

Progress in the Chemistry of Dihydrogen Trioxide (HOOOH)

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Abstract

During the past 15 years, there has been considerable progress in understanding of the chemistry of dihydrogen trioxide (HOOOH). In this account, the preparation, characterization and structure (^1H , ^{17}O NMR, IR, quantum chemical methods), kinetics and mechanism of decomposition, and reactivity of this simplest of polyoxides are discussed. Dihydrogen trioxide is, in organic oxygen bases as solvents, far more stable than previously believed. For example, the half-life of HOOOH in acetone- d_6 is 16 ± 2 min; however, it decomposes rather quickly in water solutions ($t_{1/2} \approx 20$ ms) at room temperature. HOOOH is most likely involved in oxidation processes that span atmospheric, environmental, and biological systems.

Key words: ozone, low-temperature ozonation, dihydrogen trioxide HOOOH, density-functional theory, ab-initio, molecular-structure, hydrogen-bonds, HOOO anion, HOOO radical, alkyl hydrotrioxides ROOOH, thermal-decomposition

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Introduction

Polyoxides are compounds of the general formula RO_nR , where R is hydrogen or other atoms or groups, and $n \geq 3$. These species may be regarded as higher homologues of hydrogen peroxide, alkyl hydroperoxides (ROOH), and dialkyl peroxides (ROOR), and are believed to be key intermediates in atmospheric chemistry, the chemistry of combustion and flames as well as in biochemical oxidations.¹

Because the chemistry of alkyl hydrotrioxides (ROOOH) and dialkyl trioxides (ROOOR) has been rather well documented in recent years,¹ we will concentrate here mainly on the formation, characterization, decomposition, and reactivity of dihydrogen trioxide (HOOOH), i.e., the simplest of polyoxides. This is to the

best of our knowledge the first review devoted entirely to dihydrogen trioxide. The proposed IUPAC name for HOOOH is trioxidane.

Origins of Dihydrogen Trioxide Chemistry

Although hydrogen peroxide has been known since 1818 (L. J. Thenard), the existence of higher oxides of hydrogen was a subject of heated controversy and speculation ever since 1880, when M. Berthelot proposed the possibility of transient existence of dihydrogen trioxide as an intermediate in the decomposition of hydrogen peroxide.² Fifteen years later, Mendeleev

suggested dihydrogen tetraoxide (HOOOOH) as still another unstable intermediate in the same reaction.³ All these suggestions were soon forgotten because there were no methods available at that time to test these hypotheses.

In 1917 Rothmund and Burgstaller were the first to investigate the kinetics of the reaction between ozone and hydrogen peroxide.⁴ Several groups of workers later suggested the free radical nature of this reaction with the involvement of HO•, HOO•, the superoxide anion (O₂^{•-}), and the ozonide radical anion (O₃^{•-}) as intermediates. The potential involvement of HOOOH, resulting from recombination of HO• and HOO• radicals, was also considered.^{5–7}

In the 1950s and 1960s several groups of researchers studied the dissociation of water vapor by means of an electrical discharge.⁸ When the discharged vapor stream was chilled quickly to –190 °C, a glassy solid was obtained, which upon warming yielded large amounts of oxygen and hydrogen peroxide. This was, together with the heat evolved, taken as a proof for the involvement of H₂O₃ and H₂O₄ in these reactions.

Direct Spectroscopic Detection of Dihydrogen Trioxide

UV and IR spectra. The modern chemistry of HOOOH began in 1963, when Czapski and Bielski reported the production of an intermediate, believed to be dihydrogen trioxide (on kinetic grounds), in the pulse radiolysis of acidified air-saturated aqueous solutions.⁹ Later Bielski and Schwartz provided the first UV spectroscopic evidence for the existence of HOOOH in the pulse radiolysis of air-saturated perchloric acid solutions.^{10,11} A UV absorption spectrum very similar to, but more intense than, that of HOOH was reported.

These authors also estimated the maximum half-life for HOOOH in aqueous solutions of 17 seconds in 0.027 M acid at 0 °C.

The first attempts to detect hydrogen polyoxides by IR were made in the late 1960s and 1970s, when Nekrasov et al. studied the low-temperature (–198 °C) reaction of ozone with atomic hydrogen in liquid ozone as well as the dissociation of water and hydrogen peroxide vapor with subsequent freezing of the products into the matrix. The IR spectra of the products showed some new bands, which were tentatively assigned to H₂O₃ and H₂O₄, but no unambiguous interpretation of the IR spectra could be made at that time.¹²

Giguère et al. were the first to report in a series of papers fundamental skeletal vibrations of H₂O₃ and H₂O₄ and their deuterated analogs by studying IR and Raman spectra of the products from electrically dissociated mixture of water, hydrogen peroxide and oxygen.¹³ However, the highest concentration of H₂O₃ produced in the glassy solid was below 5% (only one tenth as much for H₂O₄). They also reported that H₂O₃ begins to decompose at about –55 °C (H₂O₄ at about –100 °C), and estimated that at room temperature it could survive only a small fraction of a second.

A recent report by Engdahl and Nelander presented the IR spectroscopic identification of dihydrogen trioxide in argon matrices obtained by photolyzing the ozone-hydrogen peroxide (or DOOD and HOOD) mixtures.¹⁴ All fundamental vibrations of HOOOH were observed, and they agree well with the MP4/6-31G(d,p)¹⁴ and B3LYP/6-31G(d,p)¹⁵ calculations (Table 1). Several bands of DOOOD, HOOOD, and H¹⁶O¹⁶O¹⁸OH (¹⁸O₃ and H₂O₂) have also been measured. The strongest bands are the torsions, the OH stretches, and the antisymmetric HOO bands. The antisymmetric O-O stretch at 776 cm⁻¹ may be used to detect HOOOH even in the presence of high water concentrations.

Biographical Sketch



Božo Plesničar studied chemical technology at the University of Ljubljana, from which he received his Ph.D. degree (Chemistry) in 1966. In 1966/1967, he spent one year as a postdoctoral research associate with Professor N. A. Milas at the Massachusetts Institute of Technology (MIT) (Cambridge, USA), and again in 1970 half a year as a NSF postdoctoral fellow with Professor Glen A. Russell at the Iowa State University (Ames, USA). He started at the University of Ljubljana in 1974 as a Dozent, and was promoted to Full Professor in 1985. His present research interests in the field of physical organic chemistry include the characterization of reactive intermediates formed in the oxidation of various organic substrates with ozone (ROOOH, HOOOH). In 2004, he received the Zois Award for research excellence in the field of Organic Chemistry.

Table 1. Observed and calculated ((MP4/6-31G(d,p))^a and [B3LYP/6-31G(d,p)]^b) fundamentals of HOOOH (trans) and DOOOD in wave-numbers (cm⁻¹).^c

	HOOOH	DOOOD
v ₁ (symmetric OH stretch)	3529.6 (3529.6) [3533.1]	2610.4 [2582.2]
v ₂ (antisymmetric OH stretch)	3529.6 (3529.6) [3528.4]	2610.4 [2579.0]
v ₃ (antisymmetric HOO bend)	1359.1 (1359.2) [1353.6]	1007.3 [1013.6]
v ₄ (symmetric HOO bend)	1347.4 (1347.6) [1349.6]	(NR) ^d [1004.2]
v ₅ (symmetric OO stretch)	821.0 (820.4) [899.5]	(NR) ^d [892.8]
v ₆ (antisymmetric OO stretch)	776.3 (776.1) [770.2]	762.6 [769.8]
v ₇ (OOO bend)	509.1 (509.2) [506.5]	(NR) ^d [492.6]
v ₈ (antisymmetric torsion)	387.0 (387.0) [410.4]	301.6 [317.1]
v ₉ (symmetric torsion)	346.4 (345.9) [346.9]	273.5 [252.8]

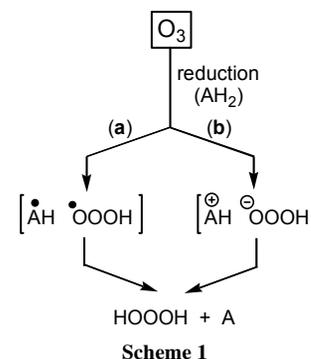
^a Ref. 14. ^b Ref. 15. ^c Calculated fundamentals are listed in parentheses. ^d NR; not reported.

Methods of Preparation of Dihydrogen Trioxide in Organic Solvents. NMR (¹H and ¹⁷O) and IR Spectra

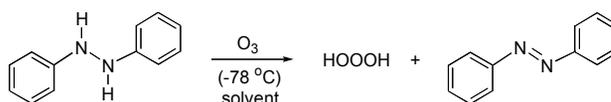
All the samples of HOOOH obtained by one of the above-mentioned procedures, contained very small amounts of the trioxide (< 5%), and were thus unsuitable for studying its chemistry in detail. Therefore, a method was needed to prepare relatively highly concentrated solutions of HOOOH in various organic solvents in order to allow an unambiguous spectroscopic identification and characterization, and to enable the study of the decomposition and reactivity of this polyoxide. Basically, three methods emerged for the preparation of HOOOH in solutions of organic solvents: (a) reduction of ozone; (b) decomposition of hydrotrioxides; and (3) the reaction of ozone with hydrogen peroxide.

(a) Reduction of ozone. Several compounds (reducing agents-AH₂), i.e., 1,2-diphenylhydrazines,^{16,17} 2-ethylanthrahydroquinone,¹⁶ isopropyl alcohol,¹⁸ isopropyl methyl ether,¹⁸ and cumene¹⁹ were found to react with ozone in various organic solvents at low temperatures

to form HOOOH. The results of theoretical studies (the gas-phase and the solution-phase) showed that the reaction proceeds by either a step-wise radical process (path a) involving the abstraction of the hydrogen atom from the substrate by ozone to form the hydrotrioxyl radical, HOOO•,^{17,19} or an ionic process (path b) that involves the abstraction of the hydride ion to form the hydrotrioxide anion, HOOO⁻.^{20,21} These hydrotrioxide species, i.e., HOOO•²² and HOOO⁻,²³ the existence of which was recently confirmed by a combination of experimental and quantum chemical studies,^{22,23} react further by abstracting the hydrogen atom and the proton, respectively, to form HOOOH (Scheme 1).



The ozonation of 1,2-diphenylhydrazine (hydrazobenzene) in acetone-*d*₆ at -78 °C is, at least at present, the method of choice for the preparation of relatively highly concentrated solutions of HOOOH (up to 0.1 M) without the interfering presence of organic hydrotrioxides (ROOOH) (Scheme 2).^{16,17} Besides 1,2-diphenyldiazene (azobenzene), 1,2-diphenyldiazene-N-oxide (azoxybenzene), and hydrogen peroxide are also formed in this reaction. This method allows the use of commercially available 1,2-diphenylhydrazine without any further purification. Methyl acetate or *tert*-butyl methyl ether can also be used as solvents. ¹H and ¹⁷O NMR,¹⁷ and IR²⁴ spectra of dihydrogen trioxide obtained in this way are shown in Figure 1.



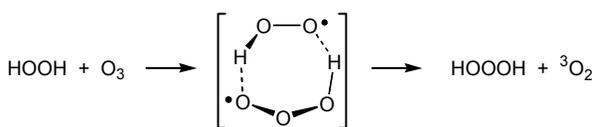
Most recently, Wentworth et al. prepared HOOOH free of the contamination products, i.e., 1,2-diphenyldiazene and 1,2-diphenyldiazene-N-oxide, by the low-temperature ozonation (-78 °C) of the resin-bound 1,2-diphenylhydrazine in acetone-*d*₆ or tetrahydrofuran-*d*₁₀.²⁵ The oxidized resin can be removed by

phenyls (PCBs), benzene, toluene, ethylbenzene, and xylene (BTEX), trinitrotoluene (TNT), and some other waste constituents.^{28b}

More recently, the reaction between O_3 and HOOH has become of biological interest since a research group from the Scripps Research Institute (La Jolla, California), led by Lerner, Wentworth, and Eschenmoser, has discovered that all antibodies are capable of catalyzing the oxidation of water by singlet oxygen (Δ^1O_2) to generate HOOH and an oxidant with the chemical signature of O_3 . These authors postulated that antibodies carry the reaction through HOOOH as a key reaction intermediate. All these discoveries have important implications for pathological processes in living systems.²⁹

Wentworth et al. have recently reported that HOOOH is actually formed during the thermal reaction of HOOH with O_3 in acetone- d_6 or tetrahydrofuran- d_{10} at $-78\text{ }^\circ\text{C}$ in concentrations of approximately 2.9 mM (acetone- d_6). The trioxide was characterized by ^1H NMR spectroscopic analysis (OOOH absorption at $\delta = 13.6 \pm 0.2$ ppm).²⁵

By using quantum chemical methods, Xu and Goddard have proposed that in the gas phase the reaction between HOOH and O_3 proceeds via a planar seven-membered-ring triplet biradical intermediate (with the triplet and singlet states being almost degenerate) to yield HOOOH and 3O_2 (Scheme 4).¹⁵ The enthalpy of the overall reaction was found to be exothermic by 32.3 kcal/mol, with the highest enthalpy of activation of 4.8 kcal/mol (B3LYP/6-31G(d,p)). Alternatively, Lesko et al. have recently, in order to explain hydrogen isotope effects on the reaction of HOOH with O_3 in water, concluded that HOOO $^-$ anion is involved in these reactions. The conjugate base of HOOOH is most likely formed from a reaction between the HOO $^-$ anion and O_3 .³⁰ Clearly, further studies are needed to clarify the mechanistic details of this interesting and important reaction.



Structure, Acidity, and Thermochemical Data

Structure. Because the structure of HOOOH has not been determined by direct methods yet, we have to rely on the results of theoretical studies. A number of *ab initio* studies on the monomeric dihydrogen triox-

ide were published.^{31–37} All of them indicate a zig-zag skew-chain structure with C_2 symmetry so that both HOOO dihedral angles are equal and opposite. The calculated geometry parameters for the monomeric form of HOOOH are, together with, for comparison, the experimental values for HOOH shown in Figure 2.^{37,38}

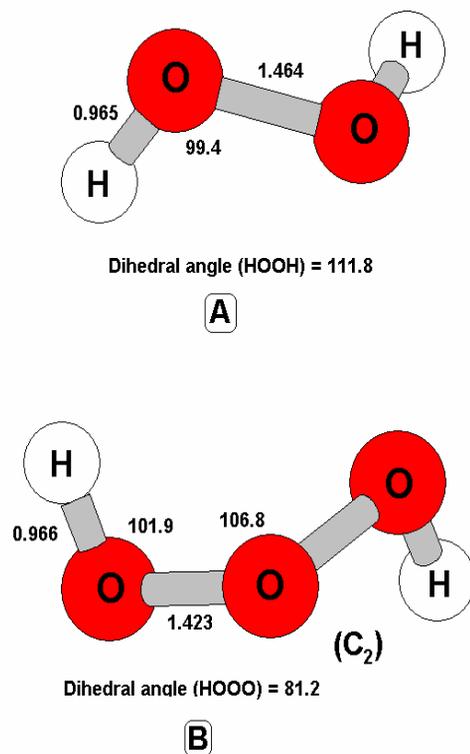


Figure 2. (A) Experimental geometry parameters for HOOH (IR, microwave spectroscopy)(Ref 38). (B) CCSD(T)/6-311++G(3df,3pd) geometrical parameters for HOOOH (Ref. 37). Bond lengths and angles are in Ångstroms and degrees, respectively.

The dipole and the hyperconjugation effects were found to be predominant factors governing the conformational behavior of HOOOH. The shortening of the O-O in this polyoxide relative to the O-O bond in HOOH was also explained by hyperconjugation arguments.^{32,36}

Theoretical studies indicate that self-association, i.e., dimerization/oligomerization, is most likely the characteristic structural feature of HOOOH. Our preliminary studies indicate that various dimeric^{27,39} and trimeric (as well as tetrameric) structures of HOOOH (Figure 3) are plausible in “inert”, i.e., non-basic solvents.³⁹ However, basic solvents ($B =$ oxygen base) are able to complex with such aggregates, and, if basic enough, disrupt the hydrogen bonds in these aggregates to form 1:1 and/or 1:2 hydrogen-bonded complexes with HOOOH.^{17b,18b} For an example, see Scheme 5.

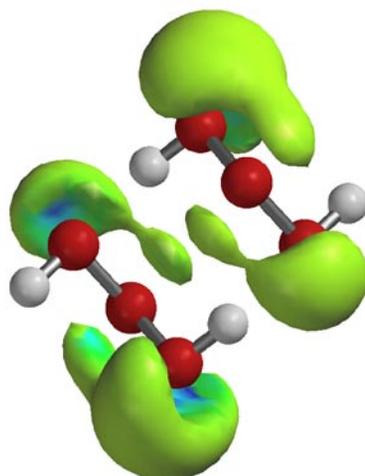


Figure 3A

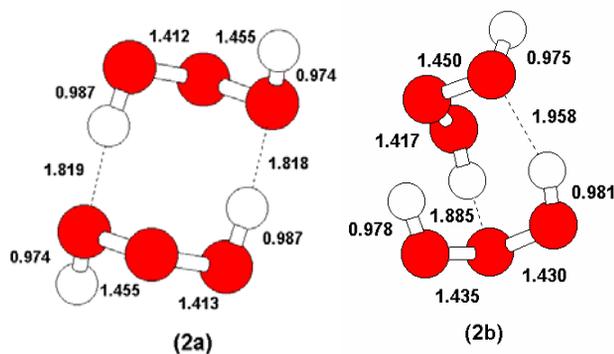


Figure 3B

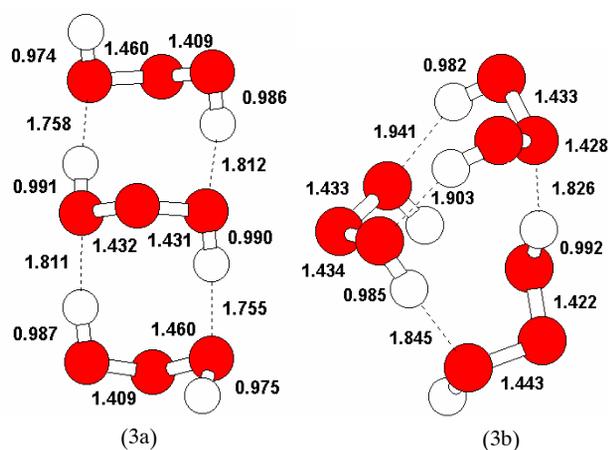
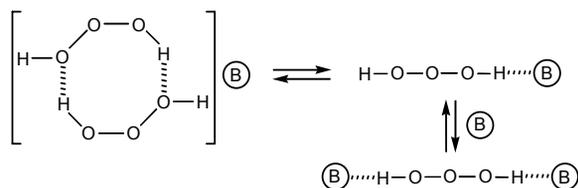


Figure 3C

Figure 3. (A) The dihydrogen trioxide dimer **2a**: equipotential surfaces. (B) The two most stable structures (among several distinct entities) of HOOOH dimers (**2a**, BE = 9.2 kcal/mol, per H-bond, 4.6 kcal/mol; **2b**, BE = 9.0 kcal/mol, per H-bond, 4.5 kcal/mol). (C) The two most stable structures of HOOOH trimers (**3a**, BE = 21.1 kcal/mol, per H-bond, 5.2 kcal/mol; **3b**, BE = 21.5 kcal/mol, per H-bond, 5.3 kcal/mol; B3LYP/6-31G(d,p), BSSE corrected).



Scheme 5

Because water and hydrogen peroxide were always present in solutions of HOOOH (prepared by either of the methods mentioned above), theoretical studies on HOOOH-HOH (BE = 8.2 kcal/mol; B3LYP/6-31G(d,p), BSSE corrected) and HOOOH-HOOH (BE = 8.0 kcal/mol) as well as HOOOH-HOH-HOOH complexes were also of interest.^{17,39} As will be discussed later, these structures have a considerable effect on the decomposition of HOOOH.

It is interesting to mention that, the dihydrogen trioxide-water dimerization energy is 0.8 kcal/mol (B3LYP/6-31G(d,p), BSSE corrected) smaller than that for the dihydrogen trioxide dimer, suggesting that the self-association of HOOOH is slightly favored with respect to its solvation by one molecule of water. This, together with a relatively good solubility of HOOOH in less polar solvents, might indicate that HOOOH is more lipophilic than water (and most likely more lipophilic than HOOH as well).

There is at present no direct evidence for the various self-associated HOOOH entities and for intermolecularly hydrogen-bonded HOOOH-oxygen base complexes. However, a study of the temperature dependence of the OOOH absorption of HOOOH in acetone-*d*₆, methyl acetate, and *tert*-butyl methyl ether revealed a small but definitive upfield shift of the OOOH absorption that was observed with increasing temperature^{18b} (see Table 2). This corresponds to the appearance of larger clusters of HOOOH both at low temperatures and at higher HOOOH concentrations. Interchange between all these forms, which contributes to narrow time-averaged features, must be fast since no exchange broadening of the OOOH absorption was observed even at the lowest temperature investigated (−100 °C, dimethyl ether). The observed OOOH chemical shift thus reflects both the hydrogen-bond strength and their extent in these entities.^{18b}

Acidity. The proton affinity of HOOOH ($\Delta H(298) = 365.7$ kcal/mol) clearly indicates that this polyoxide is more acidic than HOOH ($\Delta H(298) = 376.6$ kcal/mol) and HOH ($\Delta H(298) = 391.3$ kcal/mol).^{23,37} A peculiar structure of the HOOO[−] anion is worth mentioning here. Namely, according to CCSD(T)/6-311++G(3df,3pd) calculations, the singlet state of the HOOO[−] anion possesses a strong HOO-O bond with some double bond character, while a weakly covalent

Table 2. Proton chemical shifts, rate constants, frequency factors, and activation energies for the decomposition of the dihydrogen trioxide (HOOOH) formed in the ozonation of 1,2-diphenylhydrazine in various solvents.^a

solvent	<i>T</i> (°C)	δ (ppm)	$10^4 k(T)$, s ^{−1}	E_a (kcal mol ^{−1})	log <i>A</i>
acetone- <i>d</i> ₆	−20	13.11	0.1	16.7 ± 1.5	9.4 ± 1.0
	−10	13.02	0.25		
	0	12.93	1.4		
	10	12.84	2.5		
	20	12.75	6.8		
methyl acetate	−10	12.47	0.4	16.5 ± 1.5	9.5 ± 1.1
	0	12.38	1.43		
	10	12.29	4.3		
	15	12.25	7.2		
	20	12.21	12.4		
<i>tert</i> -butyl methyl ether	−10	12.62	0.38	15.3 ± 1.3	8.3 ± 0.9
	0	12.55	0.95		
	10	12.50	2.4		
	20	12.41	5.7		
	25	12.39	11.4		
30	12.36	17.0			

^a *c*(HOOOH) = 0.002–0.01 M. Standard deviations ≤ ±10%. By following the decay of the HOOOH ¹H NMR absorption.

HO-OO bond is extraordinarily long (1.80 Å, i.e., the longest O-O bond ever found for a peroxide). In aqueous solution, the HOOO[−] anion adopts a geometry that closely resembles that of HOOOH (HOO-O = 1.388 Å, HO-OO = 1.509 Å, $\tau(\text{HOOO}) = 78.3^\circ$), and can thus be regarded as the conjugate base of HOOOH. The other metastable form, i.e., the triplet form of the HOOO[−] anion (10.9 kcal/mol more stable than the singlet), was actually found to be a weakly bounded ($\Delta H(298) = 2.1$ kcal/mol) van der Waals complex between the HO[−] anion and triplet oxygen.³⁷

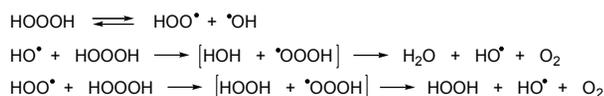
It is quite likely that solvation will somewhat reduce the gas-phase acidity differences among these species. Namely, the HOO[−] anion, and particularly the HO[−] anion, possess a more localized negative charge, and can thus be better solvated by water molecules than the HOOO[−] anion. The estimated p*K*_a value for HOOOH is 9.5 ± 0.2 in water at 25 °C (p*K*_a(HOOH) = 11.6 in water at 20 °C).^{11,37}

The calculated bond dissociation energies (BDE) for HOOOH are: BDE(HOO-OH) = 33.9 kcal/mol and BDE(HOOO-H) = 81.3 kcal/mol.³⁶ The enthalpy of formation of HOOOH, $\Delta H_f^\circ(298)$, is −22.7 kcal/mol³⁷ (−24 ± 3 kcal/mol).^{22i,22k}

Decomposition of Dihydrogen Trioxide

The decomposition of HOOOH has been studied in the last decade, both by experiment and theory.^{16–18} Several experimental facts emerged. Firstly, the kinetics of decomposition of HOOOH, measured by following the decay of the OOOH ¹H NMR absorption, was found to obey cleanly first-order kinetics over at least 3–4 half-lives in acetone-*d*₆, methyl acetate, and *tert*-butyl methyl ether (Table 2). Secondly, singlet oxygen (¹O₂) and water were the main decomposition products found. The studies are underway to determine unambiguously, whether hydrogen peroxide and ozone are also formed in these reactions.

Several mechanisms for the decomposition of HOOOH were proposed to accommodate the experimental data. Nangia and Benson proposed a radical chain mechanism for the decomposition of HOOOH (Scheme 6).⁴⁰ The activation energy of this chain reaction mechanism would be lower than the BDE of the HOO-OH bond (33.9 kcal/mol).³⁶ However, the initially formed HOOO[•] radical would break down to the HO[•] radical and triplet oxygen. This, together with relatively low experimental log *A* values for the decomposition of HOOOH,^{17a,18} seem not to support this mechanistic proposal.



Scheme 6

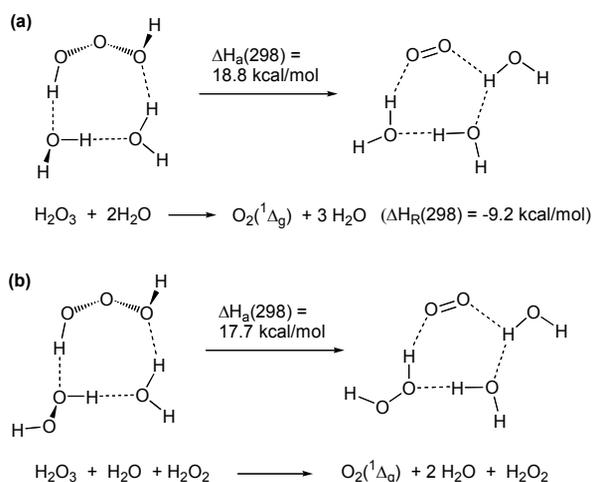
The activation energy for the intramolecular proton-transfer was calculated to be far too high (≈ 49 kcal/mol)^{23a} for the reaction to proceed on the singlet surface. Therefore, still some other mechanistic possibilities, including those involving water and hydrogen peroxide were considered. Namely, as stated before, water (and hydrogen peroxide as well) were always present in solutions of HOOOH prepared by either of the methods mentioned in sufficient amounts to complex all the HOOOH present. Water was found to be labeled with ¹⁷O (ozonation with ¹⁷O₃) indicating that, at least in part, it was formed by the decomposition of HOOOH during the ozonation procedure.^{17a}

The kinetic and activation parameters for the decomposition of HOOOH are in accord with the mechanism depicted in Scheme 7 involving (a) two molecules of water, acting as a bifunctional catalyst or (b) hydrogen peroxide and one molecule of water. Namely, the calculated activation enthalpies, i.e., 18.8 and 17.7 kcal/mol,^{17a} respectively, are very similar to the

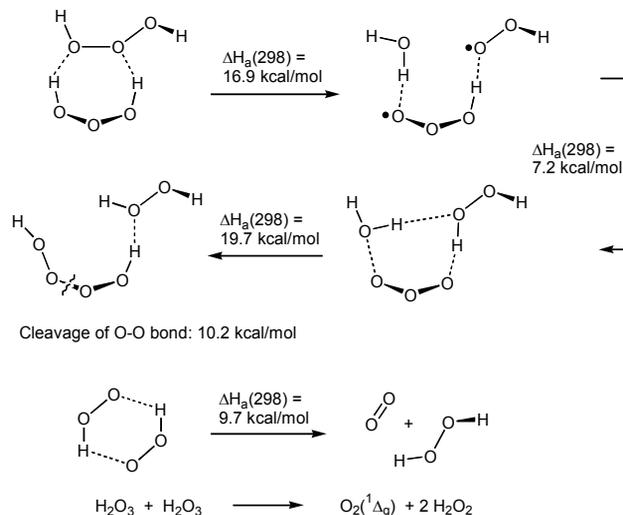
measured Arrhenius energies (16.5 ± 1.5 kcal/mol)^{17a} (see Table 2).

The half-life of HOOOH at room temperature (20 °C) is 16 ± 2 min in all solvents investigated. This is in contrast with the half-life of HOOOH in water, which was estimated to be just a fraction of a second ($t_{1/2} \approx 20$ ms).

Xu, Muller, and Goddard investigated still some other plausible decomposition pathways of HOOOH.⁴¹ In one of them (Scheme 8), the decomposition is initiated in the dimer of *cis*-HOOOH (each of the HOOOH molecules adopts the 2.4 kcal/mol less stable *Cs*-symmetrical *cis* conformation) to form ¹O₂ and two HOOH molecules via intermediate O₃ and dihydrogen tetraoxide (H₂O₄) complexes. The activation enthalpy of the rate-determining step of the process was calculated to be 19.7 kcal/mol.

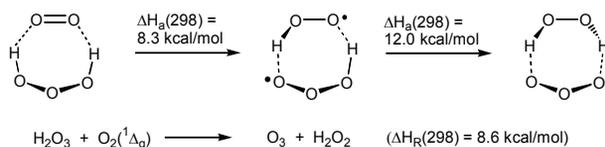


Scheme 7



Scheme 8

Alternatively, dihydrogen trioxide can react with singlet oxygen to form ozone and hydrogen peroxide (Scheme 9). The activation energy of this process is 12.0 kcal/mol.⁴¹



Scheme 9

All these mechanistic possibilities for the decomposition seem to explain relatively high losses of HOOOH (up to 50%) during the ozonation procedures for making this polyoxide.^{16,17a,18}

Some oxygen bases (B), for example ethers,^{17,18} appear to slow down the decomposition of HOOOH. Namely, somewhat smaller rates for the decomposition of HOOOH in various ethers, compared to the values in other solvents (acetone-*d*₆, methyl acetate), may reflect the lower solubility of water in these solvents and consequently the formation of relatively strongly hydrogen-bonded HOOOH-B^{17b} and/or B-HOOOH-B complexes^{17b,18} (as already discussed above), thus preventing the donation of a hydrogen atom (proton) to the other end of the molecule. In such cases, homolytic contributions to the decomposition pathways for HOOOH, particularly at higher temperatures, might play a more important role.

A proton transfer from dihydrogen trioxide to the HO⁻ anion without any barrier was calculated when HO⁻ was brought near HOOOH.³⁶

The base-catalyzed reaction of HOOOH + HO⁻ → HOH + HOOO⁻ is exothermic by 26.9 kcal/mol.³⁷ The hydrogen-bonded H₂O-HOOO⁻ complex decomposes quickly into singlet oxygen and HO⁻, most likely without activation energy. (The overall reaction HOOOH + HO⁻ → HO⁻ + Δ¹O₂ + HOH is exothermic by 12.6 kcal/mol; HOOO⁻ (singlet) → Δ¹O₂ + HO⁻ is endothermic by 14.3 kcal/mol). Therefore, the decomposition of HOOOH will be very fast in the presence of a very strong base.^{36,37} This prediction was actually confirmed by experiment. It is also interesting to note that HOOOH decomposes very fast in various organic solvents in the presence of triphenylphosphine-oxide, which apparently is basic enough to abstract the proton from HOOOH.⁴²

The acid-catalyzed decomposition most likely involves conversion of HOOOH into the protonated form, HOOOH₂⁺ (protonation by H₃O⁺ of one of the terminal oxygen atoms),^{35,36} with subsequent fragmentation of this species to Δ¹O₂ and HOH. This process is most likely heavily assisted by clusters of water molecules, which delocalize the positive charge, and thus

stabilize the system.³⁶ The details of the acid-catalyzed decomposition of HOOOH are not known at present. It is interesting to mention that, the protonation energy of HOOOH was calculated to be 160.8 kcal/mol, while the predicted binding energy of Li⁺ to HOOOH was 33 kcal/mol (QCISD/DZ+P level).³⁵ Therefore, it is quite probable that both adducts, i.e., HOOOH₂⁺ and Li⁺-HOOOH, might be observable by mass spectrometry.

In the trioxide CF₃OOOCF₃⁴³ (the first X-ray structure of a trioxide^{43a}), neither the acid- or base-catalyzed nor the solvent-assisted decomposition pathways are possible. The radical fragmentation was found to be a predominant mechanistic feature. The BDE of the CF₃O-OOCF₃ bond is estimated to be 30.1 kcal/mol, while the experimental value was found to be 30.3 kcal/mol.^{43c,43d} Although this value is slightly smaller than the BDE for the HO-OOH bond (33.7 kcal/mol), the perfluoroalkylated trioxide is much more stable. It actually does not decompose until at or above 25 °C thus convincingly demonstrating that, if proton-transfer pathways are blocked, the stability of the trioxides is increased.

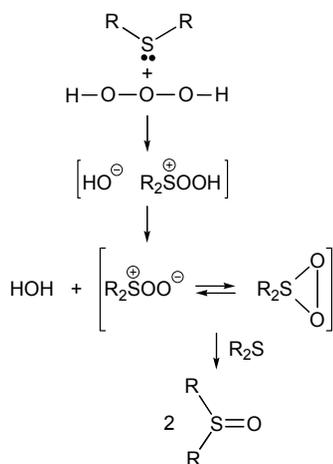
Reactivity of Dihydrogen Trioxide

Very little of a definitive nature is known about the reactivity of HOOOH against various organic substrates. It was reported that solutions of HOOOH reacted with thianthrene 5-oxide (introduced by Adam et al. as a chemical probe for differentiating between the electrophilic versus nucleophilic nature of various oxidants⁴⁴) as an electrophilic oxidant, i.e., *X*_{Nu} values of 0.17 ± 0.01 were obtained in acetone and methyl acetate, respectively. HOOOH was found to be more electrophilic than ozone in these reactions (*O*₃, *X*_{Nu} = 0.24, methylene chloride; 0.59, acetone).¹⁶

Oxidation of substituted phenyl methyl sulfides with solutions of HOOOH (competition experiments in acetone or methyl acetate at -40 °C) gave Hammett ρ values (vs σ) of -1.90 ± 0.02. Only sulfoxides were formed in these reactions. Control experiments showed that HOOH does not react with the sulfides under the conditions investigated.^{16,17}

While they are certainly alternative explanations possible for the oxidation of sulfides to sulfoxides with HOOOH (for example, single-electron-transfer processes, and the involvement of HOOO[•] or HOOO⁻ species), we believe that the mechanism which involves the rate-determining attack of the sulfur atom on the middle oxygen atom in HOOOH might be one of them (Scheme 10).

The question of Brønsted and Lewis acid catalysis in oxidations with HOOOH also awaits to be explored.



Scheme 10

Conclusions and Outlook

We have demonstrated that HOOOH, characterized by ^1H and ^{17}O NMR, and IR spectroscopy, can be prepared by the low-temperature reduction of ozone with various organic reducing agents in oxygen bases (acetone- d_6 , methyl acetate, *tert*-butyl methyl ether) as solvents. The ozonation of 1,2-diphenylhydrazine (1,2-DPH) in acetone- d_6 is, at least at present, the method of choice for the preparation of relatively highly concentrated solutions of HOOOH (up to 0.1 M) without the interfering presence of organic hydrotrioxides (ROOOH). Using a variety of DFT methods in connection with the B3LYP functional, a stepwise mechanism involving the hydrotrioxyl radical (HOOO \cdot) formed by the abstraction of the N-hydrogen atom by ozone to form a radical pair, (PhNNHPh \cdot •OOH), was found. The HOOO \cdot radical then abstracts the remaining N(H) hydrogen atom from the PhNNHPh \cdot radical to form HOOOH and the diazene, or recombines with RNNHR \cdot to form the hydrotrioxide, RN(OOOH)NHR. The homolytic decomposition of the latter most likely explains the presence of other reaction products, i.e., 1,2-diphenyldiazene-N-oxide and hydrogen peroxide.

The use of the resin-supported 1,2-DPH, introduced recently by Wentworth et al., enables the preparation of HOOOH free of the contamination products arising from the oxidation of 1,2-DPH.

Water, always present in solutions of HOOOH after the ozonation procedure, plays a crucial role as a bifunctional catalyst in a “pericyclic” decomposition process of this polyoxide to produce water and singlet oxygen ($\Delta^1\text{O}_2$). The possibility that HOOH is, besides water, also involved in the decomposition of HOOOH, also cannot be ruled out. The half-life of HOOOH in acetone- d_6 is 16 ± 2 min at 20°C , while it is much shorter in water (≈ 20 ms).

The Scripps researchers found that all antibodies have the ability to catalyze the oxidation of water by singlet oxygen to generate HOOH and ozone. They proposed HOOOH as a key intermediate in these reactions. All these species may participate in pathological processes in living systems (atherosclerosis, neurodegenerative disorders, cancer). A recent report that HOOOH was found in quantifiable amounts in the thermal reaction of O_3 with HOOH (“peroxone process”) for the first time demonstrates that, a link exists between these three oxidants, and that HOOOH might actually be involved in oxidation processes that span atmospheric, environmental, and biological systems.

Further studies of reactions of HOOOH with either (a) ozone, hydrogen peroxide, singlet oxygen, superoxide anion, or itself (in dimers and/or oligomers), or (b) reactions of HOOOH with various organic substrates (acid- or base-catalyzed), will certainly provide further surprises in this interesting field of research. And finally, the question “How long can you make an oxygen chain?” is still a very relevant and challenging one.

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Povzetek

V zadnjih petnajstih letih je bil narejen zelo pomemben napredek pri poznavanju kemije divodikovega trioksida (HOOOH). Ta pregledni članek opisuje pripravo, karakterizacijo in strukturo (^1H , ^{17}O NMR, IR, kvantno-kemijske metode), kinetiko in mehanizem razpada ter reaktivnost tega najenostavnejšega polioksida. Divodikov trioksid je v organskih kisikovih bazah kot topilih precej bolj stabilen kot so menili do sedaj. Tako je, naprimer, razpolovni čas HOOOH v acetonu- d_6 16 ± 2 minut ($20\text{ }^\circ\text{C}$), medtem ko v vodi razpade zelo hitro ($t_{1/2} \approx 20$ ms). Divodikov trioksid najbolj verjetno sodeluje kot reaktivni intermediat pri oksidacijskih procesih v atmosferi, okolju in v bioloških sistemih.