Lifetime of Tetrahedral Intermediates. In a recently advanced theory of stereoelectronic control of the hydrolysis of carboxylic acid esters and amides, it is proposed that the nature of the products obtained is governed by the conformation of the tetrahedral intermediate formed during the course of these reactions.[25] This theory requires tetrahedral intermediates to be relatively short lived; specifically in its application to cyclic, e.g., six-membered ring, systems it implies that these intermediates react before chair-chair interconversions can take place.[26] Since these tetrahedral intermediates in the case of ester hydrolysis are in fact the same as the hydrogen ortho esters detected in the present study, the measurements of their lifetimes made here have a direct bearing upon this assumption of the stereoelectronic theory. In particular, the data of Table II show that, under certain conditions, tetrahedral intermediates are relatively stable, with lifetimes approaching one second. Since chair-chair interconversions generally occur in times much shorter than this, this assumption of the stereoelectronic theory cannot be universally correct.

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Supplementary Material Available: Tables S1-S4 of rate constants (7 pages). Ordering information is given on any current masthead page.

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The Substituent Effect on the Thermal Decomposition of Acetal Hydrotrioxides. Polar and Radical Decomposition Paths

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Abstract: Low-temperature ozonation of aliphatic and aromatic acetals leads to oxygen-rich intermediates, acetal hydrotrioxides **1-3**, the NMR spectra of which show two absorptions at δ 13 ppm downfield from Me_4Si. Decomposition of these compounds, which affords among other products singlet oxygen and peroxides, involves nonradical and radical processes. The kinetics of decomposition has been studied by NMR spectroscopy and activation parameters have been determined. Electron-withdrawing substituents in **3** accelerate decomposition in diethyl ether while electron-donating groups retard it (Hammett ρ value 1.2 ± 0.2). Considerable charge separation in the transition state for the decomposition has been proposed.

Introduction

The chemistry of organic polyoxides of the type RO_nR (R = alkyl; n = 3, 4) has been a matter of considerable interest during the past 2 decades.[1] Spectroscopic[1k,n] and theoretical[2] evidence has been given in recent years for their existence. Much less is known about alkyl hydropolyoxides, RO_nH. Alkyl hydrotrioxides have been proposed as unstable intermediates in ozonation of various organic compounds, i.e., ethers,[3] silanes,[4] amines,[5] alcohols,[6] ketones,[6a,8] and aldehydes.[6b,9] It was only recently that Murray et al. reported the first spectroscopic evidence for their existence.[9b]

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Table I. Kinetic and Activation Parameters of the Decomposition of Acetal Hydrotrioxides

hydrotrioxide	solvent	temp, °C[a]	k_1, s^{-1} [b]	E_a, kcal/mol	log A	δ OOOH (Me_4Si) −55 °C
1a		−10	2.7×10^{-2}	20.7	15.6	12.8 13.3
		−20	5.6×10^{-3}			(1:2.5)
	CH_2Cl_2[c]	−10	4.0×10^{-2}			12.7 13.1
	$(C_2H_5)_2O$[c]	−10	2.9×10^{-2}	16.1	11.8	12.8 13.2
		−20	8.5×10^{-3}			(1:2)
1b		−10	1.1×10^{-1}	14.5	11.1	12.8 13.2
		−20	3.7×10^{-2}			(1:1.5)
	$(C_2H_5)_2O$[c]	−10	7.6×10^{-2}	13.2	9.8	12.8 13.2
		−20	2.8×10^{-2}			(1:1)
2a	CH_2Cl_2[c]	−20	6.4×10^{-2}	20.5	16.6	13.20 13.25
		−30	1.2×10^{-2}			(1:1)
	$(C_2H_5)_2O$[c]	−30	6.6×10^{-2}	15.9	13.1	13.10 13.15
		−40	1.6×10^{-2}			
2b	CH_2Cl_2[c]	−20	3.8×10^{-2}	18.7	14.7	13.2
		−30	8.1×10^{-3}			
	$(C_2H_5)_2O$[c]	−40	1.1×10^{-2}			13.4
2c	$(C_2H_5)_2O$[c]	−40	2.7×10^{-2}			13.9
3a	$(C_2H_5)_2O$[c]	−30	7.6×10^{-2}	19.8	16.7	13.00 13.30
		−35	2.8×10^{-2}			(1:2.5)
		−40	1.3×10^{-2}			
3b	$(C_2H_5)_2O$[c]	−30	6.6×10^{-2}	19.0	15.9	13.00 13.30
		−35	2.9×10^{-2}			
		−40	1.2×10^{-2}			
3c	$(C_2H_5)_2O$[c]	−30	6.3×10^{-2}	19.5	16.4	12.85 13.15
		−35	3.1×10^{-2}			(1:3.5)
		−40	1.1×10^{-2}			
3d	$(C_2H_5)_2O$[c]	−35	3.2×10^{-2}	18.4	15.4	12.85 13.15
		−40	1.4×10^{-2}			
3e	$(C_2H_5)_2O$[c]	−25	2.8×10^{-1}	25.1	21.6	12.65 12.95
		−30	9.5×10^{-2}			(1:2)
		−35	3.2×10^{-2}			
3f	$(C_2H_5)_2O$[c]	−25	4.4×10^{-2}	17.2	13.7	12.85 13.10
		−30	2.0×10^{-2}			(1:4)
		−35	1.0×10^{-2}			
3g	$(C_2H_5)_2O$[c]	−20	2.1×10^{-1}	21.4	17.8	13.05 13.25
		−25	8.1×10^{-2}			
		−30	3.1×10^{-2}			
		−35	1.4×10^{-2}			

[a] Temperature range was dictated by both solubility problems and fast decomposition with gas evolution. [b] Standard deviations ±8%. [c] Acetal (20 mmol), 30%, solvent, 70% (by weight). The yield of hydrotrioxides estimated by NMR was 70–85%.

As a part of our continuous interest in polyoxides we report additional experimental evidence for the existence of hydrotrioxides in the low-temperature ozonation of acetals.[10] Deslongchamps et al. have already proposed hydrotrioxides as possible intermediates in analogous reactions.[11]

Results and Discussion

Ozonation of aliphatic and aromatic acetals (ozone–oxygen or ozone–nitrogen mixture) either neat (aliphatic acetals) or in diethyl ether, methylene chloride, and ethyl acetate below −55 °C produces unstable intermediates which upon warming to room temperature decompose vigorously. The low-temperature NMR spectra of these species show two absorptions at δ ca. 13 ppm downfield from Me_4Si. Since their position does not change much with dilution they are tentatively assigned to the OOOH absorptions of the intramolecularly hydrogen bonded six-membered rings of the acetal hydrotrioxides **1–3**[12] (Figure 1).

The decomposition of these intermediates was investigated by following the decay of OOOH absorptions and was found to obey first-order kinetics. The NMR data, along with kinetic and activation parameters for the decomposition, are collected in Table I.

The origin of the two absorptions for the OOOH protons remains uncertain. It is interesting to mention that Murray et al. made a similar observation in the case of 2-methyltetrahydrofuran hydrotrioxide.[9b,13] Both peaks show a tendency to merging and broadening at higher temperatures. A characteristic feature is rather small splitting for **2a** (Figure 2). We assume that this phenomenon might be due either to the presence of two forms of the acyclic acetal hydrotrioxides with OOOH hydrogen bonded to one or the other of available oxygen atoms (nonequivalency of the two acetal oxygens with respect to OOOH group)[14] or the presence of two conformational forms (chair–boat) of the six-membered ring with R groups on the acetal oxygen axial or equatorial. The five-membered ring in **2** is nearly planar thus not allowing appreciable conformational changes.[14b,15]

Activation parameters reported in Table I are in good qualitative agreement with those reported for other trioxides.[1c,9b,16-18] A limited number of solvents suitable for the study of decomposition of compounds under investigation show that the effect of solvent is rather small. Comparable rate constants were obtained by studying decomposition of **1a** in the parent acetal, diethyl ether as well as methylene chloride.

Electron-withdrawing groups in **3** accelerate decomposition while electron-releasing groups retard it. A Hammett plot of the rates of decomposition of substituted derivatives of **3** in diethyl ether vs. σ values gives a fair correlation with $\rho = 1.2 \pm 0.2$ (Figure 3). A similar trend of the substituent effect on decomposition of substituted derivatives of **2** has been ob-

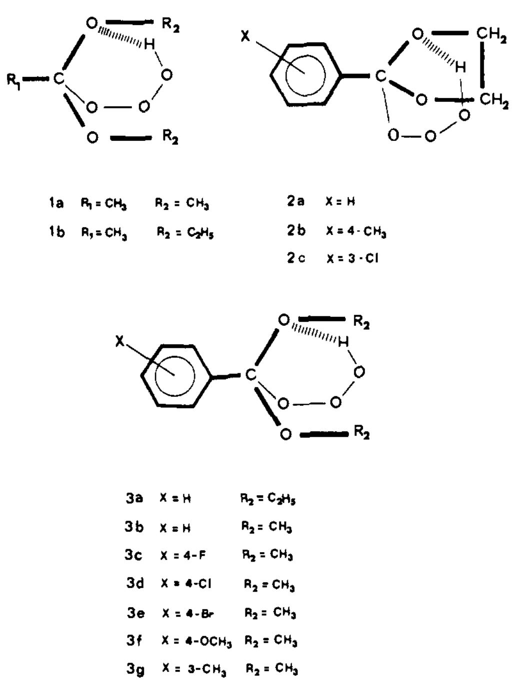


Figure 1. Acetal hydrotrioxides **1-3**.

Table II. Singlet Oxygen Determination[a]

hydrotrioxide	tetraphenylcyclopentadienone, %	1,3-diphenylisobenzofuran, %
1b	20 ± 5[b]	54 ± 5[d]
2a	55 ± 3[c]	85 ± 8[d]
3a		46 ± 5[d]
3d	30 ± 5[c]	55 ± 8[d]

[a] Percent of absorbed ozone available to react with the reagent. [b] Neat or in methylene chloride. [c] Methylene chloride. [d] Ethyl acetate. Ozonation was performed with ozone-oxygen stream.

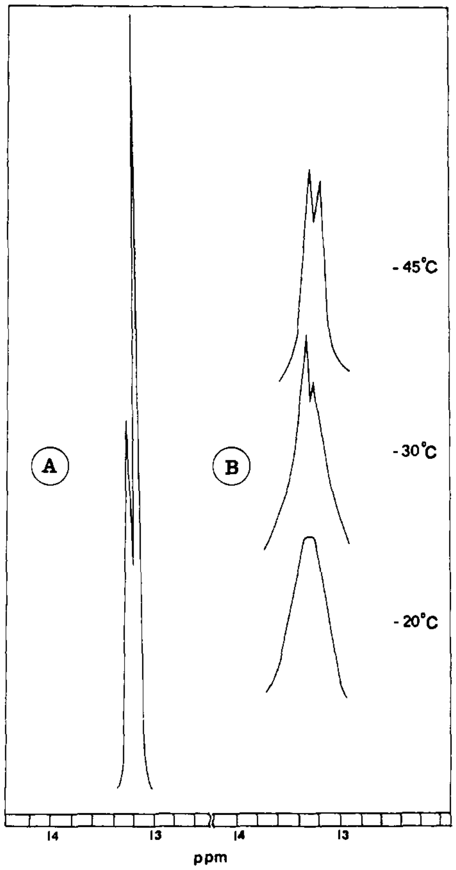


Figure 2. Segments of NMR spectra of **2a**: (A) in diethyl ether at −50 °C; (B) in methylene chloride.

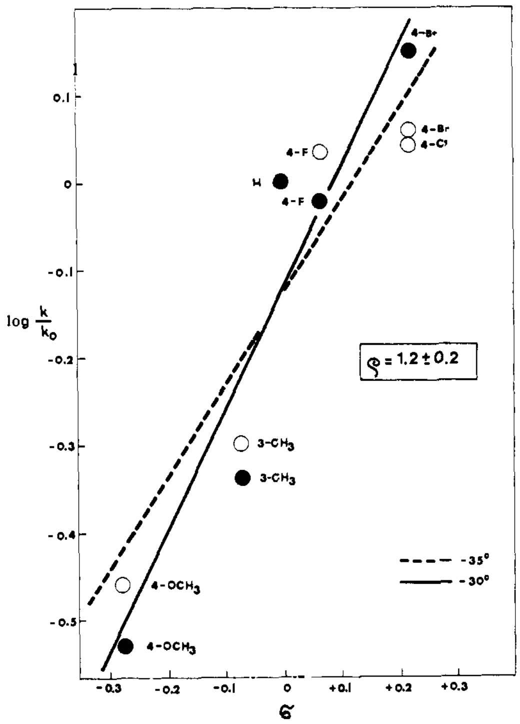


Figure 3. Correlation of logarithms of first-order rate constants for the decomposition of **3** in diethyl ether vs. Hammett σ constants.

served.[19] Considerable charge separation in the transition state for the decomposition is thus indicated.

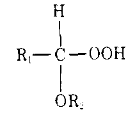
All of the hydrotrioxides investigated decompose in the temperature range −45 to −10 °C to produce singlet oxygen as determined by typical singlet oxygen acceptors (Table II). The highest yields were obtained by using 1,3-diphenylisobenzofuran, which is known as one of the best singlet oxygen acceptors.[20] Since there is some evidence that both scavengers used may not be unambiguous as detectors of singlet oxygen, we studied decomposition of **2a** in the presence of 1,2-dimethylcyclohexene. This compound has been known to distinguish between oxidation by singlet oxygen and a free-radical autoxidation on the basis of a different distribution of products for the two reactions.[21] Although only 20-30% of the absorbed ozone was available to react with this reagent, it was shown that the reacting species is singlet oxygen. Namely, 1-methyl-2-methylenecyclohexanol was found to be the major reaction product (80-90%).

A detailed study of the decomposition products of **1b** (ozonation with ozone-nitrogen mixture) by gas-liquid chromatography (GLC) showed ethyl acetate (0.80-0.85 mol/mol of absorbed ozone), ethanol (0.75-0.80 mol), water, acetaldehyde, acetic acid, ethyl formate, diethyl carbonate (0.06-0.12 mol), and a mixture of gases. Preparative thin layer chromatography (TLC) of the decomposition mixture at 5 °C on silica plates afforded α-hydroperoxydiethyl ether and α,α-diethoxydiethyl peroxide as well as hydrogen peroxide. Both organic peroxides account for roughly 5-7% of the decomposition products. The same types of peroxides were isolated in the decomposition of aromatic acyclic acetal hydrotrioxides, **3**.

Hydrogen peroxide has also been found in all these cases.[22]

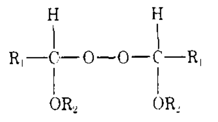
Table III. Spectral and Analytical Data of Peroxides **4** and **5**, Isolated from the Decomposition Mixture of Hydrotrioxides **1** and **3**

4a, $R_1 = CH_3$; $R_2 = C_2H_5$
b, $R_1 = C_6H_5$; $R_2 = CH_3$
c, $R_1 = C_6H_5$; $R_2 = C_2H_5$
d, $R_1 = 4\text{-}FC_6H_4$; $R_2 = CH_3$



$R_1-C(H)(OR_2)-OOH$

5a, $R_1 = CH_3$; $R_2 = C_2H_5$
b, $R_1 = C_6H_5$; $R_2 = CH_3$
c, $R_1 = C_6H_5$; $R_2 = C_2H_5$
d, $R_1 = 4\text{-}FC_6H_4$; $R_2 = CH_3$
e, $R_1 = 4\text{-}ClC_6H_4$; $R_2 = CH_3$



$R_1-C(H)(OR_2)-O-O-C(H)(OR_2)-R_1$

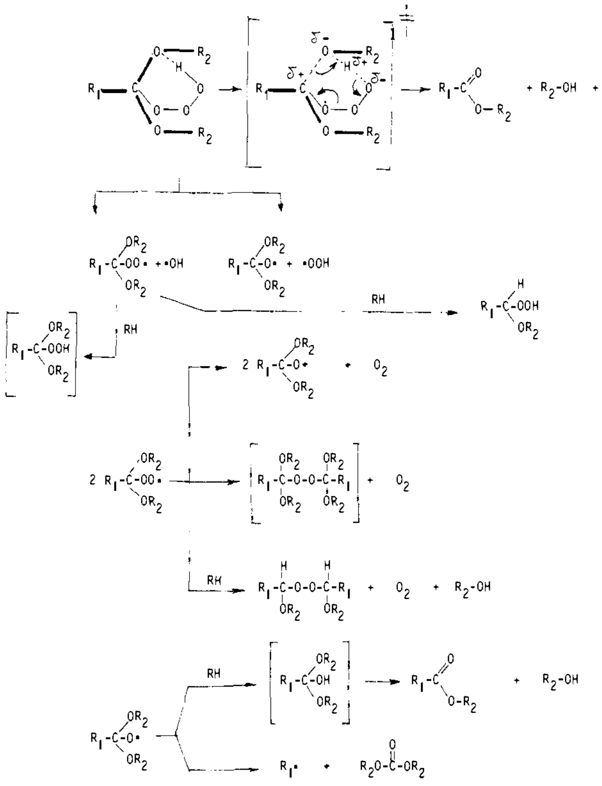
compd	^1H NMR[a]	IR[b] (ν_{OH}), cm^{-1}	elemental anal., % calcd	found
4a[c]	9.95 (br s, 1 OOH), 5.10 (q, 1 CH), 3.83 (m, 2 CH_2), 1.30 (m, 6 CH_3) $J_{CH_3CH_2} = 6$ Hz	3530, 3400 (br)		
4b	9.04 (br s, 1 OOH), 7.40 (m, 5 C_6H_5), 5.73 (s, 1 CH), 3.60 (s, 3 OCH_3)	3510, 3390 (br)	C 62.33 H 6.54	62.37 6.42
4c	9.20 (br s, 1 OOH), 7.50 (m, 5 C_6H_5), 5.88 (s, 1 CH), 3.87 (m, 2 CH_2), 1.18 (t, 3 OCH_3)	3520, 3390 (br)	C 64.27 H 7.19	64.57 7.07
4d	8.75 (br, 1 OOH), 7.33 (m, 4 4-FC_6H_4), 5.80 (s, 1 CH), 3.64 (s, 3 OCH_3)	3520, 3380 (br)		
5a	5.10 (q, 1 CH), 3.83 (m, 2 CH_2), 1.32 (m, 6 CH_3), $J_{CH_3CH_2} = 6$ Hz			
5b[d]	7.33 (m, 5 C_6H_5), 5.77 (s, 1 CH), 3.55 (s, 3 OCH_3)			
5c	7.40 (m, 5 C_6H_5), 5.93 (s, 1 CH), 3.80 (m, 2 CH_2), 1.25 (m, 6 CH_3)			
5d	7.20 (m, 4 4-FC_6H_4), 5.77 (s, 1 CH), 3.55 (s, 3 OCH_3)		C 61.93 H 5.21	62.25 5.81
5e	7.44 (s, 4 4-ClC_6H_4), 5.83 (s, 1 CH), 3.62 (s, 3 OCH_3)		C 55.99 H 4.72	56.01 4.90

[a] $CDCl_3$, δ from Me_4Si. [b] CCl_4 (1–2% solutions). [c] Prepared also independently by the displacement method with 100% hydrogen peroxide (A. Rieche and C. Bischoff, *Chem. Ber.*, **94,** 2722 (1961)). [d] Prepared also independently by ozonolysis of *trans*-stilbene in methanol (W. P. Keaveney, M. G. Berger, and J. J. Pappas, *J. Org. Chem.*, **32,** 1537 (1967)). **4a, 4d, 5a, 5b,** and **5c** are too volatile for elemental analysis.

It is interesting to mention that a previous attempt to isolate peroxidic products in the autoxidation of aliphatic and aromatic acyclic acetals failed.[23]

On the basis of the above-mentioned results we conclude that the formation of a large part of ethyl acetate, ethanol, and singlet oxygen can be tentatively ascribed to a nonradical decomposition while the presence of the other decomposition products suggests an alternative free-radical decomposition process accounting for roughly 20 ± 5% of the products (Scheme I).[24-26]

Scheme I



Experimental Section

Low-temperature NMR spectra were recorded on a JNM-C60H1 spectrometer equiped with a variable-temperature probe. IR spectra were recorded with a Perkin-Elmer 727B or 180 Model instrument. UV and visible spectra were obtained on a Perkin-Elmer Hitachi 200 spectrophotometer while a CEC 21-110C instrument was used to obtain mass spectra.

Materials. Acyclic[27] and cyclic[28] acetals were prepared by known procedures. The deuterated (C–D) derivative of the dimethyl acetal of benzaldehyde was prepared by the literature procedure.[29] All the acetals were checked by GLC, NMR, IR, and elemental analysis and found to be over 99% pure. Methylene chloride, diethyl ether, and ethyl acetate were purest commercially available products which were dried and distilled before use. Namely, it was found that water in these solvents prevents the observation of the OOOH absorptions.

Ozonations. Ozone was produced in a Gallenkamp ozonator which delivers an oxygen–ozone stream containing ca. 0.2 mmol of ozone per min.

Ozonation of the neat substrates (20 mmol) and solutions in diethyl ether, methylene chloride, and ethyl acetate (30% by wt) were carried out at −60 to −55 °C in the dark. Total ozonation times were 3 h for aliphatic acetals and 1 h for aromatic compounds. After ozonation the reaction mixture was thoroughly flushed with dried N_2 to remove excess ozone.

Kinetic Studies. Parts of the reaction mixture were transferred to a series of NMR tubes and the decay of the OOOH proton signals was followed by integrating the peak area with time at various temperatures (Me_4Si as an internal standard). The plots of the logarithm of peak areas vs. time were linear over several half-lives. Each rate constant is an average of at least three runs. First-order rate constants were obtained from a linear least-squares program.

Product Analysis. Singlet oxygen was determined by adding the acceptor (twofold excess per absorbed ozone) to the ozonized acetal at −50 to −40 °C and the reaction mixture allowed to warm up slowly to room temperature. The amount of absorbed ozone available to react with tetraphenylcyclopentadienone and 1,3-diphenylisobenzofuran was determined by measuring the decrease in absorbance at 510 and 405 nm, respectively. The corresponding reaction products, i.e., *cis*-dibenzoylstilbene (mp 214–215.5 °C, lit.[20] 215.9–216.3 °C) and *o*-dibenzoylbenzene (mp 143–145 °C, lit.[20] 146–147 °C), were isolated, although in lower yields, on silica gel chromatography columns according to the procedure of Wasserman et al.[20] Singlet oxygen determination (decomposition of **2a**) with 1,2-dimethylcyclohexene was performed by determining the amount of 1-methyl-2-methylenecyclohexanol (after sodium sulfite reduction of the corresponding hydroperoxide).[9b,21]

Decomposition products of **1b** (ozonation with an ozone-nitrogen stream[30]) were determined by a combination of techniques. All products except peroxides were determined by GLC on Porapak Q columns (80-160 °C) using calibrated internal standards and known reference materials. All the products were collected and identified by IR, NMR, and mass spectrum. The peroxidic materials were separated from the rest of the material on preparative silica plates (Merck Kieselgel 60 F_{254}, chloroform-*n*-hexane-methanol (10:10:1)). Preparative TLC was also used for the isolation of other peroxides reported in Table III (R_f, alkyl hydroperoxides 0.2-0.3; dialkyl peroxides, 0.5-0.6; hydrogen peroxide, 0.0).

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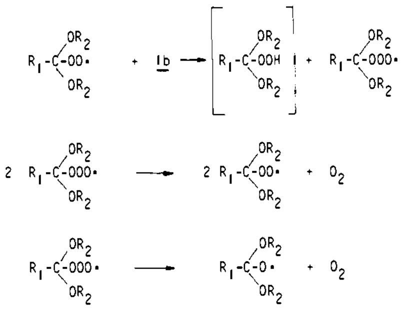

(26) Relatively smaller evolution of gas has been observed in most cases even after the disappearance of the OOOH absorption. This might be due to the decomposition of peroxides and/or polyoxides formed by radical recombinations.[1]

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