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Evidence for the $HOOO^-$ Anion in the Ozonation of 1,3-Dioxolanes: Hemiortho Esters as the Primary Products

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Reactions of ozone with organic materials are at the focus of current interest. Ozonation reactions play important role in the polluted atmosphere,[1] for wastewater purification,[2] in ozone toxicity studies,[2] and in chemical synthesis.[3] Ozone can initiate oxidation (e.g., by O_3 addition and subsequent OO bond rupture, or alternatively by O transfer to a heteroatom such as N, S, etc.), abstract a H atom ($HO_3^\bullet$ formation), or even abstract a hydride ion (HO_3^- formation). The latter reactions are discussed in connection with the antibody-catalyzed oxidation of water by singlet dioxygen[4] and have led to an increased interest into the elusive HO_3^- anion.[5]

In this work, we study HO_3^- formation by using dioxolanes as suitable model systems that support hydride abstraction by ozone due to the fact that generation of a dioxolyl cation is electronically supported. Deslongchamps and Moreau first reported that aldehyde acetals reacted with ozone to give esters in high yield.[6a] Deslongchamps et al. also demonstrated that acetals react with ozone when they can take a conformation where each oxygen has an electron lone pair oriented antiperiplanar to the C−H bond ("Deslongchamps' hypothesis of stereoelectronic control").[6b,7] More recently, they also reported that synperiplanar oxygen lone pairs play a similar role in influencing this oxidation reaction.[6c]

Acetal hydrotrioxides (ROOOH), which have been proposed as the labile intermediates in most investigations of the ozonolysis of acetals, have actually been detected in these reactions.[8] Several different mechanisms for the oxidation of the C−H bonds in acetals by ozone to form hydrotrioxides (ROOOH) have been proposed: (a) a concerted 1,3-dipolar insertion,[9] (b) a mechanism involving H-atom abstraction by ozone to form a radical pair ($R^\bullet\ {}^\bullet OOOH$),[7a] and (c) a hydride-ion transfer to form a carbenium ion and the hydrotrioxide ion ($R^+\ {}^-OOOH$).[7a,10,11] Unfortunately, an unambiguous substantiation of either of the proposed mechanisms is still lacking.

Here we report that low-temperature ozonation of 2-methyl-1,3-dioxolane (**1a**) in acetone-d_6, methyl acetate, and *tert*-butyl methyl ether produced both the corresponding acetal hydrotrioxide ROOOH (**3a**) and the hemiortho ester (**2a**)[12] in molar ratio 1:5 (−78 °C). Both intermediates were fully characterized by ^1H, ^{13}C, and ^{17}O NMR spectroscopy (Table 1), and at higher temperatures, they both decomposed to the corresponding hydroxy ester. The kinetic and activation parameters of the decomposition of acetal hydrotrioxide **3a** (Table 2) indicate that the homolytic cleavage of the RO−OOH bond to produce $RO^\bullet$ and ${}^\bullet OOH$ radicals is the first step of the decomposition process. These radicals either abstract the hydrogen atom from the substrate R−H to produce the hemiortho ester **2a** and hydrogen peroxide or react in the solvent cage to produce **2a** and singlet oxygen, Δ^1O_2.[13,14] However, kinetic and activation parameters of the decomposition of **2a** indicate polar decomposition pathways, most likely involving water as the catalyst.[15,16] Similar observations were also made during the study of the ozonation of 1,3-dioxolane (**1b**).

Table 1. Selected ^1H, ^{13}C, and ^{17}O NMR Chemical Shifts of the Hemiortho Esters (**2**), and the Acetal Hydrotrioxides (**3**) in Acetone-d_6 at −60 °C[a]

species	^1H NMR			^{13}C NMR			
X	X	R[b]	CH_2	C(1)	R[b]	CH_2	^{17}O NMR[c]
(**2a**) OH	6.42	1.49	3.89 4.02	119.90 122.06	23.09 24.79	64.58 65.67	96.0
(**3a**) O3O2O1H	13.66	1.61	4.05 4.12	124.47 125.52	20.44 20.48	66.44	305 (O1) 355 (O3) 455 (O2)
(**2b**) OH	6.63	6.01	3.86 4.02	112.44		64.10	
(**3b**) OOOH	13.94	6.49	4.04 4.08	116.82 117.41		64.74 64.92	

[a] **2** = (0.8 ± 0.2) M. Molar ratio **2a**:**3a** = 5:1, **2b**:**3b** = 4:1. (In the case of 2-phenyl-1,3-dioxolane; molar ratio **2c**:**3c** = 10:1). Initial concentration of **1** = (1.0 ± 0.2) M; time of ozonation, 20 min; flow of O_3 in O_3/O_2 or O_3/nitrogen mixture, 0.1−0.2 mol/min. [b] For R, see Scheme 1. [c] The ozonation was performed by ^{17}O-enriched O_3, obtained by the passage of ^{17}O-enriched oxygen (58% $^{17}O_2$, ISOTEC) through a semimicro ozonator.[14b]

We have recently determined that the $HOOO^-$ anion can adopt a singlet or triplet state.[5] Although the singlet $HOOO^-$ anion in the gas phase possesses, according to CCSD(T) calculations, the longest OO−OH bond ever reported for a peroxide (1.80 Å), the anion is remarkably stable in the gas phase at 298 K. Despite its peculiar structure, it is a covalently bonded molecule rather than a van der Waals complex, which can be concluded from the analysis of the geometry, electron density distribution, and simple bonding models. Nonspecific solvation in aqueous solution substantially increases the stability of the singlet $HOOO^-$ anion as is reflected by its geometry and particularly an OO−OH bond of 1.51 Å.[5] Similar conclusions hold for an acetone solution. Ozone abstracts hydride from 2-methyl-1,3-dioxolane, thus forming a stable carbenium ion and the $HOOO^-$ anion in an exergonic reaction ($\Delta_R G$ = −28.9 kcal/mol, PISA/B3LYP/6-311++G(3df,3pd)[17−19] with ϵ = 20.7 for acetone[20]) (Scheme 1), while the hydrogen abstraction reaction yielding $HOOO^\bullet$ and a dioxolane radical is slightly endergonic ($\Delta_R G$ = 0.2 kcal/mol) under the same conditions.

The ion pair, $R^+\ {}^-OOOH$, can then collapse directly in the solvent cage to either the tetrahedral intermediate, that is, the hemiortho ester (**2a**) ($\Delta_{Ra}G$ = −40.3 kcal/mol) or the hydrotrioxide (**3a**) ($\Delta_{Rb}G$ = −29.5 kcal/mol), where the former process is favored in line with the calculated charge distribution of the O3O2O1H anion

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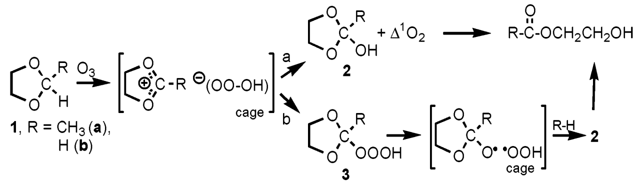
Table 2. Kinetic and Activation Parameters for the Decomposition of the Hemiortho Ester **2a** and the Hydrotrioxide **3a** in Various Solvents[a]

		R–OH (**2a**)					R–OOOH (**3a**)				
			$k \times 10^4$,[b] s^{-1}					$k \times 10^4$,[b] s^{-1}			
solvent	T, °C	δ, ppm	OH[d]	CH_3	E_a, kcal/mol	log A	δ, ppm	OOOH[e]	CH_3	E_a, kcal/mol	log A
acetone-d_6	−15	5.84	3.15	3.23	12.5 ± 1.2[c,d]	7.2 ± 0.8	13.11				
	15						12.58	3.73	3.83	17.5 ± 1.6[c,e]	9.9 ± 1.1
methyl acetate	−15	5.32	11.74	11.27	14.5 ± 1.3[d]	9.5 ± 1.0	12.67				
	15						12.33	5.54	5.34	19.0 ± 1.5[e]	11.2 ± 1.1
tert-butyl methyl ether	−15	5.51	0.82		14.8 ± 1.5[d]	8.4 ± 1.1	12.80				
	15						12.60	1.40		24.7 ± 1.7[e]	15.0 ± 1.2

[a] **2a** = (0.08 ± 0.02)M. [b] Standard deviations ≤±10%. [c] **2b**:acetone-d_6, E_a = 13.1 ± 1.1 kcal/mol, log A = 8.1 ± 0.9. **3b**: acetone-d_6, E_a = 20.0 ± 1.5 kcal/mol, log A = 12.5 ± 1.1. [d] Following decay of the OH absorption. [e] Following decay of the OOOH absorption.

Scheme 1



suggesting a $HO^{\delta-}{\cdot\cdot}O_2^{\delta-}$ structure with a relatively large negative charge at position O1 and a smaller one at O3.

Hydrotrioxide **3a** decomposes to $RO^\bullet$ and $HOO^\bullet$ radicals in an endergonic process ($\Delta_R G$ = 19.2 kcal/mol in acetone solution). The $RO^\bullet$ radical can easily abstract an H atom to form **2a**. This, together with considerably greater kinetic stability of **3a,** as opposed to that of **2a** (see Table 2), suggests that the hemiortho ester **2a** is preferentially formed by ion pair recombination involving the HO_3^- anion rather than via hydrotrioxide **3a**.[21]

Finally, the hydrogen trioxide (HOOOH), observed recently in the low-temperature ozonation of isopropyl alcohol, isopropyl methyl ether, and various hydrocarbons,[14a−c] was not detected in the ozonized solutions of acetals under investigation. This corresponds to the fact that H-atom abstraction by ozone to form $HOOO^\bullet$ radicals (and subsequently HOOOH) is energetically disfavored when dioxolanes are dissolved in acetone, thus underlining the important role of the HO_3^- anion in ozone reactions[22] involving substrates with the potential of forming relatively stable carbenium ions in solution.

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Supporting Information Available: Details of calculations and structures and complete kinetic data for the decomposition of **2** and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) A radical inhibitor, i.e., 2,6-di-*tert*-butyl-4-methylphenol has a relatively small effect on the rates and the activation parameters for the decomposition of **3a** and **3b.** This, together with relatively low yields of H_2O_2 formed in these reactions, supports an "in cage" reaction as the predominant reaction pathway. (b) The formation of Δ^1O_2 in the decomposition of the hydrotrioxide of 2-propyl-1,3-dioxolane has been confirmed by chemiluminescence measurements. (Khurshan, S. L.; Khalizov, A. F.; Avzyanova, E. V.; Yakupov, M. Z.; Shereshovets, V. V. *Russ. J. Phys. Chem.* **2001**, *75*, 1225.). See also ref 8.
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(15) Water was always present in the reaction mixture in small but sufficient amounts to participate in the reaction (molar ratio **2a**:H_2O = 1:2 in acetone-d_6 (by ^1H NMR)). Also, the addition of water (4 ± 1 vol %) to acetone-d_6 solutions (−60 °C) did not change significantly the kinetic and activation parameters of the decomposition of either **2a** or **3a**.
(16) Somewhat smaller activation parameters for the decomposition of **3a** and **3b** in acetone-d_6 and methyl acetate as compared to values in *tert*-butyl methyl ether might reflect the fact that the decomposition is proceeding by several simultaneous first-order processes involving radical (predominant) and nonradical pathways. Among the latter, water-assisted decomposition might be more important in acetone than in *tert*-butyl methyl ether (different solubility of water in these solvents).[14b]
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(21) **2a** was found to be enriched with ^{17}O in the OH group as indicated by its ^{17}O NMR spectrum, which appears to indicate the reaction of the carbenium ion with $HOOO^-$ anion in the solvent cage.
(22) Supporting the hydride abstraction mechanism is the observation that ethyl diethoxy acetate is inert toward O_3 and that electron-withdrawing groups in benzaldehyde acetal[6b] and 2-phenyl-1,3-dioxolane[9] retard the ozonolysis of these substrates.

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