

Hemiortho Esters and Hydrotrioxides as the Primary Products in the Low-Temperature Ozonation of Cyclic Acetals: An Experimental and Theoretical Investigation

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Abstract: Low-temperature ozonation ($-78\text{ }^{\circ}\text{C}$) of 1,3-dioxolanes **1a–1f** and 1,3-dioxanes **1g** and **h** in acetone- d_6 , methyl acetate, and *tert*-butyl methyl ether produced both the corresponding hemioortho esters (**2a–h**, ROH) and acetal hydrotrioxides (**3a–h**, ROOOH) in molar ratios ROH/ROOOH ranging from 0.5 to 23. Both types of intermediates were fully characterized by ^1H , ^{13}C , and ^{17}O NMR spectroscopy. DFT calculations suggest that ozone abstracts a hydride ion from **1** to form an ion pair, $\text{R}^+ \text{ } ^-\text{OOOH}$, which subsequently collapses to either the corresponding hemioortho ester (ROH) or the acetal hydrotrioxide (ROOOH). Hemioortho esters decomposed quantitatively into the corresponding hydroxy esters. Experimentally obtained activation parameters for the decomposition of **2a** ($E_a = 13.5 \pm 1.0$ kcal/mol, $\log A = 8.3 \pm 1.0$) are in accord with a highly oriented transition state involving, according to B3LYP calculations ($\Delta H_a(298) = 13.2$ kcal/mol), two molecules of water as a bifunctional catalyst. This mechanism is also supported by the magnitude of the solvent isotope effect for the decomposition of **2e**, i.e., $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 4.6 \pm 1.2$. Besides the hydroxy esters and oxygen ($^3\text{O}_2/{}^1\text{O}_2$), dihydrogen trioxide (HOOOH) was formed in the decomposition of most of the acetal hydrotrioxides (ROOOH) investigated. The activation parameters for the decomposition of the hydrotrioxides **3a–e** in various solvents were $E_a = 20 \pm 2$ kcal/mol, $\log A = 13.5 \pm 1.5$. Several mechanistic possibilities for the decomposition of ROOOH were tested by experiment and theory. The formation of the hydroxy esters and oxygen could be explained by the intramolecular transfer of the proton to form the hydroxy ester. The assistance of water in the decomposition of ROOOH to form the hydroxy esters, either directly or via hemioortho esters, was also investigated. According to DFT calculations, the formation of a hydroxy ester via hemioortho ester is energetically more favorable ($\Delta H_a(298) = 14.5$ kcal/mol), again due to the catalytic effect of two water molecules. HOOOH generation requires the involvement of water in the decomposition of ROOOH where the direct formation out of ROOOH is energetically preferred. The energy for a reaction between two molecules of water and singlet oxygen ($\Delta^1\text{O}_2$) is too high to occur in solution.

Introduction

The cleavage of acetals, and particularly cyclic acetals, has been proven to yield synthetically useful derivatives.^{1–3} In 1971, Deslongchamps and Moreau first reported that aldehyde acetals and 1,3-dioxolanes react with ozone when they can take a conformation where each oxygen has an electron lone pair oriented antiperiplanar to the C–H bond.^{2b,3} More recently the synperiplanar oxygen lone pairs were found to play a similar role in influencing these oxidations.^{2c}

Several mechanisms for the oxidation of acetals have been proposed: (a) a concerted 1,3-dipolar insertion of ozone into the C–H bond to form the corresponding hydrotrioxides (ROOOH),^{1,4} (b) a hydride-ion transfer to form a carbenium ion and the hydrotrioxide ion ($\text{R}^+ \text{ } ^-\text{OOOH}$),^{3a,5} and (c) a H-atom abstraction by ozone to form a radical pair ($\text{R}^{\bullet} \text{ } ^{\bullet}\text{OOOH}$) with subsequent collapse into ROOOH.^{3a,6}

We have recently, in a preliminary form, already provided evidence for the involvement of the HOOO[−] anion in the ozonation of 1,3-dioxolanes.⁷ It was found that at low temper-

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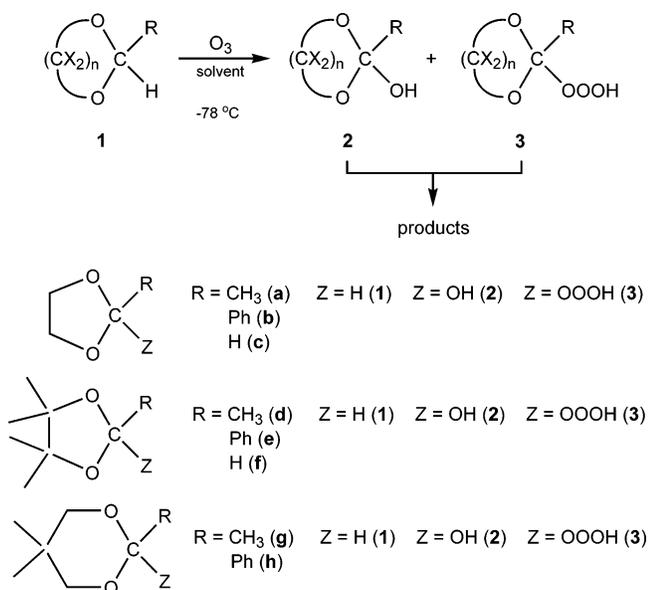
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Chart 1



ature (-78°C) 2-methyl-1,3-dioxolane (**1a**) in various solvents produced both the hemioortho ester **2a** and the corresponding hydrotrioxide **3a**. Both of these intermediates decomposed to the corresponding hydroxy ester at higher temperatures. This, together with some preliminary quantum chemical calculations,⁷ suggested the mechanism (b), which involves the HOOO^- anion, in the form of an ion pair, $\text{R}^+ \text{OOOH}^-$, subsequently collapsing to either the hemioortho ester or the acetal hydrotrioxide. It should be noted that theoretical and experimental evidence for the existence of the elusive HOOO^- anion (the conjugate anion of HOOOH) has recently been provided.⁸ The goal of the present investigation is to elucidate, by a combination of experimental and quantum chemical means, the mechanism of (1) the formation of hemioortho esters and hydrotrioxides generated in the low-temperature ozonation of cyclic acetals and (2) the decomposition of these initially formed labile intermediates. Previously, we have shown that the ozonation of cyclic acetals is, at least at present, the method of choice for the generation of hemioortho esters in relatively high yields.⁹ In the current report, the first example of a direct conversion of an acetal hydrotrioxide into dihydrogen trioxide (HOOOH) is also presented.

Experimental Section

Instrumentation. Low-temperature ^1H , ^{13}C , and ^{17}O NMR spectra were recorded on a Bruker Avance 300 DPX (^1H NMR, 300.3 MHz; ^{13}C NMR, 75.48 MHz; ^{17}O NMR, 40.70 MHz) and on Varian Unity Inova-600 spectrometers (^1H NMR, 600.09 MHz; ^{17}O NMR, 81.37 MHz) with TMS (^1H and ^{13}C NMR) and H_2^{17}O (^{17}O NMR) as internal standards. GC/MS was performed on a Hewlett-Packard 6890 chromatograph (HP-5MS column).

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- (9) The hemioortho ester **2a** (2-hydroxy-2-methyl-1,3-dioxolane) was characterized before in the hydronium ion catalyzed hydration of 2-methylene-1,3-dioxolane (Capon, B.; Ghosh, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 1765). (b) For reviews on tetrahedral intermediates, see: McClelland, R. A.; Santry, L. J. *Acc. Chem. Res.* **1983**, *16*, 394. Capon, B.; Ghosh, A. K.; Grieve, D. M. A. *Acc. Chem. Res.* **1981**, *14*, 306.

Materials. Commercially available solvents in their purest form were (except in the case of acetone- d_6 , 99.5%, Aldrich) rigorously dried and distilled according to standard procedures described in the literature.^{8d} The purity was checked by GC/MS. 2-Methyl-1,3-dioxolane (**1a**, 97%, Aldrich), 2-phenyl-1,3-dioxolane (**1b**, 99%, Aldrich), 1,3-dioxolane (**1c**, 99.7%, Aldrich), 1,3-dioxane (99%, Aldrich), 1,3-dioxepane (99%, Aldrich), ethylene carbonate (98%, Aldrich), acetaldehyde (99.5%, Merck), benzaldehyde (99+%, Aldrich), formaldehyde (37 wt. % solution in water, Merck), 4-methoxybenzaldehyde (99%, Fluka), 4-methylbenzaldehyde (98%, Fluka), 4-fluorobenzaldehyde (98%, Fluka), 4-chlorobenzaldehyde (97%, Aldrich), 4-bromobenzaldehyde (97%, Fluka), 4-cyanobenzaldehyde (95%, Aldrich), 4-nitrobenzaldehyde (95%, Fluka), acetaldehyde dimethyl acetal (95%, Aldrich), acetaldehyde diethyl acetal (99%, Aldrich), benzaldehyde dimethyl acetal (95%, Aldrich), trimethyl orthoacetate (99%, Aldrich), ethylene glycol (99%, Merck), pinacol (98%, Aldrich), and methanesulfonic acid (99% Aldrich) were used as received. 2,4,4,5,5-Pentamethyl-1,3-dioxolane (**1d**), 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolane (**1e**), 4,4,5,5-tetramethyl-1,3-dioxolane (**1f**), 2,5,5-trimethyl-1,3-dioxane (**1g**), 2-phenyl-5,5-dimethyl-1,3-dioxane (**1h**), and 2-*para*-phenyl-substituted dioxolanes (analogues of **1b** and **1e** which include the following: 2-(4-methoxyphenyl)-1,3-dioxolane, 2-(4-methylphenyl)-1,3-dioxolane, 2-(4-fluorophenyl)-1,3-dioxolane, 2-(4-chlorophenyl)-1,3-dioxolane, 2-(4-bromophenyl)-1,3-dioxolane, 2-(4-cyanophenyl)-1,3-dioxolane, 2-(4-nitrophenyl)-1,3-dioxolane, 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane, 2-(4-methylphenyl)-4,4,5,5-tetramethyl-1,3-dioxolane, 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3-dioxolane, 2-(4-cyanophenyl)-4,4,5,5-tetramethyl-1,3-dioxolane, and 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-1,3-dioxolane) were prepared according to the procedure of Fife and Jao.¹⁰

2-Hydroperoxy-2-methyl-1,3-dioxolane was prepared from 2-methoxy-2-methyl-1,3-dioxolane¹¹ with nucleophilic substitution, using H_2O_2 solution in diethyl ether (in situ prepared and rigorously dried with MgSO_4) and methanesulfonic acid as the catalyst, following the method of Rieche et al.¹² Spectroscopic data for the crude product are collected in the footnote of Table 1.

2-Hydroperoxy-2,4,4,5,5-pentamethyl-1,3-dioxolane was prepared from 2-methoxy-2,4,4,5,5-pentamethyl-1,3-dioxolane¹³ with nucleophilic substitution as 2-hydroperoxy-2-methyl-1,3-dioxolane. Spectroscopic data for crude product are collected in the footnote of Table 1.

Ozonation Procedure. Ozone–oxygen mixtures delivered at a rate of 0.1–0.2 mol of ozone min^{-1} were produced by flowing oxygen through a Welsbach T-816 ozonator.⁷ The typical time of ozonation for an almost complete consumption of the starting material was 20 min for compounds **1a–c**, 10 min for compounds **1d–f**, and 60 min for compounds **1g** and **h**. Ozone–nitrogen mixtures were obtained as already reported.^{8d} The concentration of ozone in the gas stream was measured according to the literature procedure.^{8d} ^{17}O -enriched ozone was generated by flowing ^{17}O -enriched oxygen (58% $^{17}\text{O}_2$, ISOTEC) through a semimicro ozonator.⁷

WARNING: Although we have not had any accidents in handling solutions of peroxides and polyoxides formed in the ozonation reactions, care should be exercised in handling dried and concentrated solutions of these potentially hazardous compounds.

Product Analysis. Reaction products of the ozonation of cyclic acetals, **1**, were determined by a combination of methods. The products, 2-hydroxyethyl acetate, 2-hydroxyethyl benzoate, 2-hydroxyethyl formate, ethylene carbonate, 2-hydroxy-1,1,2-trimethyl-propyl acetate, 2-hydroxy-1,1,2-trimethyl-propyl benzoate, 2-hydroxy-1,1,2-trimethyl-propyl formate, 3-hydroxy-2,2-dimethyl-propyl acetate, and 3-hydroxy-2,2-dimethyl-propyl benzoate were determined by GC/MS, using

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Table 1. Comparison of Selected ^1H , ^{13}C , and ^{17}O NMR Chemical Shifts for Some Hemiortho Esters (**2**) and Hydrotrioxides (**3**) in Acetone- d_6 at $-60\text{ }^\circ\text{C}^a$

species Z	^1H NMR			^{13}C NMR				^{17}O NMR	
	Z	R ^b	CH ₂	CH ₃	C(1)	R ^b	CH ₂		CH ₃
(2a) OH ^c	6.42	1.49	3.89 4.02		119.9 122.1	23.09 24.79	64.58 65.67		96.0
(3a) O3O2O1H ^c	13.66	1.61	4.05 4.12		124.5 125.5	20.44 20.48	66.44		305 (O1) 355 (O3) 455 (O2)
(2b) OH	7.15		4.04 4.17		119.5	141.5 ^d	65.32		92.8
(3b) O3O2O1H	13.91		4.21 4.46		121.3 124.9	136.1 ^d 138.4 ^d	65.80 67.02		306 (O1) 362 (O3) 456 (O2)
(2c) OH	6.63	6.01	3.84 4.01		112.4		64.10		84.4
(3c) O3O2O1H	13.92	6.49	4.04 4.08		116.8 117.4		64.74 64.92		302 (O1) 348 (O3) 454 (O2)
(2d) OH ^e	5.97	1.48		1.15 ^f 1.26 ^g	117.5 117.6	28.53	83.04 ^h 84.87 ^h	23.90 ^f 24.16 ^g	105.2
(3d) O3O2O1H ^e	13.56	1.68		1.21 ^f 1.30 ^g	123.6 124.1	24.57	83.43 ^h 85.67 ^h	24.06 ^f 24.28 ^g	305 (O1) 361 (O3) 450 (O2)
(2e) OH	6.42			1.08 ^f 1.38 ^g	116.9 117.0	144.6 ^d	83.78 ^h	23.77 ^f 24.16 ^g	109.3
(3e) O3O2O1H	13.32			1.16 ^f 1.42 ^g	121.7 122.6	139.8 ^d	85.63 ^h	23.88 ^f 25.15 ^g	306 (O1)
(2f) OH	6.41	5.87		1.14 ^f 1.22 ^g	116.6		82.15 ^h	22.22 ^f 22.34 ^g	60.1
(3f) O3O2O1H	13.94	6.36		1.18 ^f 1.23 ^g	125.5		84.05 ^h	23.17 ^f 23.29 ^g	306 (O1) 355 (O3) 455 (O2)
(2g) OH	5.94	1.43	3.43 ^f 3.54 ^g	0.88 ^f 1.10 ^g	109.4	26.47	69.75 ⁱ	22.54 ^f 23.04 ^g	
(3g) OOOH	13.72	1.57	3.41 ^f 3.52 ^g	0.75 ^f 1.14 ^g	112.6	23.74	71.14 ⁱ	21.82 ^f 21.63 ^g	
(2h) OH	6.53		3.38 ^f 4.10 ^g	0.83 ^f 1.20 ^g	108.7	143.1 ^d	70.22 ⁱ	22.11 ^f 22.74 ^g	61.0
(3h) O3O2O1H	13.64		3.59 ^f 4.12 ^g	0.86 ^f 1.18 ^g	114.8	139.3 ^d	71.60 ⁱ	22.49 ^f 23.47 ^g	308 (O1) 460 (O2)

^a **2** = (0.07 ± 0.02) M, **3** = (0.030 ± 0.025) M. All ^{17}O NMR spectra were recorded at $-20\text{ }^\circ\text{C}$. ^b For R, see Chart 1. ^c For comparison, 2-hydroperoxy-2-methyl-1,3-dioxolane (acetone- d_6 , 25 $^\circ\text{C}$): ^1H NMR 10.56 (s, OOH), 4.16 and 3.98 (m, CH₂), 1.47 (s, 2-CH₃). ^d Chemical shift for C(1) atom in the phenyl ring. ^e For comparison, 2-hydroperoxy-2,4,4,5,5-pentamethyl-1,3-dioxolane (acetone- d_6 , 25 $^\circ\text{C}$): ^1H NMR 11.17 (s, OOH), 1.53 (s, 2-CH₃), 1.27 and 1.18 (s, 4,5-CH₃); ^{17}O NMR (O2O1H), 231 (O1), 252 (O2). ^f Chemical shift for the substituent in trans position relative to the OH (OOH) group in the hemioortho ester (hydrotrioxide). ^g Chemical shift for the substituent in cis position relative to the OH (OOH) group in the hemioortho ester (hydrotrioxide). ^h Chemical shift for the C(4) and C(5) atom in the 1,3-dioxolane ring. ⁱ Chemical shift for the C(4) and C(6) atom in the 1,3-dioxane ring.

calibrated internal standards and known reference materials. All products were also collected and identified by ^1H , ^{13}C , and ^{17}O NMR spectroscopy. Hydrogen peroxide was determined by ^1H NMR (and ^{17}O NMR) and by other analytical methods described previously.^{8d} Singlet oxygen ($\Delta^1\text{O}_2$) was determined by adding the acceptor, i.e., tetraphenylcyclopentadienone (2-fold excess per mol of the hydrotrioxide), to the deoxygenated solution of **3** in the dark at $-78\text{ }^\circ\text{C}$, and the reaction mixture was allowed to warm slowly to room temperature. The corresponding reaction product, i.e., (Z)-1,2-dibenzoylstilbene, was isolated on a silica gel chromatographic column and checked by NMR spectroscopic comparison with an authentic sample.

Kinetic Studies. The kinetics of the decomposition of hemioortho esters (**2**), hydrotrioxides (**3**), and dihydrogen trioxide (HOOOH) was measured by following the decay of the OH (OOOH) and the corresponding CH₃, CH₂, and phenyl absorptions by ^1H NMR, using TMS as the internal standard. Kinetic and activation parameters for the first-order decay were obtained by standard procedures.⁷

Computational Methods. The theoretical investigation focused on the study of the model system 2-methyl-1,3-dioxolane (**1a**) and the reaction mechanisms resulting from its interaction with ozone. Due to the large number of systems studied, standard density functional theory (DFT)¹⁴ was employed for the calculation of all reactants, transition

states (TSs), intermediates, and products. The B3LYP hybrid functional¹⁵ in conjunction with Pople's 6-31G(d,p) basis set¹⁶ was chosen as this level of theory has been shown to provide good results for the systems under study.⁷

Geometry optimizations were carried out using standard procedures based on analytical gradients. Frequency calculations were performed to characterize the stationary points as minima or TSs, as well as for the calculation of zero-point energies (ZPE), enthalpies (H), entropies (S), and Gibbs energies (G). The effect of the solvent medium on the reaction system investigated was included through the use of the PISA continuum model¹⁷ applying the dielectric constant of acetone ($\epsilon = 20.7$),¹⁸ which was one of the solvents used in the experimental studies.

The calculation of dispersion-bonded van der Waals complexes is inherently difficult when using DFT.¹⁹ However, in the case where these

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Scheme 1

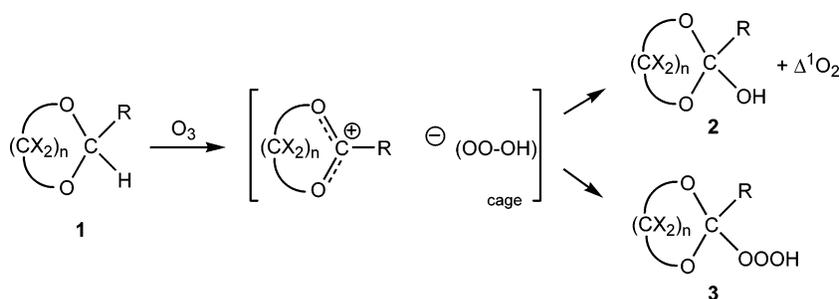


Table 2. Molar Ratio between Hemiortho Esters (**2**) and Hydrotrioxides (**3**) Formed in the Low-Temperature Ozonation of Cyclic Acetals (**1**) in Acetone- d_6 at $-60\text{ }^\circ\text{C}^a$

Species	ROH/ROOOH ^b		ROH/ROOOH	
		X = OCH ₃	X = OCH ₃	
2a/3a	5	13.2	23.0	
2b/3b	9.5	11.5	15.0	
2c/3c	4	9.5	12.2	
2d/3d	4	8.8		
2e/3e	17	5.3	12.0	Cl
2f/3f	1.2	7.4		
2g/3g	0.5	2.6	9.8	CN
2h/3h	9	1.4	9.2	NO ₂

^a **1** = (0.10 ± 0.01)M. ^b The same trend is observed in methyl acetate and *tert*-butyl methyl ether as solvents.

complexes are stabilized by H-bonding, composed of both electrostatic and covalent contributions, DFT performs reasonably well.²⁰ Thus, the optimization of van der Waals complexes was carried out in this work at the B3LYP level, and the calculation of the complexation energy was corrected using the counterpoise correction method,²¹ to eliminate the basis set superposition error (BSSE). We note that the description of dispersion-bounded van der Waals complexes would fail with B3LYP, no matter whether BSSE corrections are included or not. However, in the case of the van der Waals complexes investigated in this work, electrostatic interactions between the monomers dominate so that a description with BSSE-corrected B3LYP becomes useful.

Because of the deficiencies of DFT when calculating $\text{O}_2(^1\Delta_g)$, we calculated also the corresponding $\text{O}_2(^3\Sigma_g^-)$ energies and corrected with the experimental triplet-singlet splitting enthalpy 22.64 kcal/mol¹⁸ in the case of free or complexed $\text{O}_2(^1\Delta_g)$.

All calculations were performed with the quantum chemical packages COLOGNE 2003²² and Gaussian 98.²³

Results and Discussion

Mechanism for the Formation of the Hemiortho Esters and Hydrotrioxides of Dioxolanes. Low-temperature ozonation of dioxolanes **1a–f** in acetone- d_6 , methyl acetate, and *tert*-butyl methyl ether produced both the corresponding hemiortho esters **2a–f** and acetal hydrotrioxides **3a–f**. All these intermediates were fully characterized by ¹H, ¹³C, and ¹⁷O NMR spectroscopy (Table 1).²⁴ At higher temperatures both of these types of intermediates decompose to the corresponding hydroxy esters.

We have already presented preliminary evidence⁷ that ozone abstracts hydride from 2-methyl-1,3-dioxolane (**1a**) forming a relatively stable carbenium ion and the HOOO⁻ anion in an exothermic reaction ($\Delta G = -28.9$ kcal/mol, PISA/B3LYP/6-311++G(3df,3pd) with $\epsilon = 20.7$ for acetone), whereas the hydrogen atom abstraction to produce the HOOO[•] and the dioxolane radical is an almost thermoneutral process ($\Delta G = 0.2$ kcal/mol) under the same conditions (Scheme 1). The molar ratio, hemiortho ester/acetal hydrotrioxide, appears to reflect the relative stability and/or reactivity of the corresponding dioxolyl cations toward the HOOO⁻ anion and the HO⁻ anion, respectively (Table 2, Figure 1).^{25,26}

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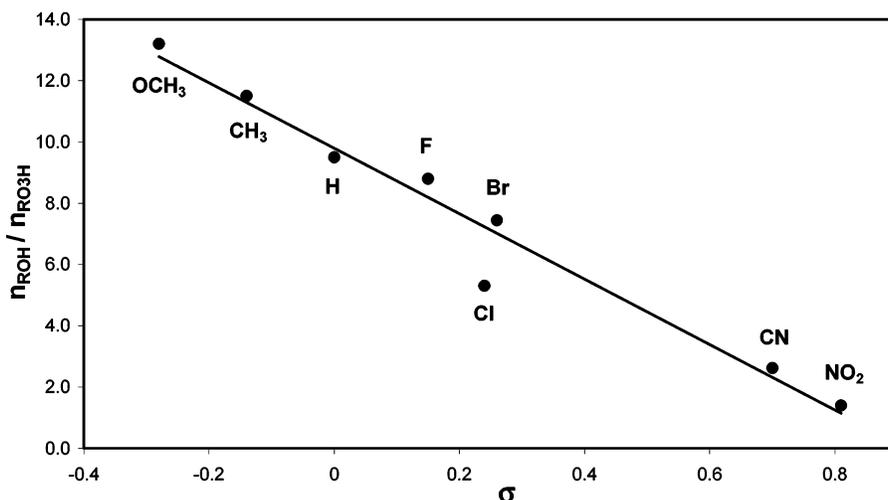


Figure 1. Molar ratio of 2-(*para*-phenyl)-substituted 2-hydroxy-1,3-dioxolane (ROH, **2**) vs 2-hydrotrioxy-1,3-dioxolane (ROOOH, **3**), formed in the ozonation of various 2-(*para*-phenyl)-substituted 1,3-dioxolanes (**1**) and correlated with Hammett σ constants.

The reaction mechanism, which leads to the formation of these products, was investigated computationally through the optimization of the structures involved in both a radical and an ionic mechanism. The formations of hemiortho esters and acetal hydrotrioxides were considered with respect to both the hydride transfer and the H-atom abstraction reactions, where the model reaction of 2-methyl-1,3-dioxolane (**1a**) with ozone was used as a template. Contrary to previous investigations (based on single-point calculations),⁷ we have reoptimized all gas-phase geometries in the solvent medium to obtain a more accurate description.

The initial H abstraction by ozone occurs after the formation of a van der Waals complex, which is stabilized by 5.0 kcal/mol ($\Delta H(298)$, BSSE corrected) below the enthalpies of the free species (Figure 2, Table 3). Once bound, the H abstraction occurs, after overcoming an activation barrier of 14.7 kcal/mol ($\Delta H_a(298)$, Table 3) in a slightly endothermic reaction to produce either the radical or ionic pair, where the radical pair is stabilized by 3.0 kcal/mol below the ionic pair in the solvent acetone (Figure 2, Table 3). This is in contrast with our previous observation that found the ionic pair to be substantially more stabilized in the solvent than the radical pair. Reoptimization of all structures within the solvent cavity is obviously important to obtain a reliable description.

Despite the loss in exothermicity for the ionic reaction, the products resulting from the reaction between ozone and dioxolane are strongly indicative of the ionic mechanism. The hemiortho ester generated in the reaction results from the collapse of the ionic pair and the simultaneous breaking of the weakest O–O bond. In the case of the ionic pair this O–O

bond is substantially weaker, as evidenced by the O–O bond length (1.662 Å, OOOH anion; 1.494 Å, OOOH radical: PISA/B3LYP/6-31G(d,p) optimization in acetone), compared with the weakest O–O bond in the radical system. However, in both cases a dissociation of the hydrotrioxide species (HOOO[•]/HOOO[−]) and subsequent formation of hemiortho ester and singlet oxygen are plausible. The telling evidence in this regard is the formation of the acetal hydrotrioxide as one of the reaction products. The formation of this species can occur through either (a) a rotation of the HOOO species in the solvent cage after the hydrogen atom or hydride ion abstraction and a subsequent collapse to form the acetal hydrotrioxide or (b) the transfer of the hydrogen atom or hydride ion between the terminal O atoms of the HOOO molecule, followed by the collapse. Proposal (a) is essentially condemned due to the taking place of the reaction in the solvent cage. The rotation of the reactive HOOO intermediate would result in the breaking of the solvent cage and the interaction of the intermediates with the surrounding medium, which is not observed. On the contrary, hemiortho esters (**2**) are found to be enriched with ¹⁷O in the OH group as indicated by its ¹⁷O NMR spectrum, which supports the reaction occurring exclusively within the solvent cage.

Proposal (b) requires the surmounting of a second TS (TS2; Table 3), whereby the hydride ion or hydrogen atom is transferred between the terminal O atoms. This TS was calculated for both an ionic (TS2a) and a radical (TS2b) mechanism at the PISA/B3LYP/6-31G(d,p) level and corrected for tunneling using the Wigner formula.²⁷ The barrier for the proton transfer is 18.7 kcal/mol less in the case of the ionic species ($\Delta H_a(298)(\text{TS2a}) = 8.4$ kcal/mol; Table 3) than for the radical HOOO system ($\Delta H_a(298)(\text{TS2b}) = 27.1$ kcal/mol; Table 3). Thus, for the radical species such a transfer reaction is clearly not energetically favorable. However, for the ionic mechanism the activation energy of the transfer reaction is lower than that of the competing reaction, i.e., the dissociation of the HOOO anion to form the OH anion and singlet oxygen ($\Delta H = 14.3$ kcal/mol; ref 8a). Therefore, on the basis of the formation of the acetal hydrotrioxide, we conclude that *the abstraction of hydrogen from dioxolane by ozone occurs via an ionic mechanism* as described above.

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(26) The larger stabilization of the carbocation generated, the easier it lets go the HOOO anion, which, once decoupled, undergoes the decomposition into singlet oxygen and the OH anion. The latter reacts (diffusion-controlled) with the cation to form the hemiortho ester (ROH). If the carbocation charge is not stabilized by delocalization or hyperconjugation, it will not let the HOOO anion go, thus forming more of the hydrotrioxide (ROOOH). Therefore, we should get more ROH for R = Ph than for R = Me or H. In the same way one can explain the effect of substituents (X) on the benzene ring with OMe having the largest stabilizing power and NO₂ the opposite. The four methyl groups in the back of **1d–1f** increase puckering and thus make it easier for the phenyl group to establish maximum conjugation and thus increasing the stability of the carbocation. This leads to more ROH.

(27) Wigner, E. Z. *Phys. Chem. B* **1932**, *19*, 203.

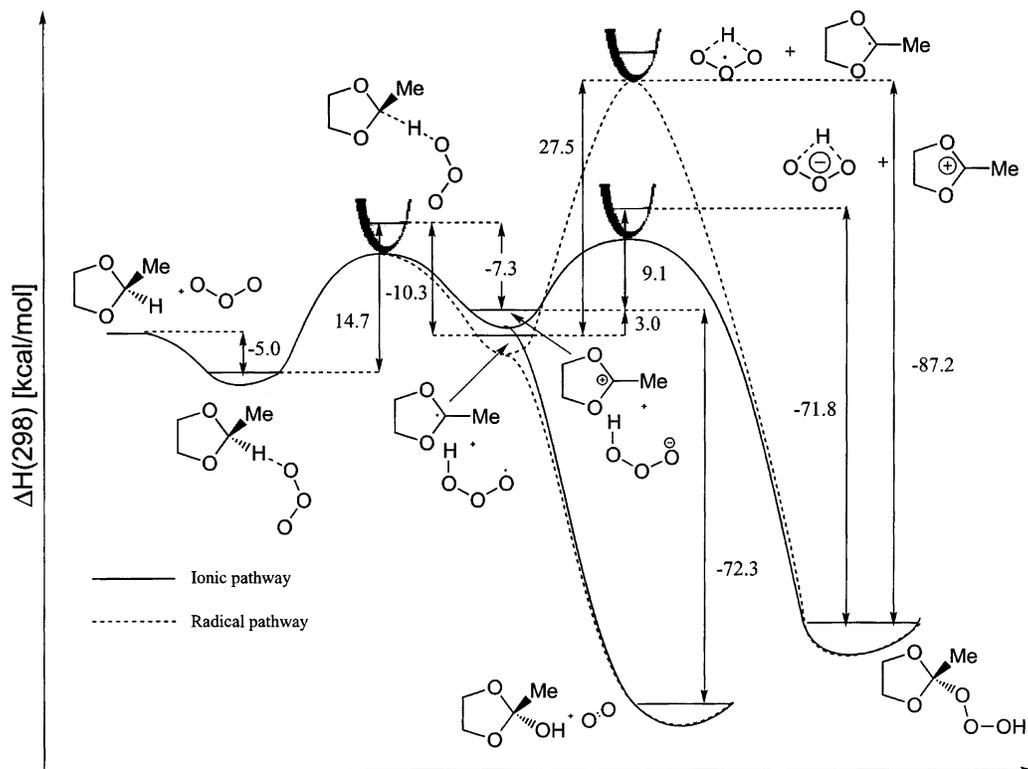


Figure 2. Energetics of the reaction of 2-methyl-1,3-dioxolane (**1a**) with ozone. All enthalpy calculations were done at the B3LYP/6-31G(d,p) level of theory. Ionic (solid lines) and radical pathways (dashed lines) are distinguished.

Table 3. Energies and Thermodynamics for the Formation of Hemioortho Ester (**2a**) and Hydrotrioxide (**3a**) of Dioxolane (**1a**)^a

system	sym	$E, \Delta E$	ΣZPE	$H, \Delta H(298)$	ΣS	$G, \Delta G(298)$	μ
dioxolane (1a)	C_1	-307.68318	80.8	-307.55728	93.4	-307.68549	1.51
ozone	C_{2v}	-225.40743		-225.39515		-225.40642	0.68
vdW ^b	C_1	-6	81.1	-5.0	92.7	-4.3	1.68
TS1	C_1	11.1	78.6	9.7	94.1	12.3	5.48
ion pair	C_s, C_1	3.4	79.0	2.4	144.0	2.9	1.25, 1.24
radical pair	C_1, C_1	0.8	79.0	-0.6	140.4	0.8	2.17, 1.50
hemioortho ester (2a)	$C_1, D_{\infty h}$	-70.6	70.7	-69.9	130.9	-70.1	2.49, 0
acetal hydrotrioxide (3a)	C_1	-62.1	82.6	-60.3	94.0	-61.7	2.2
HOOO ⁻	C_1	-226.17715	9.9	-226.15565	64.1	-226.17651	1.24
TS2a	C_1	11.9	8.0	8.4 ^c	59.8	10.9 ^c	0.42
HOOO [•]	C_1	-226.06210	11.0	-226.03935	63.1	-226.06154	1.50
TS2b	C_1	30.4	8.8	27.1 ^d	60.4	29.8 ^d	0.78

^a Relative energies, enthalpies, and free energies are reported in kcal/mol, and their absolute counterparts are given in hartrees. Entropies are in cal/(mol K), and dipole moments, in debye. All calculations performed with PISA/B3LYP in conjunction with Pople's 6-31G(d,p) basis set. The dielectric constant of acetone ($\epsilon = 20.7$) was used. In the first section of the table, relative values are taken with respect to the dioxolane–ozone system. In the second section, the energies of TS2 are relative to the preceding reactant. ^b BSSE corrected energy. Enthalpy and free energy were incremented by the BSSE correction for the energy. ^c Includes correction for tunneling of -0.7 kcal/mol. ^d Includes correction for tunneling of -0.4 kcal/mol.

Experimentally supporting the hydride abstraction mechanism are the observations that (a) ethyl diethoxy acetate is inert toward O_3 ^{2b} and (b) electron-withdrawing groups in benzaldehyde acetal^{2b} and 2-phenyl-1,3-dioxolane⁴ retard the ozonolysis of these substrates.

Mechanism for the Decomposition of the Hemioortho Esters. NMR spectroscopic evidence indicated that hemioortho esters under investigation decomposed quantitatively into the corresponding hydroxy esters. The kinetics of decomposition of **2a–h** was measured by following the decay of the OH absorption (and in some cases those of the CH_3 and CH_2 groups as well) by ¹H NMR. The first-order kinetics was observed (over 2–3 half-lives) in all solvents investigated.

The activation parameters for the decomposition of **2a** ($\Delta E_a = 13.5 \pm 1.0$ kcal/mol, $\log A = 8.3 \pm 1.0$) are in accord with a highly oriented transition state (Table 4).

It has already been suggested that water might play a significant role in the decomposition of hemioortho esters.²⁸ Therefore, we employed DFT to test the three mechanistic possibilities for the decomposition of the hemioortho ester **2a**: (a) the intramolecular proton-transfer and (b) the assistance of one or (c) two molecules of water acting as a bifunctional catalyst in these reactions (Scheme 2).

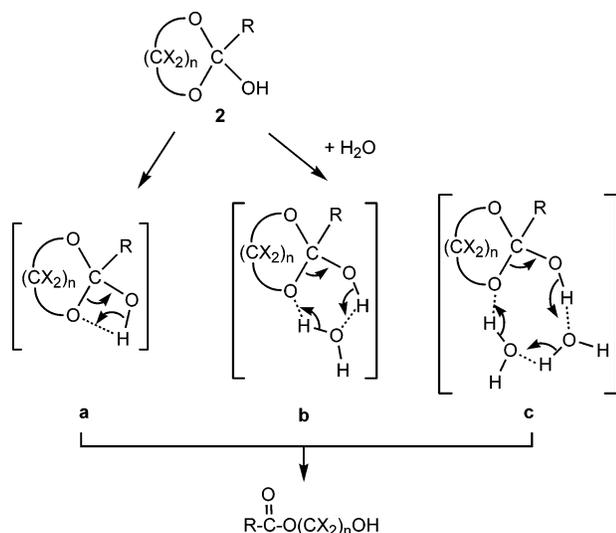
The decomposition occurring via route (a) was found to require an activation enthalpy of 35.5 kcal/mol (Table 5), which is significantly greater than that experimentally observed. However, reactions (b) and (c) are much more competitive. For a single water molecule acting as a catalyst for the H-transfer, the activation enthalpy was calculated as $\Delta H_a(298) = 14.3$ kcal/mol. This is a significant improvement over the uncatalyzed

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Table 4. Kinetic and Activation Parameters for the Decomposition of Hemiortho Esters (**2**) Formed in the Low-Temperature Ozonation of Cyclic Acetals (**1**) in Various Solvents^{a,b}

solvent	T, °C	δ , ppm	$k \times 10^4$, s ⁻¹					E _a , kcal/mol	log A
			ROH	OH ^c	CH ₃ ^d	t-CH ₃ ^e	c-CH ₃ ^f		
(2a) acetone- <i>d</i> ₆	-10	5.79	5.10	5.39			5.05 ^g	12.5 ± 1.0 ^c	7.2 ± 0.7 ^c
methyl acetate	-10	5.27	24.71	27.89				14.5 ± 1.3 ^c	9.5 ± 0.9 ^c
<i>tert</i> -butyl methyl ether	-10	5.47	1.12				0.92 ^g	14.3 ± 1.3 ^d	9.3 ± 0.9 ^d
(2b) acetone- <i>d</i> ₆	-15	6.52	5.50				5.15 ^g	14.8 ± 1.3 ^c	8.4 ± 0.8 ^c
<i>tert</i> -butyl methyl ether	-15	7.04	(3.25) ⁱ				(3.23) ^{i,g}	13.4 ± 1.2 ^g	7.2 ± 0.7 ^g
(2c) acetone- <i>d</i> ₆	-15	6.15	2.91				2.23 ^h	15.7 ± 1.5 ^c	10.1 ± 1.0 ^c
(2d) acetone- <i>d</i> ₆	-15	6.14	9.65	9.79 ^j			5.15 ^g	(13.8 ± 1.3) ^{c,i}	(8.3 ± 0.8) ^{c,i}
(2e) acetone- <i>d</i> ₆	-10	5.69	0.27		0.30	0.21	8.81 ^g	15.1 ± 1.4 ^c	9.3 ± 0.9 ^c
methyl acetate	-10	4.80	3.79		2.56			14.7 ± 1.4 ^h	8.8 ± 0.9 ^h
(2e) acetone- <i>d</i> ₆	-10	5.94	0.26		0.25	0.26	0.23 ^h	13.1 ± 1.1 ^c	8.1 ± 0.9 ^c
<i>tert</i> -butyl methyl ether	-5	5.77	0.30				0.29 ^h	15.9 ± 1.5 ^c	8.8 ± 0.9 ^c
(2f) acetone- <i>d</i> ₆	-10	5.86	3.03	3.03 ^j				12.0 ± 1.1 ^e	6.4 ± 0.6 ^e
(2g) acetone- <i>d</i> ₆	-60	5.94	16.6	16.8				15.8 ± 1.5 ^c	8.6 ± 0.8 ^c
<i>tert</i> -butyl methyl ether	-60	5.23	0.45					20.3 ± 2.0 ^c	12.6 ± 1.2 ^c
(2h) acetone- <i>d</i> ₆	-60	6.52	0.45		0.45	0.48	0.44 ^h	18.1 ± 1.8 ^h	10.6 ± 1.0 ^h
								14.6 ± 1.3 ^c	8.7 ± 0.8 ^c
								12.6 ± 1.2 ^c	10.2 ± 1.0 ^c
								13.4 ± 1.3 ^c	9.5 ± 0.9 ^c
								12.5 ± 1.2 ^c	8.7 ± 0.8 ^c

^a **1** = (0.1 ± 0.01) M, **2** = (0.08 ± 0.01). ^b Standard deviation ± 10%. ^c Following decay of the OH absorption. ^d Following decay of the 2-CH₃ absorption. ^e Following decay of the *trans*-4,5-CH₃ absorptions relative to the OH group in the hemioortho ester **2**. ^f Following decay of the *cis*-4,5-CH₃ absorptions relative to the OH group in the hemioortho ester **2**. ^g Following decay of the CH₂ absorption. ^h Following decay of the absorptions of meta and para protons in the benzene ring. ⁱ For comparison, 2-hydroxy-2-(*para*-NO₂-phenyl)-4,4,5,5-tetramethyl-1,3-dioxolane. ^j Following decay of the 2-H absorption.

Scheme 2

activation enthalpy and is already within the borders of the experimental error. The addition of a second water molecule, as shown in Scheme 2, lowers the activation enthalpy by a further 1.1 kcal/mol ($\Delta H_a(298) = 13.2$ kcal/mol). Thus, it is clear that the involvement of water, in a catalytic role, is essential for this decomposition to occur. Furthermore, the involvement of two water molecules (c) appears to be in better agreement with the experimental results, although both pathways are equally viable.

It should be pointed out that water was always present in the reaction mixture in small but sufficient amounts to participate in the reaction (molar ratio **2**/H₂O = 1:2 in acetone-*d*₆ (by ¹H NMR)). Furthermore, the addition of water (5 ± 1 vol %) to acetone-*d*₆ solutions (-60 °C) did not change significantly the kinetic and activation parameters of the decomposition of **2**.²⁹

Table 5. Energies and Thermodynamics of the Uncatalyzed and Catalyzed Decomposition of Hemiortho Ester (**2a**)^a

system	sym	E, ΔE	ΣZPE	H, ΔH(298)	ΣS	G, ΔG(298)	μ
Route (a)							
reactant	C ₁	-382.91221	78.4	-382.77937	81.99	-382.81832	2.49
TS1	C ₁	39.0	75.0	35.5	79.8	36.1	3.27
product	C ₁	-7.4	77.7	-7.4	92.2	-10.4	2.02
Route (b)							
reactant	C ₁	-459.34830	94.7	-459.18681	96.0	-459.23240	3.98
TS1	C ₁	19.2	90.6	14.3	88.3	16.6	2.51
product	C ₁	-8.9	93.6	-9.1	103.4	-11.4	1.77
Route (c)							
reactant	C ₁	-535.79300	110.6	-535.60374	106.9	-535.65453	3.11
TS1	C ₁	19.5	105.3	13.2	98.7	15.7	1.88
product	C ₁	-6.7	110.1	-6.7	111.5	-8.1	1.68

^a Relative energies, enthalpies, and free energies are reported in kcal/mol, and their absolute counterparts are given in hartrees. Entropies are in cal/(mol K), and dipole moments, in debye. All calculations performed with the B3LYP hybrid functional and Pople's 6-31G(d,p) basis set. Relative values are taken with respect to the reactant value in each route.

The involvement of water in the decomposition was also confirmed by the magnitude of the solvent isotope effect for the decomposition of **2e**, i.e., $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 4.6 \pm 1.2$,³⁰ which indicated a considerable proton transfer in the transition state of this reaction (Table 6).

Mechanism for the Decomposition of the Hydrotrioxides.

A NMR and GC/MS investigation of the products in the decomposition mixture after warming the ozonized solution of **1a–h** to room temperature in *tert*-butyl methyl ether revealed the presence of the corresponding hydroxy ester and oxygen (³O₂/¹O₂) in nearly quantitative yields.³¹ Hemiortho ester could not be detected (by NMR) during the decomposition of the

(29) We have not observed any water drop out of solution as the water/acetone mixture is cooled from -10 to -60 °C.

(30) The obtained value for the solvent isotope effect is in good agreement with that already reported by McClelland as an unpublished observation. (McClelland, R. A.; Santry, L. J. *Acc. Chem. Res.* **1983**, *16*, 394.)

(31) Small amounts of hydrogen peroxide were detected in all mixtures after the decomposition of the hydrotrioxides under investigation.

Table 6. Solvent Kinetic Isotope Effect for the Decomposition of Hemioortho Ester (**2e**) and Hydrotrioxide (**3e**), Formed in the Low-Temperature Ozonation of 2-Phenyl-4,4,5,5-tetramethyl-1,3-dioxolane (**1e**) in Acetone- d_6 with Added 5 vol % H_2O or D_2O ^{a,b}

species	T, °C	$k \times 10^4, s^{-1}$				$k_{H_2O}/k_{D_2O}^c$	E_a , kcal/mol	log A
		OOOH ^d	t-CH ₃ ^e	c-CH ₃ ^f	Ph ^g			
2e	-5		1.48 ^h	1.27 ^h	1.20 ^h	3.7		
			0.38 ⁱ	0.34 ⁱ	0.34 ⁱ			
	0		2.50 ^h	2.31 ^h	2.28 ^h	4.9	14.9 ^{e,h}	8.4 ^{e,h}
			0.51 ⁱ	0.49 ⁱ	0.44 ⁱ		14.7 ^{e,i}	7.5 ^{e,i}
	5		4.50 ^h	4.47 ^h	4.40 ^h	4.6	15.5 ^{f,h}	8.8 ^{f,h}
			1.02 ⁱ	0.98 ⁱ	0.89 ⁱ		14.9 ^{f,i}	7.7 ^{f,i}
	10		7.71 ^h	7.31 ^h	6.91 ^h	6.7	15.7 ^{g,h}	8.9 ^{g,h}
			1.17 ⁱ	1.10 ⁱ	0.98 ⁱ		14.6 ^{g,i}	7.5 ^{g,i}
	15		9.72 ^h	8.97 ^h	8.86 ^h	3.5		
			2.78 ⁱ	2.63 ⁱ	2.52 ⁱ			
3e	-25	1.00 ^h	0.87 ^h	0.98 ^h	1.6			
			0.51 ⁱ	0.64 ⁱ				
	-20	2.58 ^h	2.19 ^h		1.5	19.6 ^{d,h}	13.4 ^{d,h}	
			1.44 ⁱ			20.5 ^{e,i}	13.9 ^{e,i}	
	-15	4.88 ^h	4.10 ^h	4.30 ^h	1.5	18.6 ^{e,h}	12.5 ^{e,h}	
			2.80 ⁱ	2.77 ⁱ		20.3 ^{f,i}	13.8 ^{f,i}	
	-10	11.2 ^h	9.30 ^h		1.3	19.0 ^{f,h}	12.8 ^{f,h}	
			6.92 ⁱ					
	-5	22.2 ^h	17.3 ^h	23.2 ^h	1.6			
			11.5 ⁱ	13.9 ⁱ				

^a **1e** = (0.10 ± 0.01) M, **2e** = (0.09 ± 0.01) M, **3e** = (0.01 ± 0.005) M. ^b Standard deviation ± 10%. ^c Standard deviation ± 20%. ^d Following decay of the OOOH absorption in the hydrotrioxide **3e**. ^e Following decay of the *trans*-4,5-CH₃ absorptions relative to the OH (OOH) group in the hemioortho ester **2e** (hydrotrioxide **3e**). ^f Following decay of the *cis*-4,5-CH₃ absorptions relative to the OH (OOH) group in the hemioortho ester **2e** (hydrotrioxide **3e**). ^g Following decay of the absorptions of the meta and para protons in the benzene ring in **2e**. ^h Runs with 5 vol % H_2O in acetone- d_6 . ⁱ Runs with 5 vol % D_2O in acetone- d_6 .

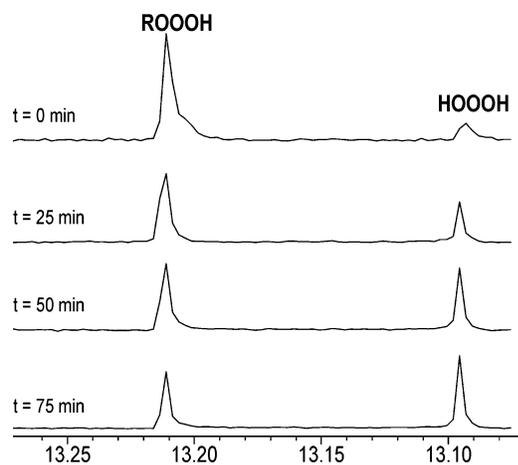


Figure 3. Segments of 1H NMR spectra of **3h** and HOOOH in acetone- d_6 at -20 °C. The disappearance of the OOOH absorption at δ 13.21 ppm, belonging to **3h**, and appearance of HOOOH as a function of time. After 150 min, the CH₃, CH₂, and phenyl NMR absorptions of **3h** completely disappeared.

hydrotrioxides. However, when acetal hydrotrioxides **3d–h** were allowed to decompose slowly (temperature range -20 to $+10$ °C), dihydrogen trioxide (HOOOH) was formed in considerable amounts with the corresponding hydroxy ester (see Figure 3). Again, no hemioortho ester could be detected during these processes. The identity of HOOOH was checked by NMR spectroscopic techniques as already described.^{8d} Also, the kinetic and activation parameters for the decomposition of this polyoxide were in accordance with those of our previous observations (see also Table 7).^{8d}

Kinetic and activation parameters for the decomposition of the hydrotrioxides **3a–h** are collected in Table 7. A radical inhibitor such as, e.g., 2,6-di-*tert*-butyl-4-methylphenol has a relatively small effect on the rates and the activation parameters

for the decomposition of **3a–h**. This observation is consistent with the proposed mechanism.

Several pathways of decomposition were studied for the prototype, 2-hydrotrioxy-2-methyl-1,3-dioxolane (**3a**), to rationalize the experimental results. The decomposition of the hydrotrioxide to form the hydroxy ester can occur in either a direct mechanism, a one-step mechanism, or via the hemioortho ester intermediate, a two-step mechanism (Scheme 3).

Three different paths were considered within the framework of a one-step mechanism: (a) an intramolecular transfer of H(OOO) between the hydrotrioxide substituent and the O in the 1 or 3 position of the ring; (b) assistance by a water molecule to catalyze the transfer in path (a) and resulting in the production of both water and O₂ ($^1\Delta_g$); (c) a conformational variation of (b), whereby the rotation of the OOOH group allows the direct formation of HOOOH in addition to the hydroxy ester.

Pathway (a) requires a rotation of the OOOH substituent into a conformation that leads to the formation of an intramolecular hydrogen bond stabilizing the molecule by 2.0 kcal/mol ($\Delta H(298)$, Table 8). The formation of the hydroxy ester then occurs in a concerted cyclic fragmentation reaction involving the cleavage of the OC–OC, O–O, and O–H single bonds and the formation of a new O–H bond as well as a C=O and O=O double bond combined with a proton transfer. This process occurs with an activation enthalpy $\Delta H_a(298) = 20.1$ kcal/mol (Table 8) and a reaction enthalpy of -21.6 kcal/mol. A van der Waals complex is generated, which is stabilized by an enthalpy of 3.3 kcal/mol (BSSE corrected value, Table 8).

The catalytic role of a water molecule is tested in pathway (b). Its effect is not nearly as pronounced as was observed in the decomposition of the hemioortho esters. Nonetheless, a slight decrease in the activation enthalpy is observed ($\Delta H_a(298) = 18.2$ kcal/mol; Table 8), whereas the reaction enthalpy is close to that of path (a) ($\Delta H_R = -19.0$ kcal/mol; Table 8). Path (b)

Table 7. Kinetic and Activation Parameters for the Decomposition of Hydrotrioxides (ROOOH, **3**) and Dihydrogen Trioxide (HOOOH), Formed in the Low-Temperature Ozonation of Cyclic Acetals (**1**) in Various Solvents^{a,b}

solvent	T, °C	R-OOOH (3)							HOOOH				
		δ , ppm	$k \times 10^4$, s ⁻¹					E_a , kcal/mol	log A	δ , ppm	$k \times 10^4$, s ⁻¹	E_a , kcal/mol	log A
			ROOOH	OOOH ^c	CH ₃ ^d	t-CH ₃ ^e	c-CH ₃ ^f						
(3a) acetone- <i>d</i> ₆	10	12.88	2.48	2.44			17.5 ± 1.6 ^c	9.9 ± 1.1 ^c					
methyl acetate	10	12.39	2.43	2.45			19.0 ± 1.5 ^c	11.2 ± 1.1 ^c					
<i>tert</i> -butyl methyl ether	10	12.63	0.63				20.5 ± 1.5 ^d	12.3 ± 1.1 ^d					
(3b) acetone- <i>d</i> ₆	10	12.99	16.60				22.8 ± 1.7 ^c	14.9 ± 1.2 ^c					
		13.23	(6.37) ^g	(5.74) ^{g,h}			(18.2 ± 1.5) ^{c,g}	(10.9 ± 1.1) ^{c,g}					
<i>tert</i> -butyl methyl ether	10	12.75	11.66				24.1 ± 1.7 ^c	15.8 ± 1.2 ^c					
(3c) acetone- <i>d</i> ₆	10	13.21	10.90	11.24 ⁱ			20.0 ± 1.5 ^c	12.5 ± 1.1 ^c					
(3d) acetone- <i>d</i> ₆	10	12.77	3.17	3.48			23.0 ± 1.7 ^c	14.3 ± 1.2 ^c	12.84	1.55	21.8 ± 2.0	13.2 ± 1.3	
methyl acetate	10	12.29	4.78	3.09			23.0 ± 1.7 ^c	14.3 ± 1.2 ^c	12.15	7.86	18.6 ± 1.8	11.0 ± 1.0	
<i>tert</i> -butyl methyl ether	10	12.54	2.71	2.63			20.6 ± 1.6 ^d	12.6 ± 1.1 ^d					
(3e) acetone- <i>d</i> ₆	-15	12.81	2.42		2.35	2.36	21.3 ± 1.6 ^c	14.5 ± 1.2 ^c	13.06				
<i>tert</i> -butyl methyl ether	-15	12.50	2.17				23.3 ± 1.7 ^c	16.1 ± 1.3 ^c	12.63				
(3f) acetone- <i>d</i> ₆	-15	13.40	48.0	46.5 ⁱ			18.6 ± 1.7 ^c	13.5 ± 1.2 ^c	13.05	0.56	15.1 ± 1.3	8.6 ± 0.7	
(3g) acetone- <i>d</i> ₆	-15	13.27	1.87	1.90	1.81	1.88	16.3 ± 1.5 ^c	10.3 ± 1.0 ^c	13.06				
	15						15.4 ± 1.6 ^d	9.6 ± 1.0 ^d	12.78	3.34	16.0 ± 1.4	8.7 ± 0.7	
methyl acetate	-15	12.63	6.23	8.50	7.25	7.24	15.2 ± 1.6 ^c	9.8 ± 1.0 ^c	12.48				
	15						16.2 ± 1.6 ^d	10.7 ± 1.1 ^d	12.23	39.2	15.6 ± 1.2	9.3 ± 0.8	
(3h) acetone- <i>d</i> ₆	-15	13.17	0.64	0.59 ^h	0.52	0.50	16.4 ± 1.5 ^c	9.8 ± 1.0 ^c	12.97				
	15						16.7 ± 1.6 ^h	10.0 ± 1.1 ^h	12.79	4.08	16.1 ± 1.2	8.9 ± 0.8	

^a **1** = (0.1 ± 0.01) M, **3** = (0.02 ± 0.01). ^b Standard deviation ± 10%. ^c Following decay of the OOOH absorption. ^d Following decay of the geminal 2-CH₃ absorption. ^e Following decay of the *trans*-4,5-CH₃ absorptions relative to the OOOH group in the hydrotrioxide **3**. ^f Following decay of the *cis*-4,5-CH₃ absorptions relative to the OOOH group in the hydrotrioxide **3**. ^g For comparison, 2-hydrotrioxy-2-(*para*-NO₂-phenyl)-4,4,5,5-tetramethyl-1,3-dioxolane. ^h Following decay of the absorptions of meta and para protons in the benzene ring. ⁱ Following decay of the geminal 2-H absorption in the hydrotrioxide **3c**.

Table 8. Energies and Thermodynamics for the Decomposition of 2-Hydrotrioxy-2-methyl-1,3-dioxolane (**3a**)^a

system	sym	$\Sigma E, \Delta E$	ΣZPE	$\Sigma H, \Delta H(298)$	ΣS	$\Sigma G, \Delta G(298)$	μ
Path (a)							
reactant	C ₁	-533.18065	82.7	-533.03877	93.4	-533.08317	2.20
H-bond	C ₁	-2.2	83.1	-2.0	92.6	-1.7	3.55
TS1	C ₁	21.3 (23.5)	80.0	18.1 (20.1)	89.0	19.4 (21.7)	3.59
prod _{comp}	C ₁	-21.5 (-19.3)	80.9	-21.6 (-19.6)	109.8	-26.5 (-24.8)	1.87
prod _{sep}	C ₁	-17.1 (4.4)	79.8	-18.3 (3.3)	141.2	-32.6 (-6.1)	2.02
Path (b)							
react _{sep}	C ₁	-609.60038	96.1	-609.43337	139.9	-609.49985	2.20
react _{comp}	C ₁	-10.0	98.9	-8.0	105.8	-2.2	3.79
TS	C ₁	13.1 (23.1)	94.6	10.2 (18.2)	100.7	17.5 (19.7)	4.57
prod _{comp}	C ₁	-28.6 (-18.6)	96.5	-27.0 (-19.0)	129.6	-28.2 (-26.0)	3.58
prod _{sep}	C ₁	-18.7 (9.9)	93.2	-20.0 (7.0)	187.7	-38.6 (-10.4)	3.58
Path (c)							
react _{sep}	C ₁	-609.60038	96.1	-609.43337	139.9	-609.49985	2.20
react _{comp}	C ₁	-10.5	97.9	-8.9	110.9	-0.2	2.46
TS	C ₁	38.2 (48.7)	94.8	35.9 (44.8)	103.7	46.7 (46.9)	1.31
prod _{comp}	C ₁	-25.1 (-14.6)	98.5	-22.9 (-14.0)	114.7	-15.3 (-15.1)	2.90
prod _{sep}	C ₁	-20.9 (4.2)	96.4	-20.5 (2.4)	153.0	-6.3 (9.0)	2.02
Path (f)							
react _{sep}	C ₁	-686.02012	109.5	-685.82796	186.4	-685.91654	2.20
react _{comp}	C ₁	-20.3	114.7	-16.5	119.8	3.4	3.26
TS	C ₁	-0.1 (20.2)	110.1	-2.0 (14.5)	113.8	19.7 (16.3)	2.83
prod _{comp}	C ₁	-30.2 (-9.9)	113.7	-26.8 (-10.3)	128.1	-9.4 (-12.8)	1.37
prod _{sep}	C ₁	-8.7 (21.5)	107.6	-10.0 (16.8)	224.0	-21.1 (-11.7)	2.49

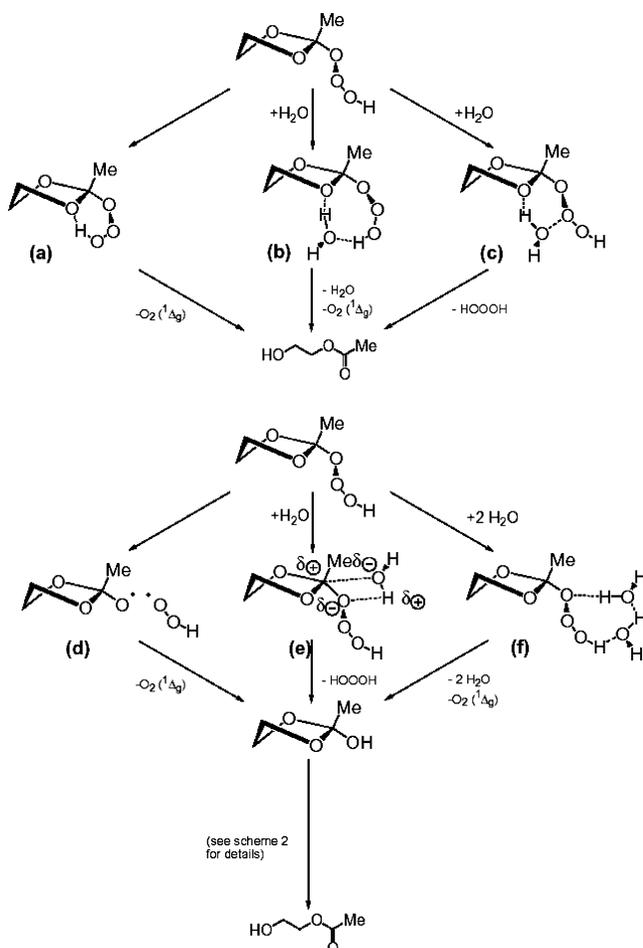
^a Relative energies, enthalpies, and free energies are reported in kcal/mol, and their absolute counterparts are given in hartrees. Entropies are in cal/(mol K), and dipole moments, in debye. All calculations performed with the B3LYP hybrid functional and Pople's 6-31G(d,p) basis set. Relative values are with respect to the reactant energy and include BSSE corrections. Where more than one structure is summarized into the results, the symmetry and dipole moment are reported for the larger structure. The values in parentheses are (a) for the complexes, relative to the reactant complex, and (b) for the separated products relative to the complexed products.

is somewhat more likely than path (a) due to the participating water molecule.

A rotation of the HOOO group is required to form the reactant complexes of paths (a) and (b). However, this rotation can be

avoided when HOOOH is produced from ROOOH and H₂O in path (c). The reaction shown in Scheme 3 proceeds with $\Delta H_a(298) = 44.8$ kcal/mol (Table 8), which is too large to provide an explanation for the appearance of HOOOH under

Scheme 3



the current experimental conditions (see below). Path (c) yields the hydroxy ester and HOOOH with $\Delta H_{\text{R}}(298) = -14.0$ kcal/mol (Table 8).

Experimentally, it was observed that the decomposition of the acetal hydrotrioxides occurred without the production of hemioortho esters. However, it was shown in the previous section that reaction of the hemioortho esters to produce the hydroxy ester occurs with a low activation barrier (13.5 ± 1.0 kcal/mol) when one or two water molecules can assist in this reaction. As this is true in the case of the decomposition of the acetal hydrotrioxides, we considered the possibility of a two-step mechanism, involving the production of the hemioortho ester and its subsequent decomposition into the hydroxy ester (Scheme 3).

Path (d) implies OO dissociation without specific assistance by the solvent or water. Assuming an OO bond dissociation energy of 30 kcal/mol (BDE of CF₃O–OOCF₃ 30.1 kcal/mol;³² BDE of HOOOH 33.7 kcal/mol; for heats of formation, see ref 8a), path (d) is less likely compared to paths (a) or (b).

A spontaneous heterolytic dissociation of ROOOH in acetone solution is not possible in view of a calculated increase in the reaction enthalpy by more than 60 kcal/mol (Table 3). The formation of the OOOH anion can only proceed by assistance of solvent and/or water molecules as formulated for path (e). A frontside attack by water (Scheme 3e) and a backside attack in

the sense of an S_N2 reaction (not shown in Scheme 3) have been investigated in this work. In both reaction modes, four O atoms and an alkyl group have to be arranged around the C atom, which leads to strong repulsion between the O atoms and an unfavorable energy. Therefore, it is not surprising that all attempts to locate a TS for path (e) (either as water-assisted ionic cleavage or S_N2 reaction) were unsuccessful.

In path (f) two water molecules catalyze the decomposition reaction. First, a diwater complex of the acetal hydrotrioxide is formed, which is 16.5 kcal/mol more stable than the separated monomers (BSSE corrected enthalpy, Table 8). A concerted fragmentation reaction can occur that is characterized by the breaking of four bonds (an O–O single bond and three O–H bonds; Scheme 3) and the simultaneous formation of four new bonds (the π -bond of O₂, (¹Δ_g), and three new OH bonds). The calculated activation enthalpy $\Delta H_{\text{a}}(298)$ is 14.5 kcal/mol. Note that the energy barrier is reduced by 5.6 kcal/mol by vibrational effects due to the loss of three OH bonds, whereas the free activation energy is 16.3 kcal/mol due to a further loss (–6 entropy units; Table 8) in entropy. The reaction is exothermic ($\Delta H_{\text{R}}(298) = -10.3$ kcal/mol; $\Delta G_{\text{R}}(298) = -12.8$ kcal/mol; Table 8), and the conservation in the number of hydrogen bonds between the reactant and product complexes implies that the complexation energy of the product should be comparable to that of the reactant. This was indeed observed ($\Delta E = -21.5$ kcal/mol; BSSE corrected).

Solvent calculations, using the dielectric constant of acetone, were carried out on the optimized structures of the reaction and were found to have a slightly negative effect on free energy changes ($\Delta G_{\text{a}}(298) = 19.5$ kcal/mol; $\Delta G_{\text{R}}(298) = -8.6$ kcal/mol) along the reaction path (f). Thus, as the subsequent decomposition to form the hemioortho ester requires less energy than the initial step, this mechanism should be competitive with and possibly dominate those of paths (a) and (b) due to the lower activation enthalpy required.

Somewhat smaller activation parameters for the decomposition of the hydrotrioxides (**3**) in acetone-*d*₆ and methyl acetate as compared to values in *tert*-butyl methyl ether suggest that the decomposition is proceeding by several simultaneous first-order processes involving paths such as (a), (b), or (f). In addition, water assisted decomposition might be more important in acetone than in *tert*-butyl methyl ether, due to the different solubilities of water in these solvents.

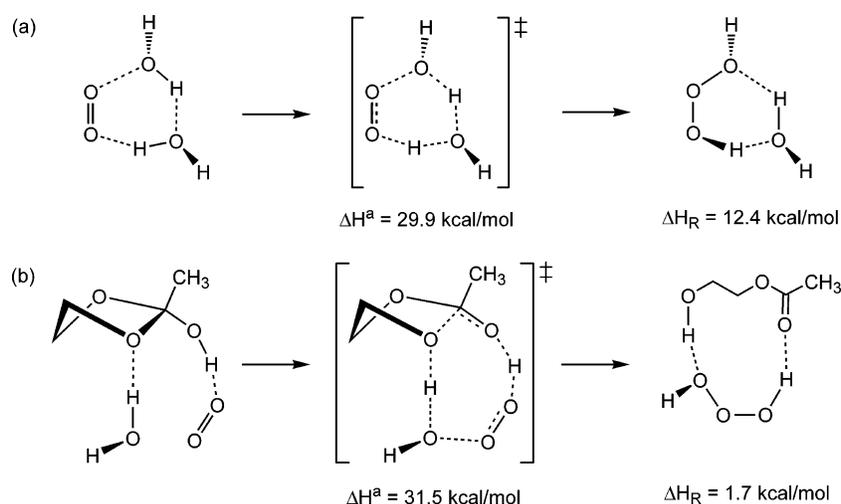
Generation of HOOOH. The generation of HOOOH, which was observed experimentally, remains to be explained. Paths (c) and (e) both propose direct mechanisms of generating HOOOH via the decomposition of the acetal hydrotrioxide. However, in both these cases the repulsion of the oxygen lone pairs was such that the barrier was found to be too large (path (c), Scheme 3) or the TS proved unattainable (path (e), Scheme 3). Thus, several mechanisms were proposed that could explain the generation of HOOOH based upon the intermediates and/or byproducts of the acetal hydrotrioxide decomposition. The most prevalent of these byproducts was O₂ (¹Δ_g).

The formation of HOOOH through pericyclic reaction involving water and O₂ (¹Δ_g) has been studied by Goddard et al.^{33,34} The cyclization reaction involving two water molecules (path (a); Scheme 4) and O₂ (¹Δ_g) requires an activation enthalpy ΔH_{a} -

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Scheme 4

Table 9. Energies and Thermodynamics for the Formation of HOOOH^a

system	sym	<i>E</i> , Δ <i>E</i>	ΣZPE	<i>H</i> , Δ <i>H</i> (298)	Σ <i>S</i>	<i>G</i> , Δ <i>G</i> (298)	<i>μ</i>
Path (a)							
react _{sep}	C _{2v}	-303.15952	29.2	-303.10215	142.0	-303.16961	2.04
react _{comp}	C ₁	-8.9	33.8	-5.9	81.3	12.3	1.34
TS1	C ₁	24.8 (33.7)	31.7	24.0 (29.9)	69.3	45.8 (33.5)	1.97
prod _{comp}	C ₁	2.8 (11.7)	35.2	6.5 (12.4)	75.9	26.3 (14.0)	1.62
prod _{sep}	C ₁	11.8 (9.0)	32.4	13.5 (7.0)	75.9	24.0 (-2.3)	1.13
Path (b)							
react _{sep}	C ₁	-609.65199	94.2	-609.48692	177.5	-609.57125	2.49
react _{comp}	C ₁	-8.7	97.6	-6.0	113.2	13.1	4.09
TS	C ₁	26.6 (35.3)	95.3	25.5 (31.5)	99.7	48.6 (48.6)	3.34
prod _{comp}	C ₁	-7.8 (0.9)	98.4	-4.3 (1.7)	115.6	14.1 (1.0)	1.63
prod _{sep}	C ₁	3.9 (11.7)	96.4	5.6 (9.9)	153.0	12.9 (1.2)	2.02

^a Relative energies, enthalpies, and free energies are reported in kcal/mol, and their absolute counterparts are given in hartrees. Entropies are in cal/(mol K), and dipole moments, in debye. All calculations performed with the B3LYP hybrid functional and People's 6-31G(d,p) basis set. Relative values are with respect to the reactant energy and are BSSE corrected. The values in parentheses are (a) for the complexes, relative to the reactant complex, and (b) for the separated products relative to the complexed products.

(298) of 29.9 kcal/mol (Table 9) in good agreement with the value given in the literature (33.1 kcal/mol).³³ Calculation of the reaction barrier with BD(T)/6-311G(d,p) did not lead to any reduction in the barrier. An additional method (path (b); Scheme 4) of HOOOH production was considered in light of the generated hemiortho ester intermediate (path (f); Scheme 3) which occurs in the decomposition of the acetal hydrotrioxide. Although the product of this reaction is more stable than in the first case ($\Delta H_R(298) = 1.7$ kcal/mol; Table 9), the activation enthalpy for the reaction is again too large ($\Delta H_a(298) = 31.5$ kcal/mol; Table 9).

In this connection some basic considerations concerning the lifetime of O₂ (¹Δ_g), its possibility to leave the solvent cage, the possibility of energy dissipation of the reaction complex, and the presence of water are appropriate. Various spectroscopic studies in connection with quenching experiment determined the lifetime of O₂ (¹Δ_g) in water and acetone-*d*₆ to be 3 and 992 μs, respectively.³⁵ This might be considered to be too short to leave the solvent cage or to undergo energy dissipation by

collisions with solvent molecules. However, a calculation of the diffusion coefficients for the reaction complexes considered in Scheme 3 based on Brownian motions, the viscosities of the solvents used (acetone, methyl acetate, *tert*-butyl methyl ether, and water as a reference), and the calculated geometries of the molecules involved revealed that the lifetime of O₂ (¹Δ_g) is sufficient for both vibrational and collisional energy dissipation. This means that the excess energy formed in reactions (a), (b), or (f) of Scheme 3 is not available to surmount a barrier of 30 kcal/mol.

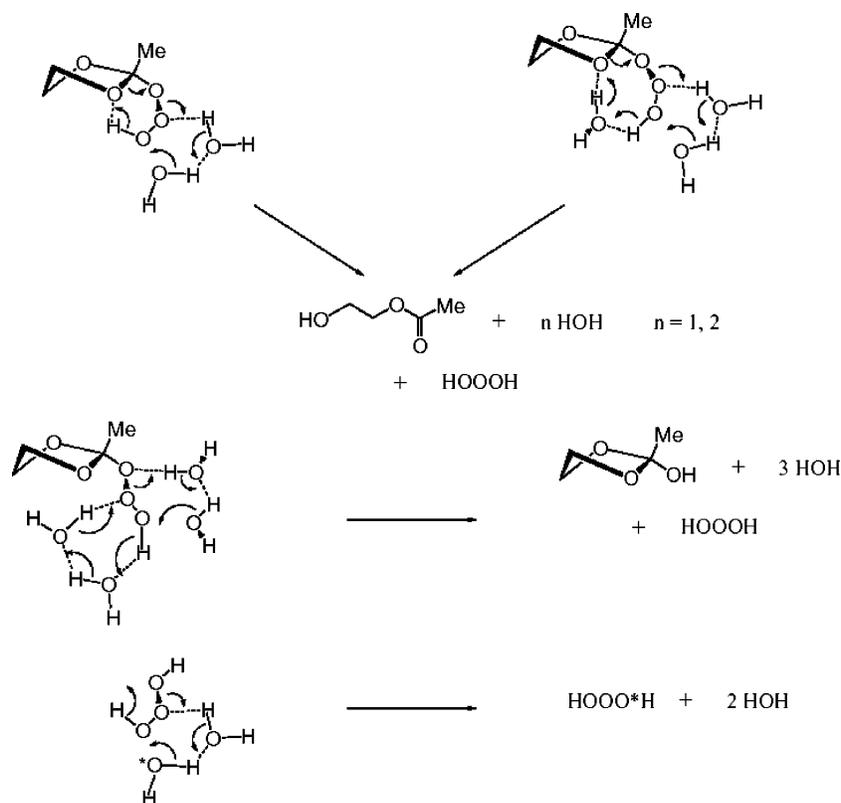
The creation of HOOOH out of O₂ (¹Δ_g) requires the formation of a new O–O bond, which is an energetically expensive process (lone pair–lone pair repulsion between the O atoms has to be overcome). Therefore, the formation of HOOOH will have a higher chance if the OOO unit is largely conserved and only an O atom is exchanged according to the rearrangement of the HOOOH–H₂O–H₂O complex shown in Scheme 5.

There are other water molecules than those considered in Scheme 3, which are H-bonded to the acetal hydrotrioxide. They can play a role in connection with the HOOOH formation from ROOOH as indicated in Scheme 5 where reactions (a), (c), and (f) of Scheme 3 were considered as starting points. Work is in progress to determine the barriers of these reactions.

(34) (a) Wentworth, P., Jr.; Jones, L. H.; Wentworth, A. D.; Zhu, X. Y.; Larsen, N. A.; Wilson, I. A.; Xu, X.; Goddard, W. A., III; Janda, K. D.; Eschenmoser, A.; Lerner, R. A. *Science* **2001**, *293*, 1806. (b) Xu, X.; Goddard, W. A., III. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 15308. (c) Wentworth, P., Jr.; Wentworth, A. D.; Zhu, X. Y.; Wilson, I. A.; Janda, K. D.; Eschenmoser, A.; Lerner, R. A. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 1490. (d) Nyffeler, P. T.; Eltepu, L.; Boyle, N. A.; Wong, C.-H.; Eschenmoser, A.; Lerner, R. A.; Wentworth, P., Jr. *Angew. Chem., Int. Ed.* **2004**, *43*, 4656.

(35) Schweitzer, C.; Schmidt, R. *Chem. Rev.* **2003**, *103*, 1685 and references therein.

Scheme 5



Conclusions

In the present study we have demonstrated that hemioortho esters (ROH) and acetal hydrotrioxides (ROOOH) are formed in good yields in the low-temperature ozonation of 1,3-dioxolanes and 1,3-dioxanes. This is an efficient new method for the preparation of the hemioortho esters under investigation.

The formation of these tetrahedral intermediates involves the abstraction of the hydride anion from the parent acetal by ozone to form an ion pair, $\text{R}^+ \text{ } ^-\text{OOOH}$. The ion pair subsequently collapses to form either the hemioortho ester or the hydrotrioxide, with an intermediate H-transfer step involved in the formation of the latter.

Water (always present in the reaction mixture) plays a crucial role in the decomposition of hemioortho esters to hydroxy esters by acting as a bifunctional catalyst. Two molecules of water are most likely involved in a cyclic transition state for these reactions (pericyclic process).

Dihydrogen trioxide (HOOOH) is (surprisingly) formed, besides the corresponding hydroxy esters and molecular oxygen ($^3\text{O}_2/{}^1\text{O}_2$), during the decomposition of the hydrotrioxides. Several mechanistic possibilities for the formation of these products were tested: (a) intramolecular transfer of the proton in ROOOH to form ROH and singlet oxygen ($\text{O}_2 \text{ } ^1\Delta_g$); (b) the homolytic scission of the RO–OOH to form the radical pair, $\text{RO}^\bullet \text{ } ^\bullet\text{OOH}$, with subsequent formation of the hydroxy ester (via hemioortho ester) and oxygen ($^3\text{O}_2/{}^1\text{O}_2$); and (c) the assistance of one or more water molecules in the decomposition of ROOOH. Dihydrogen trioxide (HOOOH) is most likely formed

directly from ROOOH–water complexes, whereas the reaction of singlet oxygen with water is energetically too demanding to take place under the conditions of the ROOOH decomposition investigated.

Experimental evidence has been provided which shows, for the first time, that ozone is converted into HOOOH via ROOOH. This new pathway of the HOOOH production sheds a new light on the mechanism of ozonation reactions. This simplest of polyoxides most likely participates in various reactions in biological, environmental, and atmospheric systems. Theoretical work on the elucidation of this reaction mechanism is currently in progress.

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Supporting Information Available: Complete kinetic and activation parameters for the decomposition of hemioortho esters (2), hydrotrioxides (3), and dihydrogen trioxide (HOOOH). Geometries and energy data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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