Characterization and Reactivity of Hydrogen Trioxide (HOOOH): A Reactive Intermediate Formed in the Low-Temperature Ozonation of 2-Ethylanthrahydroquinone

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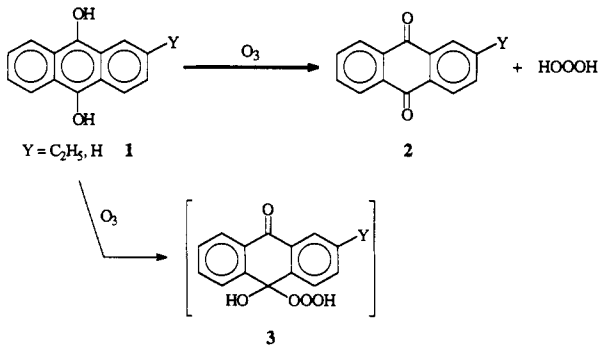
Although the existence of organic hydrotrioxides, ROOOH, is now well documented, very little of a definitive nature is known about the simplest polyoxide, hydrogen trioxide (HOOOH).[1] Giguere et al.[2] presented infrared and Raman spectroscopic evidence for the presence of HOOOH in the products from electrically dissociated water and related hydrogen–oxygen-containing systems at cryogenic temperatures. A UV absorption spectrum very similar to that of hydrogen peroxide was assigned to HOOOH in the pulse radiolysis of air-saturated perchloric acid solutions.[3]

We have recently presented evidence for the involvement of a transient polyoxide, which we tentatively assigned to HOOOH, in the decomposition of dimethylphenylsilyl hydrotrioxides in acetone-d_6 and methyl acetate.[4] Here we report our interim studies directed toward the preparation and characterization of HOOOH by other routes.

The oxidation of substituted anthrahydroquinones by atmospheric oxygen has been used successfully for large-scale production of hydrogen peroxide for a long time.[5] We found that, by using ozone instead of oxygen for the oxidation of anthrahydroquinone, hydrogen trioxide (HOOOH) and the corresponding quinone are formed as the main products.

Ozonation of 2-ethylanthrahydroquinone (**1**) (0.2 ± 0.1 M) with either an ozone–nitrogen or ozone–oxygen mixture in acetone-d_6 and methyl acetate at −78 °C produced an oxygen-rich intermediate, characterized by a typical OOOH absorption at 13.6 ± 0.2 ppm, downfield from Me_4Si.[6] The appearance of this absorption was accompanied by the simultaneous disappearance of **1** and the appearance of 2-ethylanthraquinone (**2**) as evidenced by ^1H and ^{13}C NMR spectroscopy. Since no other ^{13}C NMR resonances that could be attributed to an organic hydrotrioxide were detected, at least above -40 °C, the observed OOOH absorption was tentatively assigned to hydrogen trioxide (HOOOH). The yield of HOOOH was estimated to be 40 ± 10% (per mole of **2** formed). However, it was evident from ^1H NMR spectra that, besides HOOOH, still another transient hydrotrioxide was formed in these reactions, as indicated by the presence of another low-field OOOH absorption (δ 13.8 ± 0.1 ppm, −78 °C). This hydrotrioxide was evidently less stable than HOOOH. Nevertheless, its concentration was too low (<10%) to allow a detailed ^{13}C NMR identification. We tentatively assigned the OOOH absorption at δ 13.8 ppm to hydrotrioxide **3**. Similar observations were made by studying the low-temperature ozonation of anthrahydroquinone.[7] In both cases, small amounts of HOOH (<6%; TLC and iodometry[6g]) were detected in the decomposition mixtures. Control experiments showed that **1** does not react with oxygen under the conditions investigated.



Hydrogen trioxide began to decompose appreciably at around −40 °C to produce singlet oxygen, Δ^1O_2 (9,10-dimethylanthracene endoperoxide,[8] 30 ± 10% yield). Niu and Mendenhall have already used the criterion of singlet oxygen evolution (IR emission at 1270 nm) to demonstrate the involvement of a polyoxide, believed to be HOOOH, in the low-temperature ozonation of hydrazobenzene (route B) in toluene.[9]

Solutions of HOOOH reacted with thianthrene 5-oxide[10] (at −40 °C) as an electrophilic oxidant, i.e., X_{Nu} values of 0.18 and 0.19 were obtained in acetone and methyl acetate, respectively. Total yield of the products (thianthrene 5,5-dioxide, thianthrene 5,10-dioxide, and practically negligible amounts of thianthrene 5,5,10-trioxide) was 12 ± 2%. The presence of the radical scavenger galvinoxyl did not inhibit these oxygen-transfer reactions. It is interesting to note that HOOOH is more electrophilic than O_3 in these reactions (O_3, X_{Nu} = 0.24, methylene chloride;[10] 0.59, acetone; 0.54, methyl acetate). A series of competition experiments with substituted phenyl methyl sulfides (XPhSMe; X = 4-Cl, H, 4-Me, 4-MeO) gave Hammett ρ values (vs σ) of −1.89 ± 0.01 for the oxidation of these sulfides with HOOOH (acetone, methyl acetate). Only sulfoxides were formed in all these reactions (HOOOH by route B: X_{Nu} = 0.17 ± 0.01, ρ = −1.90 ± 0.02). Control experiments showed that HOOH does not react with the sulfides under the conditions investigated.

The decay kinetics of HOOOH was studied by monitoring the disappearance of the OOOH absorption and was strictly first order in both solvents investigated. We anticipated that small amounts of an organic hydrotrioxide might induce the decomposition of HOOOH. Therefore, we studied the decomposition of HOOOH also in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BMP). The kinetic and activation parameters (from

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(4) Plesničar, B.; Cerkovnik, J.; Koller, J.; Kovač, F. *J. Am. Chem. Soc.* **1991**, *113*, 4946. Considerably higher yields of HOOOH were formed in the decomposition of trimethylsilyl hydrotrioxide (J. Cerkovnik and B. Plesničar, unpublished results).
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(7) For a discussion of plausible reaction mechanisms, see: Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1982; Vol. 2.
(8) Corey, E. J.; Taylor, W. C. *J. Am. Chem. Soc.* **1964**, *86*, 3881. Corey, E. J.; Mehrotra, M. M.; Khan, A. U. *J. Am. Chem. Soc.* **1986**, *108*, 2472.
(9) Niu, Q.; Mendenhall, G. D. *Abstracts of Papers*, 45th American Chemical Society Fall Scientific Meeting, Midland, MI; American Chemical Society: Washington, DC, 1989; p 32. These authors reported that when hydrazobenzene (6×10^{-3} M) in toluene was ozonized at −78 °C, a significant evolution of $^1O_2$ was observed when the mixture was warmed up to −20 °C. The yields of oxygen and azobenzene were 75 and 78%, respectively. A minor amount of azoxybenzene (13%) was also formed. We made nearly identical observations by running the reaction in acetone-d_6, except, as expected, for the yield of $^1O_2$ (9,10-dimethylanthracene endoperoxide, 30 ± 10%). Professor Mendenhall informed us of their observation of an OOOH absorption at 13.2 ppm at low temperatures in toluene, assigned to HOOOH. (Personal communication, Nov. 14, 1992.)
(10) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202.
(11) In neither of these cases (routes B and C) did BMP have any measurable effect on the rate of the decomposition of HOOOH in acetone-d_6.

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Table I. Kinetic and Activation Parameters for the Decomposition of Hydrogen Trioxide (0.15 ± 0.05 M) Generated by the Low-Temperature Ozonation of 2-Ethylanthrahydroquinone (Route A) and Hydrazobenzene (Route B) and in the Decomposition of Dimethylphenylsilyl Hydrotrioxide (Route C) in Various Solvents. Temperature Dependence of the OOOH Absorption

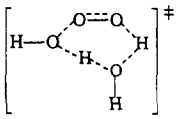
route	solvent	T, °C	δ(OOOH), ppm	10^4k,[a] s^{-1}	E_a, kcal/mol	log A
A	$(CD_3)_2CO$	−20	13.22	1.4[b] (2.7)[b]		
		−10	13.13	2.4	11.2	5.8
		0	13.03	7.4 (15.6)	(13.0)	(7.7)
		10	12.92	13.7 (33.9)		
A	$CH_3CO_2CH_3$	−20	12.85	3.2[b] (4.0)[b]		
		−10	12.73	5.8 (13.6)	10.8 (12.5)	5.8 (7.5)
		0	12.63	10.7 (33.7)		
		10	12.53	37.2 (55.5)		
B	$(CD_3)_2CO$	−30	13.36	0.8[b]		
		−20	13.26	2.0		
		−10	13.15	5.3	11.3	6.1
		0	13.00	7.7		
		10	12.90	27.4		
C	$(CD_3)_2CO$[d]	−20	13.02	4.0[b]	11.0	6.1

[a] Standard deviations, ±10%. [b] For route A, entries not in parentheses are for runs with 2,6-di-*tert*-butyl-4-methylphenol, BMP (0.2 M), and entries in parentheses are for runs without BMP. All entries for routes B and C are for runs without BMP. [d] Reference 4.

least-squares analysis) for the decomposition of HOOOH, generated by routes A, B, and C, are collected in Table I.

Although BMP reduced the rate of decomposition of HOOOH, it had only a relatively small lowering effect on the activation parameters. Kinetic and activation parameters for the decomposition of HOOOH generated from 1 (route A) thus became nearly identical with those for the decomposition of the trioxide, produced by the other two routes.[11] This, together with almost the same position of the OOOH absorption in all three cases, strongly supports the identification and characterization of this polyoxide as HOOOH.

The relatively low E_a and log A values,[12] together with the results of ESR spin trapping experiments,[13] appear to suggest that, at least in solutions of the solvents under investigation, "polar" pathways are preferable to the radical ones proposed previously for the decomposition of HOOOH.[14] Recent ab initio calculations on intramolecular proton transfer in HOOOH showed that the activation energy for this process is too high to proceed on the singlet potential surface (48.0 kcal mol^{-1}, MP4/6-31G**//MP2/6-31G*;[15a] 55.2 kcal mol^{-1}, MP4/6-31G**//6-31G, and 51.5 kcal/mol, 6-31G//6-31G[15b]). Thus, unless intramolecular proton transfer is assisted in some way, as for example by the solvent oxygen base, B (as in HOOOH...B complexes), we prefer intermolecular proton transfer in a dimeric (or oligomeric) assembly of HOOOH.[4] Water present in the system could also participate in the decomposition of HOOOH by acting either (a) as a base to deprotonate HOOOH to form $HOOO^-$, which then breaks down to HO^- and $^1O_2$,[4,16] or (b) as a bifunctional catalyst, as shown below:



However, preliminary results on a study of the decomposition of HOOOH in ethers, for example, *tert*-butyl methyl ether, showed that these relatively strong oxygen bases retard the decomposition of the polyoxide in comparison with acetone-d_6 and methyl acetate (hydrogen bond acceptor basicities: ethers > ketones > esters[17]), presumably by forming relatively stable intermolecularly hydrogen bonded B...HOOOH...B complexes. At the same time, the decomposition of HOOOH in nonbasic solvents (toluene-d_8, for example) is relatively much faster.

In conclusion, HOOOH is more stable in solutions than previously believed (up to +20 °C). Consequently, substantial amounts of this important intermediate might be present in the atmosphere[15a,18] as well as in biological systems.[19]

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(12) (a) Pryor et al. (ref 6d) have reported activation parameters for the decomposition of cumyl hydrotrioxide (0.4 M in acetone-d_6), E_a = 16.0 kcal/mol and log A = 10.4. In the presence of BMP, the decomposition of the hydrotrioxide is retarded and the activation parameters become E_a = 23.9 kcal/mol and log A = 16.4, in agreement with thermochemical predictions for the homolytic scission of the RO–OOH bond. (b) The bond dissociation energy, D(HO–OOH), was recently estimated to be 31.7 ± 1.4 kcal/mol: Francisco, J. S.; Williams, I. H. *Int. J. Chem. Kinet.* **1988**, *20*, 455.

(13) No spin adduct could be detected when a degassed sample of HOOOH in acetone-d_6, generated by either of the routes investigated, was allowed to warm from −40 to +20 °C in the presence of phenyl-*N*-*tert*-butylnitrone (PBN) in the ESR cavity.

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(15) (a) Gonzales, C.; Theisen, J.; Zhu, L.; Schlegel, H. B.; Hase, W. L.; Kaiser, E. W. *J. Phys. Chem.* **1991**, *95*, 6784; **1992**, *96*, 1767. (b) Koller, J.; Plesničar, B. Unpublished results.

(16) One of the referees has suggested the possibility of $HOOO^-$ nucleophilically attacking HOOOH to produce HOO^- and hydrogen tetraoxide (HOOOOH), which could break down to HOOH and $^1O_2$. In view of the low stability of $HOOO^-$,[4] as well as a relatively small amount of HOOH (<6%) detected in the decomposition mixture. this alternative pathway appears less likely.

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(18) See, for example: Mozurkewich, M. *J. Phys. Chem.* **1986**, *90*, 2216. DeMore, W. B. *J. Phys. Chem.* **1982**, *86*, 121. Kaufman, F. *Science* **1985**, *230*, 393. Dransfeld, P.; Wagner, H. Gg. *Z. Naturforsch.* **1987**, *42a*, 471. Toohey, D. W.; Anderson, J. G. *J. Phys. Chem.* **1989**, *93*, 1049 and references cited therein.

(19) Sawyer, D. T. *CHEMTECH* **1988**, *18*, 369. Deby, C. *La Recherche* **1991**, *228*, 57 and references cited therein.