H	$CDCl_3$	1.35 (d)	3.05 (s)	4.12 (q)	79.7	143.9	56.1	24.0
		$(CD_3)_2CO$				79.7	144.4	56.2	24.7
	OOH	$CDCl_3$	1.60 (s)	3.35 (s)	8.85 (s)	106.7	140.5	49.9	24.6
		$(CD_3)_2CO$			10.6 (s)	106.4	142.5	49.7	25.4
CH_3	OOH		1.52 (s)		10.95 (s)	84.0	145.5		26.6
OCH_3	OOOH	$(CD_3)_2CO$	1.60 (s)	3.25 (s)	13.19, 13.54 (1:1.2)	108.1[b]	134.3		26.0
		$CH_3CO_2C_2H_5$	1.57 (s)		12.90, 13.15 (1:1.2)	108.1			
		$(C_2H_5)_2O$	1.80 (s)		12.81, 13.04 (1:(7–10))	(103.2, 104.1)[c]			
CH_3	OOOH	$(CD_3)_2CO$	1.64 (s)[d]		13.67 (s)[d]	104.3	134.5[d]		
OH	H		1.33 (d)	5.3 (s)	4.65 (q)	69.9	147.3		25.1
	OOOH				13.20, 13.23 (1.2:1)	105.26[e]			
		$(C_2H_5)_2O$			12.95, 13.12 (1:1)	105.15[c]			

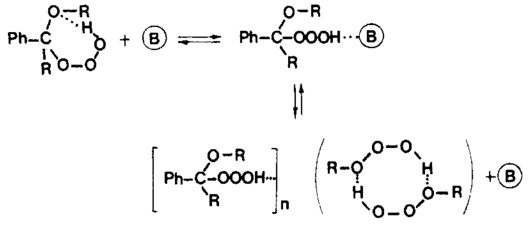
[a] At −60 °C. [b] All attempts to replicate an absorption of lower intensity at δ 110.2, reported originally in ref. 1b, failed. [c] 0.3–0.5 M. [d] From ref 4b. [e] Hydrotrioxides produced by ozonizing (+)-**3a** or (−)-**3a** δ_{COOOH} = 105.26.

$\Delta\delta$ = 0.15, −90 °C). The relative intensities of these absorptions changed somewhat from one experiment to the other.[6] The "coalescence" was observed around −55 °C. The same phenomenon was observed also on adding DMAA to solutions of **4a** at −40 °C. The splitting was in this case accompanied by a downfield shift of both signals together with the change in the relative intensities of both signals. Again, we were able in some experiments to observe additional splitting of these two signals (Figure 4). We were unable to investigate the origin of this OOOH splitting, i.e., whether it represents a J coupling or $\Delta\delta$, due to the low concentrations of the hydrotrioxide in Freon 11/12 and its fast decomposition in diethyl ether and Freon 11/12 in the presence of DMAA (see footnote 25). The same problems were encountered also in attempts to study ^1H NMR spectra of **4a** in other nonpolar solvents.

The ratio of intensities of the OOOH absorptions for the corresponding hydrotrioxides **4a** in ethyl acetate and acetone-d_6 and for hydrotrioxides **4a** and **6a** in ethyl acetate–DMAA solutions, generated from racemic **1a** and **3a**, was approximately 1:1. This upfield:downfield OOOH absorption ratio changed to 1:(1.4 ± 0.1) when (−)-**1a** and to 1:(1.7 ± 0.1) when (−)-**3a** were used as precursors of hydrotrioxides **4a** and **6a**, respectively. When (+)-**1a** and (+)-**3a** were ozonized in ethyl acetate, the intensity ratio was found to be 1:(1.1 ± 0.1) and 1:(1.5 ± 0.1), respectively.

The characteristic ^{13}C NMR signals of hydrotrioxides are, together with those of other benzylic compounds, collected in Table I. The absorptions at δ 108.16 and 105.26 (acetone-d_6, −60 °C) were, by comparison with the corresponding absorptions of other benzylic derivatives, tentatively assigned to the benzyl carbon of the hydrotrioxides **4a** and **6a**, respectively.[7] Addition of an excess of DMAA (DMAA:hydrotrioxide = 20:1) to solutions of **4a** and **6a** in acetone-d_6 caused a small upfield shift of the benzyl carbon absorptions. This was somewhat more pronounced in the case of **4a** ($\Delta\delta_{COOOH}$ = 0.17, **4a**; $\Delta\delta_{COOOH}$ = 0.05, **6a**). It is interesting to note that two COOOH absorptions with the largest upfield shift were observed for **4a** in diethyl ether (104.2, 103.1 ppm).[8] At the same time, δ_{COOOH} is 105.3 ppm for **6a** in the same solvent, i.e., not much different from the values for the same absorption in other solvents investigated.[9]

Scheme I



Splitting of the ^1H NMR OOOH absorptions was already reported for 2-methyltetrahydrofuran[4a] and acetal hydrotrioxides.[1a] On the basis of the relative concentration independence of the position of OOOH absorptions, this phenomenon was originally assigned to the presence of two forms of the hydrotrioxide with OOOH bonded intramolecularly to either of the lone pairs of the tetrahedral oxygen atom or to two conformations of the six-membered ring with R groups on the oxygen atom axial or equatorial. The present results seem to indicate that the structure of the hydrotrioxides under investigation is more complex than originally believed.

The relatively low concentrations of hydrotrioxides obtained, as well as the rather limited temperature range over which these sensitive intermediates could be studied, prevented more detailed concentration dependence and temperature variation studies of the OOOH absorption. Nevertheless, it was evident that their position did not change much with dilution,[10] thus indicating, that at least in part, the hydrotrioxides under investigation are present in solutions in the intramolecularly hydrogen-bonded form. On the other hand, we believe that, in analogy with hydroperoxides,[11] oxygen bases are able to disrupt the chelate ring with subsequent formation of intermolecularly hydrogen-bonded associates[12] and/or

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(6) The presence of various amounts of the decomposition products in the samples of **4a** in Freon 11/12 could be the cause of these variations (1:5 ± 2, upfield:downfield).

(7) The downfield shift of the ^{13}C NMR COOOH absorptions in **4a** and **6a** (acetone-d_6), compared to the corresponding carbon atom in cumyl hydrotrioxide,[4b] can be attributed to the presence of relatively strong electron-withdrawing groups (OCH_3, OH) in these hydrotrioxides and/or the presence of relatively strong hydrogen bonds in these species.

(8) The upfield COOOH absorption was less intense. It appears that the concentration of hydrotrioxide **4a**, as well as the presence of its decomposition products, influences the appearance of the COOOH absorptions as singlets or doublets in the ^{13}C NMR spectra. It should be pointed out that the highest concentrations of **4a** were obtained in diethyl ether as solvent (^{13}C NMR, [**4a**] = 0.3–0.5 M).

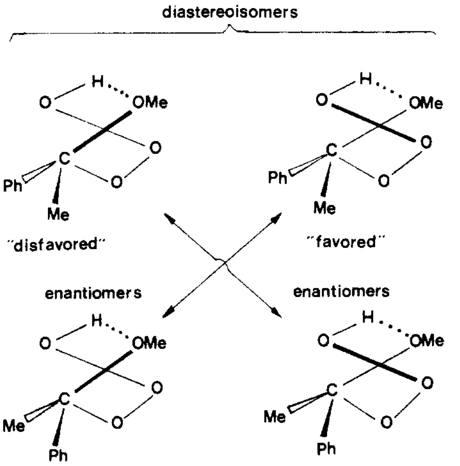
(9) The interpretation of the NMR data for **6a** is additionally complicated by the fact that the OH group can act as both hydrogen bond donor and hydrogen acceptor. At the same time, the hydroxy oxygen is a weaker proton acceptor than an ether oxygen atom.

(10) The largest variations in the position of both OOOH absorptions ($\Delta\delta_{OOOH} \approx 0.3$) were observed in diethyl ether. However, these variations appeared to be a result of different amounts of the decomposition products in the samples of **4a** rather than the change of hydrotrioxide concentration. In all cases, however, the relative position of both OOOH absorptions remained unchanged.

(11) Richardson, W. H. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 5.

(12) Symons, M. C. R. *Chem. Soc. Rev.* **1983**, 1.

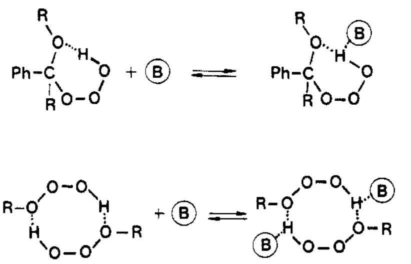
Scheme II



favor the formation of such associates in the process of formation of hydrotrioxides, as shown in Scheme I.

The change in the relative intensities for OOOH absorptions in the ^1H NMR spectra of hydrotrioxides, generated by ozonizing enantiomeric starting materials **1a** and **3a** in ethyl acetate or acetone-d_6, seems to support the belief that the NMR doublets are due to the self-associated entities and not to different hydrogen-bonded species.[13] Inspection of molecular models of either dimeric or intramolecularly hydrogen-bonded forms of hydrotrioxides reveals nearly optimal hydrogen-bonding geometries, with O–H···O bonds very nearly linear.[14] Thus, these forms should be more stable than the opened hydrotrioxide or the hydrotrioxide–oxygen base adduct. We believe that possible strong hydrogen bonds are the driving force for the formation of two distinct dimeric forms of hydrotrioxides, i.e., "cis" and/or "trans" homochiral (*R*,*R*, *S*,*S*) and heterochiral (*R*,*S*, *S*,*R*) ensembles in solutions of chiral hydrotrioxides.[13] On the basis of the expected strengths of hydrogen bonds in these associates, as well as the observations made in the present study, we prefer the possibility of "slow" (slow on the NMR time scale) exchange of participating molecules in the hydrotrioxide dimeric entities.[15] However, it should be pointed out that there is no straightforward interpretation possible of the results obtained by studying the NMR spectra of hydrotrioxides generated by ozonizing enantiomeric substrates. That is, there is at present no consensus of opinion as to whether the formation of hydrotrioxides of ethers and alcohols proceeds by retention or inversion/racemization of substrates.[16,17]

Scheme III



At the same time, there is also no information about possible preference for association of enantiomeric molecules of the same and the opposite configuration. Assuming that dimerization is an important structural feature of hydrotrioxides, our results seem to indicate that there are some selective processes (chiral recognition and/or stereoelectronic control) involved in the formation of the hydrotrioxide associates.

The possibility that the NMR doublets are due to the presence of two pairs of diastereoisomeric forms of the intramolecularly hydrogen-bonded forms with a chemical shift of the sensor nuclei being different in both forms also cannot be ruled out. Such diastereoisomeric pairs are shown in Scheme II. With a relatively strong intramolecular hydrogen bonding, it is hard for the hydrotrioxide ring to flip over from one side of the C–OR bond to the other side. According to this interpretation, the same ratio of favored and disfavored diastereoisomers would be formed from either enantiomeric hydrotrioxide.

Downfield shift of both OOOH absorptions (^1H NMR) upon addition of various amounts of DMAA to solutions of **4a** and **6a** in Freon 11/12, ethyl acetate, acetone-d_6, or diethyl ether, seems to indicate increased formation of the hydrotrioxide–oxygen base adduct, which is in equilibrium with the dimeric and/or chelated forms of the hydrotrioxide, or is due to increased solvation of the latter two forms of the hydrotrioxide,[18,19] as shown in Scheme III. We prefer the possibility of solvation of the dimeric and/or chelated forms of the hydrotrioxide as the most likely explanation for the observed phenomena (at least for **4a** in acetone-d_6 and ethyl acetate).[20] It appears, thus, that the carbonyl oxygen bases investigated serve as "chemical shift" reagents for these hydrotrioxides. We also believe that the structure of hydrotrioxides **4** and **6** is critically dependent on the reaction conditions during the process of their formation (solvent, concentration of the hydrotrioxide formed, and the presence of decomposition products).

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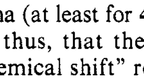
(13) Self-induced NMR nonequivalence through the formation of diastereoisomeric dimers has received considerable attention recently: (a) Pirkle, W. H.; Hoover, D. J. *Top. Stereochem.* **1982**, *13*, 316. (b) Harger, M. J. P. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1882. (c) Dobashi, A.; Saito, N.; Motoyama, Y.; Hara, S. *J. Am. Chem. Soc.* **1986**, *108*, 307.

(14) Although it is difficult to speculate about the relative strengths of the various types of hydrogen bonds possible in hydrotrioxides of benzylic ethers and alcohols, it seems reasonable to predict that the strength of the intramolecular hydrogen bonding in the chelated form is considerably smaller compared to the total binding energy in dimeric entities. However, it should be pointed out that the concentration of the chelated form in solutions of these hydrotrioxides need not be small. Specifically, the formation of the cyclic dimer requires a greater number of bonds in a suitable conformation (larger decrease of entropy) than that for the intramolecularly hydrogen-bonded monomer, thus reducing the probability of its formation. It is interesting to mention that the calculated binding energy in the cyclic dimer of CH_3O_3H (dimers arranged with the oxygen atom next to carbon acting as a proton acceptor) is more negative by 3.2 kcal/mol (4-31G/4-31G, complete geometry optimization) compared to the corresponding value for the cyclic dimeric CH_3O_2H. (Koller, J.; Hodošček, M.; Plesničar, B., to be submitted.) It has already been suggested that dimeric cyclization is the most characteristic feature of the association of alkyl hydroperoxides (RO_2H).[11]

(15) If the exchange of participating molecules in these dimers were slow on the NMR time scale (strong intermolecular hydrogen bonds), mixtures of enantiomeric hydrotrioxides would in principle show two OOOH absorptions, with the position of both signals independent of the enantiomeric ratio and their relative intensities equal to the ratio of the diastereoisomeric dimers.[13b] For a discussion of chemical shifts under fast interassociate exchange conditions, see ref 13.

(16) Of the mechanisms previously proposed for the formation of hydrotrioxides, i.e., a hydride abstraction and the concerted insertion of the ozone into a C–H bond in saturated compounds, we prefer the former mechanistic possibility.[4b,17] We found that, at least in the solvents investigated, the benzylic alcohol **3** reacted much faster than benzylic ethers **1** and **2** to form the corresponding hydrotrioxides. The hydrogen-bonded carbocation



$$\left[\mathrm{Ph}-\overset{\overset{\delta-\ \ \delta+}{\mathrm{O-H\cdots B}}}{\underset{\mathrm{CH_3}}{\mathrm{C}^{+}}}\ {}^{-}\mathrm{OOOH}\right]$$

is presumably better stabilized compared to the carbocation formed from the benzylic ethers. This mechanism implies the possibility of racemization or inversion of enantiomeric substrates.

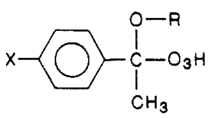
(17) (a) Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105. (b) See also: Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1983; Chapter 2.

(18) It has already been pointed out that the hydrogen bonding of a strong acceptor base to a hydroxy group increases the ability of that hydroxyl to participate in intramolecular hydrogen bonding.[19]

(19) Lemieux, R. U.; Pavia, A. A. *Can. J. Chem.* **1969**, *47*, 4441. Christofides, J. C.; Davies, D. B.; Martin, J. A.; Rathbone, E. B. *J. Am. Chem. Soc.* **1986**, *108*, 5738.

(20) Assuming that the intramolecular hydrogen bonding persists in all solvents investigated, faster interconversion between "favored" and "disfavored" forms in Freon 11/12 than in diethyl ether is indicated. The complexation of the chelated six-membered hydrotrioxide ring with the oxygen base (carbonyl oxygen bases and presumably the parent ethers and alcohols as well) may cause the disfavored form to become favored (and vice versa); at the same time, the interconversion of the two structures appears to be slowed down relative to Freon 11/12 and diethyl ether.

Table II. Kinetic and Activation Parameters for the Decomposition of Hydrotrioxides[a]



	R	X	solvent	temp,[b] °C	$10^2 k_1$,[c] s^{-1}	E_a, kcal/mol	log A
4a	CH_3	H	$(CH_3)_2CO$	−10	24.7	19.9	16.0
				−15	11.5		
				−15	(9.57)[d]	(20.6)[d]	(16.4)[d]
				−20	5.31		
				−25	2.52		
				−30	1.04		
				−30	(0.80)[d]		
4b	CH_3	CH_3		−10	12.9	17.6	13.8
				−15	6.19		
				−20	3.58		
				−25	1.67		
				−30	0.79		
4f	CH_3	Br		−20	15.8	20.4	16.8
				−25	7.07		
				−30	2.96		
4a	CH_3	H	$CH_3CO_2C_2H_5$	−15	9.01	18.0	14.2
				−15	(8.90)[d]	(19.3)[d]	(15.3)[d]
				−20	4.44		
				−25	2.17		
				−25	(1.95)[d]		
4b	CH_3	CH_3		−15	6.39	15.3	11.8
				−20	3.12		
				−25	1.72		
				−30	1.01		
4d	CH_3	F		−20	3.80		
				−25	1.88		
4f	CH_3	Br		−10	14.4	14.8	11.5
				−15	8.47		
				−20	4.69		
4a	CH_3	H	Freon 11/12	−20	1.86		
				−25	1.04		
			$(C_2H_5)_2O$	−35	10.9	15.1	12.9
				−35	(11.0)[d]	(15.5)[d]	(13.3)[d]
				−40	5.10		
				−45	2.67		
				−45	(2.60)		
4b	CH_3	CH_3		−35	11.9	18.8	16.4
				−40	4.76		
				−45	1.83		
				−50	0.67		
4c	CH_3	OCH_3		−30	14.0	16.0	13.7
				−35	5.14		
				−40	3.85		
				−45	1.64		
4d	CH_3	F		−35	7.83	15.5	13.2
				−40	3.42		
				−45	1.85		
4e	CH_3	Cl		−40	12.0	16.8	14.8
				−45	4.08		
				−50	2.34		
				−55	0.91		
4f	CH_3	Br		−35	23.0	16.9	14.7
				−40	10.3		
				−50	1.17		
				−55	0.39		
5a	C_2H_5	H		−25	5.26	15.4	12.3
				−30	2.63		
				−35	1.39		
				−40	0.70		
5b	C_2H_5	CH_3		−30	2.87	14.6	11.6
				−35	1.42		
				−40	0.78		
5e	C_2H_5	Cl		−35	5.58	19.2	16.4
				−40	2.13		
				−45	0.86		
				−50	0.33		
5f	C_2H_5	Br		−35	4.04	17.6	14.8
				−40	1.51		
				−45	0.69		
				−50	0.27		
6a	H	H	$(CH_3)_2CO$	−15	11.3	16.9	13.4
				−20	4.76		
				−25	2.63		
				−30	1.20		
				−35	0.66		
			$CH_3CO_2C_2H_5$	−15	14.5	17.0	13.6
				−20	6.75		
				−25	3.68		
				−30	1.91		
				−35	0.87		
				−40	0.41		
			$(C_2H_5)_2O$	−20	5.43	16.8	13.3
				−25	2.76		
				−30	1.42		

[a] 0.1–0.3 M. [b] Temperature range was dictated by both solubility problems and fast decomposition of hydrotrioxides. [c] Average values of at least three runs. Standard deviations ±9%. [d] Runs in the presence of 2,4,6-tri-*tert*-butylphenol (TBP) (molar ratio, TBP:hydrotrioxide = (2–3):1).

Hydrogen bonds, once formed in these species, appear to be relatively strong.[21]

Decomposition. All of the hydrotrioxides investigated decompose in the temperature range −40 to −10 °C to produce among other products singlet oxygen, Δ^1O_2, as determined by typical singlet oxygen acceptors.

A study of the decomposition products of **4a** in acetone or ethyl acetate (~0.15 M) (ozonation by an ozone–nitrogen mixture) by gas–liquid chromatography (GLC) showed acetophenone (50 ± 7% yield/mol of absorbed ozone), methanol (14 ± 2%), methyl benzoate (20 ± 3%), benzoic acid (5 ± 1%), hydrogen peroxide, and singlet oxygen (45 ± 7%, 1,3-diphenylisobenzofuran; 22 ± 3%, tetraphenylcyclopentadienone). Acetophenone (65 ± 9%), water, benzoic acid, (5 ± 1%), hydrogen peroxide, and singlet oxygen (60 ± 9%, 1,3-diphenylisobenzofuran; 25 ± 4%, tetraphenylcyclopentadienone) were found to be the major products in the decomposition of **6a** in both solvents.

Small amounts of a metastable, as yet not completely identified hydroperoxide (δ_{OOH} 8.8 ± 0.3, acetone, −5 °C) were detected at higher temperatures in the decomposition mixture of **4a**. This peroxide was definitely not α-methyl-α-methoxybenzyl hydroperoxide. This hydroperoxide, which was previously believed to be too unstable for isolation, was obtained pure (>99%) by the displacement method from acetophenone dimethyl ketal and 100% H_2O_2 in diethyl ether.[22] Since it appears that the same hydroperoxide was also formed in small amounts during the decomposition of **6a**, we believe this peroxide might be α-hydroxy-α-methylbenzyl hydroperoxide. All attempts to prepare this compound by independent routes failed.

The kinetics of decomposition of hydrotrioxides was measured by following the decay of OOOH absorptions and was found to obey first-order kinetics over 1–2 half-lives in all solvents investigated except Freon 11/12, where the disappearance of **4a** was roughly first-order only over a narrow temperature range (−25 to −10 °C). Besides the decomposition products already men-

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[21] It is interesting to mention in this connection that the exchange of the hydrogen atom (RO_3H) for deuterium (treatment of **4a** in ethyl acetate or acetone-d_6 with CH_3OD) was very slow under the conditions investigated (<−55 °C).

[22] α-Methyl-α-methoxybenzyl hydroperoxide (**7**) was found to be stable in solutions of **4a** in ethyl acetate or acetone at temperatures below −50 °C. However, when this hydroperoxide was added to **4a** at temperatures above −35 °C, it decomposed rather quickly. A vigorous evolution of gas (presumably oxygen) was observed even when **7** was added to the decomposition mixture of **4a** at 10 °C, thus confirming the presence of another peroxidic species in the system.

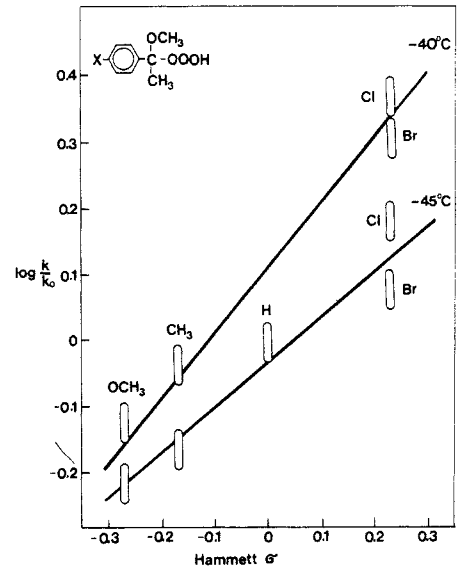


Figure 5. Correlation of logarithms of first-order rate constants for the decomposition of **4a** in diethyl ether vs the Hammett σ constants.

tioned, small amounts of an unidentified polymerized material were also found among the decomposition products in this solvent.

The kinetic and activation parameters for the decomposition of the hydrotrioxides under investigation in various solvents are collected in Table II.[23,24] In the case of the decomposition of **4a** in ethyl acetate and acetone, the disappearance of each of the two OOOH absorptions was followed separately, and it was found that both absorptions disappeared with approximately the same rate.

Comparable rate constants were obtained for the decomposition of the hydrotrioxides in all solvents investigated, except for **4a–f** in diethyl ether, where a somewhat faster decomposition, cleanly of first-order kinetics, was observed. Although we do not know the origin of this phenomenon at present, we believe that it is due to a particular structural feature of these hydrotrioxides (solvation) in diethyl ether (see discussion above) and not to induced decomposition of **4** in this solvent.[25] It is interesting to note that α-methyl-α-methoxybenzyl hydroperoxide is particularly stable in diethyl ether. Notice also that the rate of the decomposition of **6a** in diethyl ether is comparable to that in other solvents. At the same time, a study of the decomposition of **4a** in ethyl acetate, acetone, or diethyl ether in the presence of 2,4,6-tri-*tert*-butylphenol or 2,6-di-*tert*-butyl-4-methylphenol as inhibitors showed only a relatively small reduction in the rates together with slightly increased activation energies of decomposition. The effect of radical inhibitors appears, thus, to be less dramatic than that found for the decomposition of cumyl hydrotrioxide.[4c]

Activation parameters reported in Table II are comparable with those reported for structurally similar acetal hydrotrioxides.

Electron-withdrawing groups in **4** and **5** accelerate decomposition, while electron-donating groups retard it. The only exceptions are fluoro-substituted hydrotrioxides **4d** and **5d**, which decomposed somewhat slower than unsubstituted derivatives **4a** and **5a**. Since only a limited number of substituted derivatives could be studied in some solvents, only rough estimates of the Hammett ρ values were possible. A plot of the rates of decomposition of substituted derivatives of **4** in ethyl acetate vs σ values gave ρ = 0.7 ± 0.1. In diethyl ether (see Figure 5) and acetone, the ρ are 1.0 ± 0.2 and 1.4 ± 0.2, respectively. A comparable value of ρ = 1.2 ± 0.2 was obtained for the decomposition of hydrotrioxides of substituted benzaldehyde dimethyl acetals in diethyl ether.[1a]

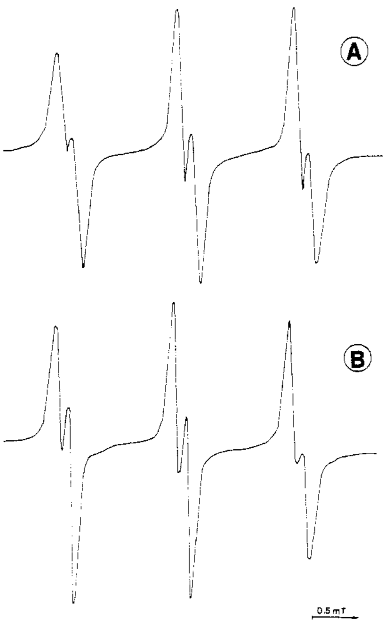
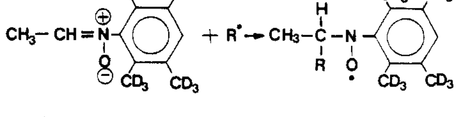


Figure 6. ESR spectra resulting from (A) mixing a degassed sample of **4a** with MDN in ethyl acetate in the dark at −58 °C and (B) the induced decomposition of hydroperoxide **7** in the presence of di-*tert*-butyl diperoxyoxalate (**8**) and MDN in ethyl acetate (<−25 °C), recorded at −58 °C.

ESR Spin Trapping. It has already been suggested that the induced decomposition of hydrotrioxides to produce alkyltrioxyl radicals (ROOO•) might be an important decomposition pathway in this class of polyoxides.[1a,4c] Since we were not able to observe by direct ESR any radical during the decomposition of **4a**,[26] the ESR spectroscopic technique of spin trapping, i.e., addition of a transient radical, R•, to a spin trap, T, to form a persistent spin adduct, RT•, has been used.[27] In an attempt to confirm the involvement of trioxyl radicals in the decomposition of hydrotrioxides, we have studied the decomposition of **4a** in ethyl acetate in the presence of methyl-*N*-durylnitrone (MDN). This nitrone has recently been shown to be a better spin trap than phenyl-*N*-(*tert*-butyl)nitrone (PBN) to distinguish peroxyl radical from alkoxyl radical.[28]



Mixing a degassed sample of **4a** (150–200 mM) with MDN in ethyl acetate (**4a**:MDN = (20–30):1) at −70 °C as nearly in the dark as practical produced an ESR spectrum that showed no proton hyperfine splitting (A_N = 1.180 mT) until about −60 °C,

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(23) According to the statistical procedures for the analysis of kinetic data elaborated by Exner,[24] the decomposition of **5** is evidently isokinetic with the isokinetic temperature β = 208 K (−65 °C) (experimental error, s_{00} = 0.020; ψ test = 0.066; isokinetic standard deviation, s_0 = 0.018). The remaining two series, i.e., decompositions of **4** in all solvents (series b) and decompositions of **4** in diethyl ether (series c), are not isokinetic. Considering the relatively large errors in E_a, the hypothesis that these two series are isoenthalpic appears most likely. The analysis of kinetic data for the decomposition of acetal hydrotrioxides, for which measurements at three temperatures are available[1a] (**3a**, **3b**, **3c**, **3f**, and **3g**), shows that this series is also isoenthalpic (s_{00} = 0.037, s_0 = 0.045, s_∞(isenthalpic) = 0.043), but in fact there are negligible differences between the individual reactions (ψ = 0.40). Thus, it seems safe to conclude that the decomposition of all these hydrotrioxides is dominated by entropy factors (kinetic steric effects and/or solvent effects, affecting simultaneously the geometry of the transition state and the force constants).

(24) Exner, O. In *Progress in Physical Organic Chemistry*; Streitwieser, A., Jr., Taft, R. W., Eds.; Wiley: New York, 1973; Vol. 10, p 411.

(25) It is interesting to mention that decomposition of **4** and **5** proceeds much faster and with lower activation energies in the presence of DMAA.

(26) Pryor et al. reported the ESR spectrum of the peroxyl radical formed in the low-temperature reaction of ozone with cumene.[4b]

(27) For reviews, see: Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31. Janzen, E. G. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic: New York, 1980; Vol. IV, Chapter 4, Perkins, M. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 1.

(28) (a) Niki, E.; Yokoi, S.; Tsuchiya, J.; Kamiya, Y. *J. Am. Chem. Soc.* **1983**, *103*, 1498. (b) Konaka, R.; Terabe, S.; Mizuta, T.; Sakata, S. *Can. J. Chem.* **1982**, *60*, 1532.

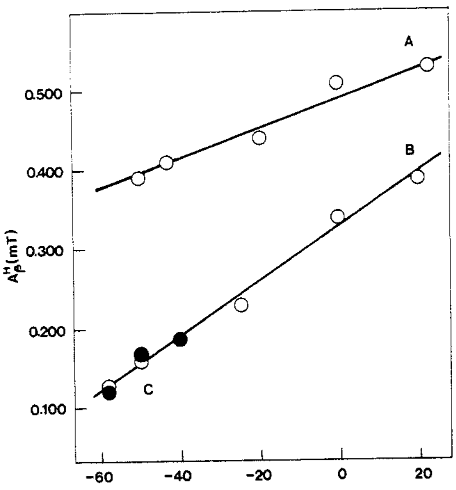
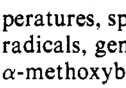


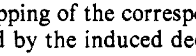
Figure 7. Temperature dependence of hydrogen splitting constants, A_β^H, of spin adducts generated (A) by a short UV irradiation of dialkyl peroxide **9** in the presence of MDN in ethyl acetate, (B) by the induced decomposition of hydroperoxide **7** in the presence of di-*tert*-butyl diperoxyoxalate (**8**) and MDN in ethyl acetate, and (C) by mixing a degassed sample of **4a** with MDN in ethyl acetate in the dark.

when it resolved into a triplet of doublets (−58 °C, A_N = 1.180 mT, A_β^H = 0.118 mT) (Figure 6). As the temperature was raised above −58 °C, the signal grew and a second triplet of singlets (A_N = 0.710 mT) appeared. At ca. −35 °C, the original triplet of doublets began to disappear rapidly and only a triplet of relatively broad singlets remained. The hyperfine splitting constant of the latter signal, which was apparently broadened by the appearance of oxygen in the solution from decomposition of the hydrotrioxide, is consistent with acetyl-*N*-duryl nitroxide.[28] A short UV irradiation (200-W lamp, through quartz) of a sample of **4a** in the presence of MDN resulted in a rather fast appearance of a triplet of doublets (A_N = 1.185 mT, A_β^H = 0.120 mT), together with the ESR signal characteristic for acetyl-*N*-duryl nitroxide.

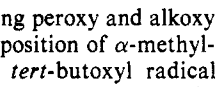
In order to identify the unstable nitroxide formed at low temperatures, spin trapping of the corresponding peroxy and alkoxy radicals, generated by the induced decomposition of α-methyl-α-methoxybenzyl hydroperoxide (**7**) by *tert*-butoxyl radical (produced by decomposition of di-*tert*-butyl diperoxyoxalate (**8**)) and by photolysis of α,α′-dimethyl-α,α′-dimethoxybenzyl peroxide (**9**), respectively, was also studied. The hyperfine splitting constants for the radical spin adduct (−58 °C, A_N = 1.185 mT, A_β^H = 0.120 MT; 20 °C, A_N = 1.200 mT, A_β^H = 0.390 mT), produced by the induced decomposition of hydroperoxide **7** in the presence of di-*tert*-butyl diperoxyoxalate (**8**) and MDN (molar ratio, **7**:**8**:MDN = 50:10:1, 200 mM (**7**)), are similar to those of the *tert*-butylperoxyl spin adduct (20 °C, benzene, A_N = 1.280 mT, A_β^H = 0.461 mT)[28,29] and are, thus, tentatively assigned to the methyl α-methoxybenzylperoxy spin adduct (see Figure 6). Somewhat lower values are expected for an α-alkoxy-substituted peroxy spin adduct; i.e., an electron-withdrawing group and nonpolar solvents favor a nonpolar resonance structure of nitroxides. A pronounced temperature dependence of the hydrogen hyperfine splitting constant indicates a considerable hindered rotation about the C–N bond with different conformations of this radical spin adduct having different energies (Figure 7).[30]


$\text{Ph}-\overset{\text{OCH}_3}{\overset{|}{\underset{\underset{\text{CH}_3}{|}}{\text{C}}}}-\text{OOH}$

7


$\text{t-BuOO}\overset{\text{O}}{\overset{\|}{\text{C}}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{OOBu-t}$

8

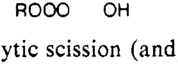

$\text{Ph}-\overset{\text{OCH}_3}{\overset{|}{\underset{\underset{\text{CH}_3}{|}}{\text{C}}}}-\text{O}-\text{O}-\overset{\text{OCH}_3}{\overset{|}{\underset{\underset{\text{CH}_3}{|}}{\text{C}}}}-\text{Ph}$

9

As the temperature was raised, a simple triplet of singlets (A_N = 0.715 mT) began to appear in the ESR spectrum at ca. 0 °C, indicating decomposition of the peroxyl spin adduct to produce acetyl-*N*-duryl nitroxide.[28] Thus, the α-methyl-α-methoxybenzylperoxy spin adduct is, as expected, somewhat less persistent than the *tert*-butylperoxy spin adduct.[28,32] The same observations were also made by generating the peroxy spin adduct by UV irradiation of **7** in the presence of MDN (ethyl acetate, −60 °C).

A short UV irradiation of dialkyl peroxide **9** (200 mM) in the presence of MDN (molar ratio, **9**:MDN = 20:1) in ethyl acetate at −50 °C produced a triplet of doublets (−50 °C, A_N = 1.210 mT, A_β^H = 0.395 mT; 20 °C, A_N = 1.220 mT, A_β^H = 0.505 mT), which was assigned to the corresponding alkoxy spin adduct. The ESR characteristics of this rather persistent radical (2 h at 20 °C), are similar to those of the *tert*-butoxyl spin adduct (20 °C, benzene, A_N = 1.410 mT, A_β^H = 0.747 mT).[28a] The temperature dependence of A_β^H for this spin adduct is shown in Figure 7.

On the basis of the above-mentioned results, we can conclude that the nitroxide obtained by mixing hydrotrioxide **4a** with MDN in ethyl acetate at low temperatures is most likely the corresponding peroxy spin adduct. However, the mechanism of its formation is not clear at present. The temperature at which it is formed is well below that of the decomposition of hydrotrioxide **4a** in the solvent investigated. At the same time, virtually no hydroperoxide **7** could be detected by NMR spectroscopy in a sample of **4a** at −60 °C. Thus, it appears that the spin trap induces decomposition of the hydrotrioxide to produce peroxy radicals by either reacting with **4a** to produce trioxidic hydroxylamine with subsequent homolytic scission (and/or oxidation)[33] of the


$R^1-\underset{\text{ROOO}}{\underset{|}{\text{CH}}}-\underset{\text{OH}}{\underset{|}{\text{N}}}-R^2$

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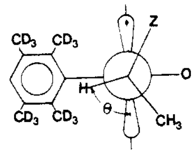
(29) Meritt, M. V.; Johnson, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 3713. Howard, J. A.; Tait, J. C. *Can. J. Chem.* **1978**, *56*, 176. Janzen, E. G.; Nutter, D. E., Jr.; Davis, E. R.; Blackburn, B. J. *Can. J. Chem.* **1978**, *56*, 2237. Zubarev, V. E.; Belevskii, V. N.; Yarkov, S. P. *Dokl. Akad. Nauk SSSR* **1979**, *244*, 1392.

(30) The adduct molecules exert a fast reorientation in the solvent. Besides this motion, the intramolecular reorientation by which the isotropic hyperfine splitting of the proton is influenced was described by three potential minima of the equilibrium conformations. Due to the asymmetric groups attached to the β carbon, a shape of the potential barrier was proposed where one of the three conformations is more probable than the rest. The fast relative reorientation of the nitroxide group with respect to the C–H of the β carbon pertains to the distribution of the conformations with respect to their potential minima differences.[31] From the experimental values for A_β^H, their temperature dependencies $\partial A_\beta^H/\partial T$, and the above assumptions of this model, the average differences ΔE and the average angle of the most stable conformation, θ, were evaluated for RO• and ROO• adducts. By fitting the experimental values with different values of the parameters B_0 and B_1 of the equation

$$A_\beta^H = B_0 + B_1 \cos^2 \theta$$

and with respect to the limiting conditions of θ and the data from other work, one obtains two sets of values for the RO• and ROO• adducts. Assuming the same values of B_0 and B_1 for both adducts, i.e., B_0 = 0 and B_1 = 7.0 mT, ΔE = 2.1 and 1.8 kcal/mol and θ = 78° and 89° for the RO• and ROO• spin adducts, respectively. On the other hand, if the minimal value for ΔE is searched, then for the RO• adduct ΔE = 1.0 kcal/mol and θ = 82° (B_0 = 0 mT, B_1 = 2.0 mT). For the ROO• adduct ΔE = 1.8 kcal/mol and θ = 89° (B_0 = 0 mT, B_1 = 7.0 mT).

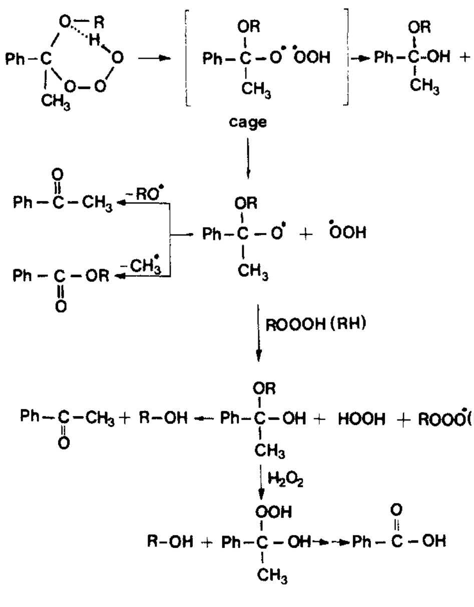


Z = RO , ROO

(31) Stone, E. W.; Maki, A. H. *J. Chem. Phys.* **1962**, *37*, 1326.

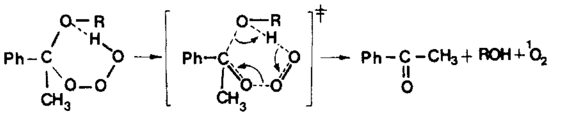
(32) Mixing a degassed sample of **4a** with phenyl-*N*-(*tert*-butyl)nitrone (PBN) in ethyl acetate at −60 °C produced an ESR signal, a triplet of doublets (−50 °C, A_N = 1.290 mT, A_β^H = 0.115 mT), which was tentatively assigned to the corresponding peroxy spin adduct. At higher temperatures (above −20 °C), this signal changed to the one characteristic of the alkoxy spin adduct (20 °C, A_N = 1.325 mT, A_β^H = 0.200 mT; −50 °C, A_N = 1.320 mT, A_β^H = 0.155 mT). In addition, a weak signal of benzoyl *tert*-butyl nitroxide, having A_N = 0.785 mT, could also be seen in the spectrum.[28a] The alkoxy spin adduct with the same ESR characteristics was observed by just mixing hydroperoxide **7** with PBN or by photolyzing peroxide **9** in the presence of PBN in ethyl acetate at low temperatures. The decomposition of **8** in the presence of **7** and PBN always resulted in the formation of the alkoxy spin adduct. Similar results were obtained in acetone as solvent.

Scheme IV



latter[28a] or interacts with the hydrotrioxide in a nonspecific manner, for example, $(ROOOH)_xT_y$, where x and y could be 1, 2, or 3.

Mechanisms for the Decomposition of the Hydrotrioxides. Basically two mechanisms can be envisaged for the decomposition of hydrotrioxides capable, at least theoretically, of existing in the chelated intramolecularly hydrogen-bonded form. Relatively low log A values for the decomposition of the hydrotrioxides of benzaldehyde, 2-methyltetrahydrofuran, and methyl isopropyl ether, as well as the formation of singlet oxygen, led Murray et al.[4a] to propose the following nonradical mechanism:



It is known from other studies, i.e., pyrolysis of halides, esters, and cyclobutanes for example,[34] that an intramolecular six-membered transition state of this type can participate of both heterolytic and homolytic character. When heterolysis predominates, one can describe such a process as pericyclic, since it implies the simultaneous breaking and formation of the bonds involved in the reaction. By knowing that the split into RO• and •OOH is the lowest energy and the fastest radical path available,[35] homolytic decomposition of such hydrotrioxides may be represented as shown in Scheme IV.

A production of a cage radical pair has already been proposed by Benson et al. for the decomposition of hydroxymethyl and acetal hydrotrioxides.[17a] The radicals formed in the cage can either diffuse out of the cage or undergo cage disproportionation to form the tetrahedral intermediates and singlet oxygen. The escaped radicals can either cleave exothermically to form, as in our case, acetophenone or methyl benzoate or abstract hydrogen from the hydrotrioxide or from another hydrogen atom donor. It is interesting to note that the abstraction of hydrogen from the hydrotrioxide produces, as already mentioned above (spin-trapping experiments), trioxyl radicals, which can also be a source of singlet oxygen:

$$ROOO^• \rightarrow RO^• + O_2\ (^1O_2 \text{ and/or } ^3O_2)$$

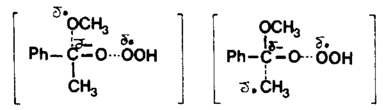
$$2ROOO^• \rightarrow 2ROO^• + O_2\ (^1O_2 \text{ and/or } ^3O_2)$$

The tetrahedral intermediate can react with hydrogen peroxide, a relatively strong nucleophile, to form the corresponding α-hydroxy hydroperoxide, which is most probably the source of benzoic acid in the decomposition of **4a** and **6a**.

Although the mechanism proposed by Murray et al. ("pericyclic mechanism") can accommodate acetophenone, methanol, and singlet oxygen, it does not account for the other products formed in the decomposition of the hydrotrioxides. All these products thus strongly indicate the involvement of homolytic pathways in these decompositions.

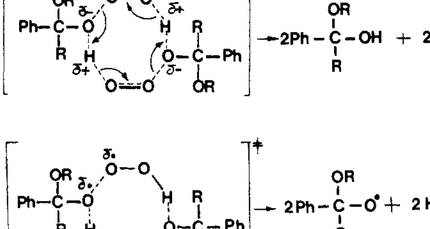
Solvent effects on the decomposition are relatively small; i.e., the relative rates of decomposition are all within a factor of 5 (15 by taking into account the decomposition of **4a** in diethyl ether). On the other hand, the rate constants for decomposition are fairly sensitive to the nature of the substituent in the para position of the phenyl ring. A transition state for decomposition containing a certain degree of polar character with some buildup of negative charge on the carbon atom next to the benzene ring (positive Hammett ρ values) is thus indicated.

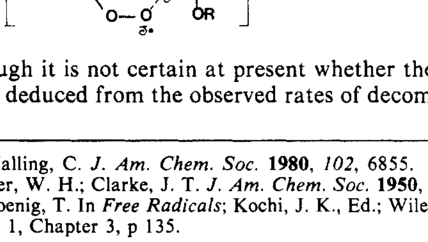
The explanation that the observed substituent effect is due to the variation of the ground-state stabilities of the hydrotrioxides seems unlikely, since it is known from other studies that increased electron density on the oxygen atoms weakens O–O bonds.[36] Unfortunately, at present one can only speculate about the possibility of the involvement of decomposition pathways with transition states in which a more or less concerted homolytic scission of two bonds takes place



or, at least, that the alkoxy radical experiences very significant perturbations of its remaining bonds.[37]

A relatively small effect of the added radical inhibitor 2,4,6-tri-*tert*-butylphenol (similar results were also observed by using 2,6-di-*tert*-butyl-4-methylphenol), i.e., somewhat reduced rates of decomposition and increased activation energies, may be attributed to the fact that the decomposition proceeds predominantly according to the "pericyclic mechanism" or involves a homolytic scission of the hydrotrioxides with subsequent cage disproportionation of the radical pair, as suggested by Benson.[17a] It should be pointed out that both mechanistic possibilities are also available for the decomposition of the dimeric hydrotrioxide entities, as shown in the following:





Although it is not certain at present whether the E_a and log A values deduced from the observed rates of decomposition are

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[33] Our preliminary results show that hydrotrioxides **4–6** (as well as acetal hydrotrioxides[1a]) oxidize sulfides to sulfoxides/sulfones and some electron-rich olefins (2,3-dimethyl-2-butene) to epoxides (the latter in low yields) in the presence of DABCO, a quencher of $^1O_2$, at low temperatures. Although we do not know for certain at present whether these species react as "electrophilic" or "nucleophilic" oxidants, the Mulliken population analysis unambiguously shows that the middle oxygen atom might be the "electrophilic" center in hydrotrioxides.[1b] Further studies on this aspect of the chemistry of hydrotrioxides are in progress.

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for one reaction pathway or represent the activation parameters for the decomposition which is proceeding by several simultaneous first-order processes, we nevertheless believe that homolysis plays an important role in the decomposition of hydrotrioxides under investigation. That is, the activation parameters are in good agreement with those reported for the decomposition of di-*tert*-butyl trioxide ($E_a = 23 \pm 3$ kcal/mol, $\log A = 17 \pm 1.5$, methylene chloride).[38]

As already pointed out above, the high reactivity of the O–H bonds of hydrotrioxides can be anticipated in analogy with hydroperoxides. We believe that this reactivity is reduced considerably due to the engagement of the O–H bonds in the hydrotrioxides in relatively strong hydrogen bonds; such hydrogen atoms become, as already reported, much less available for external reagents.[39] However, radicals derived from benzylic ethers and alcohols remaining after the ozonizing procedure may attack the hydrotrioxide (most likely the "electrophilic" middle oxygen atom) in an S_H2 type of reaction, thus causing chain decomposition. Due to the difficulties encountered in the attempt to detect hydroperoxide **7**, which should be formed in such reactions, we cannot rule out the possibility of the involvement of such a chain process in the decomposition of the hydrotrioxides.[40]

Experimental Section

Low-temperature ^1H NMR spectra were recorded with JEOL FX 100 and JEOL JNM C60HL spectrometers, and both ^1H and ^{13}C NMR spectra were recorded with a JEOL PS 100 spectrometer equipped with a JEOL variable-temperature probe. UV and visible spectra were obtained on a Perkin-Elmer Hitachi 200 spectrometer.

Materials. All solvents were the purest commercially available products (99.9%, except for acetone-d_6) and were dried and distilled before use. Alkyl α-methylbenzyl ethers **1a**, **1d**, **1e**, **1f**, **2a**, **2b**, **2e**, and **2f** were synthesized by $LiAlH_4$–$AlCl_3$ reduction of the appropriate ketals[41] according to the literature procedure.[42] Ethers **1b** and **1c** were synthesized by alkylation of the corresponding α-methylbenzyl alcohols with a methyl iodide–silver oxide mixture. α-Methylbenzyl alcohols were synthesized by $LiAlH_4$ reduction of the appropriate acetophenone.[43] Optically active methyl α-methylbenzyl ethers (**1a**) and α-methylbenzyl alcohols (**3a**) were prepared by literature procedures.[44,45] Optical purities of the enantiomers (~90% in all cases) were determined with the chiral shift reagent tris[3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III). All compounds used were checked by GLC, NMR, and elemental analysis and were found to be >99% pure. 2,4,6-Tri-*tert*-butylphenol and 2,6-di-*tert*-butyl-4-methylphenol were recrystallized from ethanol before use. The spin trap MDN was kindly provided by Dr. Konaka at Schionogi Research Laboratories. PBN was used as received from Aldrich. Di-*tert*-butyl diperoxyoxalate (**8**) was synthesized by the literature procedure.[46] Anhydrous hydrogen peroxide in diethyl ether was obtained by the method of Rieche et al.[47]

α-Methyl-α-methoxybenzyl Hydroperoxide (7). A solution of 16.6 g of acetophenone dimethyl ketal (100 mmol) and 3.6 g of anhydrous hydrogen peroxide (106 mmol) in 20 mL of diethyl ether was refluxed for 4 h. After cooling, 50 mL of diethyl ether was added. The organic layer was washed with a saturated solution of $(NH_4)_2SO_4$ (3 × 40 mL) and dried over $MgSO_4$. After removal of the solvent under vacuum, the crude hydroperoxide was purified by column chromatography (0–10 °C, silica gel 0.063–0.200 mm, *n*-hexane:chloroform:methanol = 10:10:1). After removal of the mobile phase under vacuum (<40 °C), the hydroperoxide was recrystallized from *n*-hexane: yield, 5.4 g (32%); mp 63–65 °C; ^1H NMR ($CDCl_3$, δ values in parts per million downfield from Me_4Si) δ 1.65 (s, 3 H, CCH_3), 3.42 (s, 3 H, OCH_3), 7.48 (s, 5 H, C_6H_5), 8.05 (s, 1 H, OOH). Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 63.98; H, 6.91. Iodometric titrations of samples of the hydroperoxide showed a peroxide content of >99%.

α,α′-Dimethyl-α,α′-dimethoxybenzyl Peroxide (9). A solution of 4.1 g of acetophenone dimethyl ketal (25 mmol), 4.2 g of **7** (25 mmol), and catalytic amounts of methanesulfonic acid was refluxed for 5 h. Removal of all the volatile components under vacuum (50 °C, 0.13 mbar) and recrystallization of the crude product from *n*-hexane yielded 3.5 g of **9** (47%): mp 110–112 °C; ^1H NMR ($CDCl_3$) δ 1.44, 1.54 (ds, 3 H, CCH_3), 3.05, 3.12 (ds, 3 H, OCH_3), 7.12 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 25.6, 26.4, 49.9, 50.1, 105.6, 105.8, 126.1, 126.2, 127.8, 128.0, 128.2, 141.0, 141.2. Anal. Calcd for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.20; H, 7.19.

Attempts to prepare α-hydroxy-α-methylbenzyl hydroperoxide by photochemical autoxidation of **3a** according to the procedure described by Schenk et al.[48] for the preparation of the aliphatic analogues failed.

Ozonation Procedure. Ozone–oxygen mixtures delivered at a rate of 0.1–0.3 mmol of ozone min^{-1} were produced by flowing oxygen through a Welsbach T-816 ozonator. Ozone–nitrogen mixtures were obtained by adsorption of ozone onto silica gel at −78 °C and subsequent desorption in a stream of nitrogen at higher temperatures.[49] The concentration of ozone in the gas streams was measured according to the literature procedure.[49] Ozonations were carried out in the dark (<−70 °C) to about 50–70% of the theoretical requirement of the substrate.

Product Analysis. Decomposition products of **4a** and **6a** were determined by a combination of techniques. All products, except the unidentified hydroperoxide and hydrogen peroxide, were determined by GLC (Carbowax on Chromosorb W-HP (20%), 10% OV101 on Chromosorb W-HP 80/100, 15% OV17 on Chromosorb W-HP 60, Chromosorb 102 80/100, and Porapak Q columns), using calibrated internal standards and known reference materials. All products were collected and identified by NMR and mass spectra. The ^1H and ^{13}C NMR spectra of the ozonation mixture and the standard samples were recorded at −60 °C. Hydrogen peroxide was determined by TLC (Merck Kieselgel F_{254}, chloroform:*n*-hexane:methanol = 10:10:1). Singlet oxygen determinations were performed as already described previously.[1a]

ESR Spin Trapping. ESR spectra were recorded on a Varian E9 X-band 9.7-GHz spectrometer with a cavity equipped with a quartz Dewar insert for low-temperature work. The Varian temperature controller was used to regulate the temperature in the cavity. The spectra were recorded in the dark or under low levels of light. The temperature stability of the sample was ±0.1 K. Ozone–nitrogen mixtures were used for the ozonation.

Kinetic Studies. Parts of the reaction mixture were transferred to a series of NMR tubes and stored at −198 °C until use. The decay of the OOOH proton signals was followed by integrating the peak area with time at various temperatures, using Me_4Si as an internal standard.[1a,4b] In kinetic runs with an inhibitor, a cold solution of 2,4,6-tri-*tert*-butylphenol (or 2,6-di-*tert*-butyl-4-methylphenol) in the appropriate solvent was added to deozonized solutions of the hydrotrioxide at temperatures below −65 °C.[4b] The temperature stability at the sample was ±0.2 K. The first-order rate constants were obtained from a linear least-squares program.

Acknowledgment. Thanks are expressed to Professor Glen A. Russell for many stimulating discussions and to Professor Otto Exner for suggestions concerning the statistical analysis of kinetic data. Financial support from the Research Community of Slovenia and the Yugoslav–United States Joint Fund for Scientific and Technological Cooperation, in cooperation with the National Science Foundation (Grant NSF-850937-JFP-538), is also gratefully acknowledged. We also thank Dr. Konaka for a generous gift of MDN. Thanks are also extended to M. Nemec for skillful assistance with ESR.

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