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Mechanism of the Participation of Water in the Decomposition of Hydrogen Trioxide (HOOOH). A Theoretical Study

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Abstract: Ab initio calculations at the MP4//MP2/6-31++G* level of theory have shown a substantial reduction (by 33.5 kcal/mol) of the energy barrier for the intramolecular 1,3-proton transfer in HOOOH to give water and singlet oxygen (Δ^1O_2), when a molecule of water, acting as a bifunctional catalyst, was allowed to participate in the process. The energy barriers, $\Delta E^\ddagger = 15.1$ and 26.0 kcal/mol, relative to isolated reactants and HOOOH−HOH complex, respectively, were calculated. The following gas-phase acidity order was found: HOOOH (352 kcal/mol) > HOOH (376 kcal/mol) > HOH (391 kcal/mol). $HOOO^-$ was calculated to possess an exceptionally long $HO-OO^-$ bond (1.96 Å), indicating dissociation into HO^- and O_2. It is most likely that this species does not exist as a distinguished molecular entity in water solutions of HOOOH.

Introduction

We have recently presented ^1H NMR spectroscopic and other chemical evidence for the formation of hydrogen trioxide, HOOOH, in the decomposition of silyl hydrotrioxides, $R_3SiOOOH$,[1] as well as in the low-temperature ozonation of 2-ethylanthrahydroquinone and hydrazobenzene.[2] We found that this simplest polyoxide decomposes to water and singlet oxygen, Δ^1O_2, and is more stable in various organic solvents (particularly ethers) than previously believed (up to +15 °C). Thus, considerable amounts of HOOOH might be present in the atmosphere[3] and in biological systems.[4]

The transition state for the intramolecular hydrogen transfer in HOOOH was already calculated to be too high to proceed on the singlet potential energy surface (48.0 (MP4/6-31G**//MP2/6-31G*),[5] 51.5 (6-31G//6-31G), and 55.2 kcal/mol (MP4/6-31G**//6-31G)[6]). Therefore, we have hypothesized that relatively low activation energies, $E_a = 14.0 \pm 2.5$ kcal/mol,[2,7,8] and log A values (7.5 ± 1.5) for the decomposition of HOOOH in various "basic" solvents (ketones, esters, ethers, acetonitrile), as well as the results of ESR spin trapping experiments, strongly indicate polar (rather than radical) decomposition pathways, most likely involving water (always present in the system in small amounts) acting as a catalyst in this process (Scheme 1).[2]

In order to test the above-mentioned hypothesis, we have undertaken ab initio quantum-mechanical calculations of the 1,3-hydrogen transfer in HOOOH in the presence of a water molecule.

Methods

Ab initio self-consistent field (SCF) calculations were performed using the GAUSSIAN-92[9a] and GAUSSIAN-94[9b] packages of programs. The reactants,[10] intermediates, and transition states (characterized by their single negative frequency) were optimized with gradient optimization at the MP2/6-31++G* level of theory, and the corresponding

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

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(6) Koller, J.; Plesničar, B. *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992; Unpublished results cited on p 488. Although the barrier for the 1,3-proton transfer is reproduced reasonably well at the HF level, the rupturing O_3-O_4 bond in TS-1 is longer in the MP2 than in HF (1.530 Å). Also, the O_2-O_3 bond (1.544 Å) is longer in TS-1 than in HOOOH (1.435 Å)[1] in HF. This trend was observed also by using the 6-31++G* basis set.

(7) (a) The kinetics of decomposition was measured by following the decay of the OOOH absorption (^1H NMR) of hydrogen trioxide, generated by the low-temperature ozonation of hydrazobenzene. This system provided relatively the highest yields of HOOOH without the interfering presence of organic hydrotrioxides (ROOOH), and allowed the use of a variety of solvents for kinetic measurements. (b) Our preliminary results of ^{17}O NMR spectroscopic studies on ^{17}O-enriched HOOOH revealed only one relatively strong absorption at 305 ppm (at −40 °C, relative to $H_2{}^{17}O$ in methyl acetate; $\Delta\nu_{1/2} = 540$ Hz), which we tentatively assigned to terminal oxygen atoms. This absorption, which disappeared after warmup to 15 °C, is deshielded by 118 ppm with respect to hydrogen peroxide ($H_2{}^{17}O_2$, $\delta^{17}O$ 187 ppm).

(8) Bielski and Schwartz reported that an intermediate, formed in small amounts in the pulse radiolysis of air-saturated water solutions of perchloric acid and assigned to HOOOH, decomposed ($t_{1/2} = 17$ s in 0.027 M acid at 0 °C) with the activation energy of 16.5 kcal/mol at pH 2. Bielski, B. H. J.; Schwartz, H. A. *J. Phys. Chem.* **1968**, *72*, 3836.

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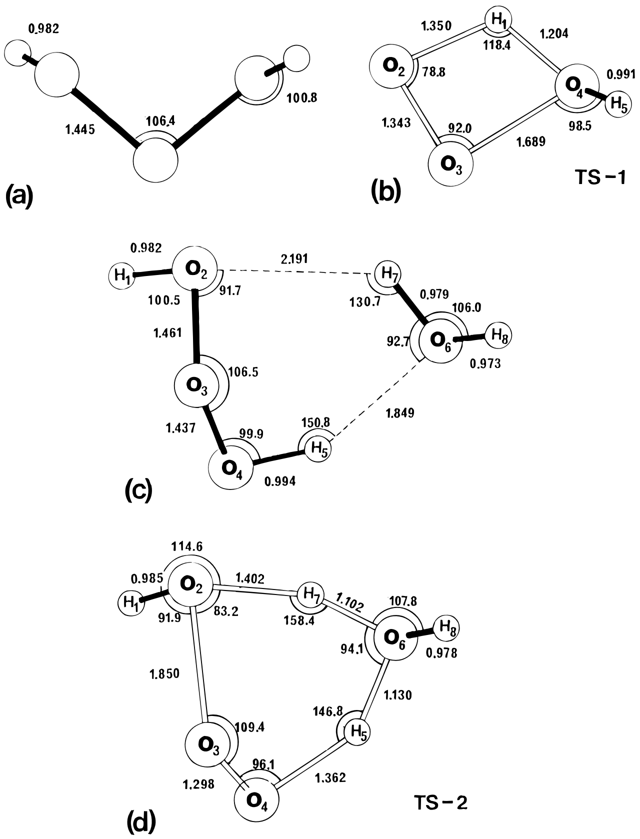
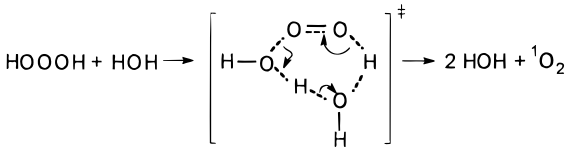


Figure 1. Optimized MP2/6-31++G* structures (in angstroms and degrees) of (a) HOOOH ($\angle HOOO = 79.6°$), (b) the transition state, TS-1, for HOOOH → HOH + $^1O_2$ ($\angle H_1O_2O_3O_4 = 4.3°$, $\angle H_5O_4O_3O_2 = 98.6°$), (c) the complex HOOOH−HOH ($\angle H_1O_2O_3O_4 = 72.9°$, $\angle O_2O_3O_4H_5 = 74.3°$, $\angle O_4H_5O_6H_7 = 0°$), and (d) the transition state, TS-2, for HOOOH + HOH → 2 HOH + $^1O_2$ ($\angle H_1O_2O_3O_4 = 66.1°$, $\angle H_5O_4O_3O_2 = 57.8°$, $\angle O_4H_5O_6H_7 = 7.0°$).

Scheme 1



energies reported were calculated at the MP4//MP2/6-31++G* level.[9c] The equilibrium geometry of hydrotrioxide anion, $HOOO^-$, was also calculated at the MP4/6-31++G** (MP4-SDTQ)[9c] level of theory. For comparison, the density functional theory methods (the Becke and Lee−Yang−Parr nonlocal gradient-corrected exchange-correlation functionals (BLYP/6-31++G*);[9d] Vosko, Wilk, and Nusair local correlation functionals (BVWN/6-31++G*)[9e]) were also used to study this species. Unrestricted MP4-SDTQ was used to study hydroxyl radical ($HO^•$) and superoxide ion (O_2^-).

Results and Discussion

The geometry parameters of the transition state for the intramolecular hydrogen transfer (reaction 1, TS-1) (Figure 1), and the computed energy barrier of 48.6 kcal/mol (Table 1) are nearly identical with those reported previously for the same process at the MP4//MP2/6-31G** level of theory.[5] Therefore, this barrier is far too high (at least for a factor 3−4) to commensurate with the observed experimental activation energies.

Table 1. Energies (au) of Reactants, Complexes, Transition Structures, and Products for the Intramolecular Proton Transfer in Hydrogen Trioxide and in the Hydrogen Trioxide−Water System

	MP2/6-31++G*	MP4//MP2/6-31++G*
	HOOOH → HOH + $^1O_2$	
HOOOH	−226.102 73 (0.0)[a]	−226.135 31 (0.0)
TS-1	−226.021 12 (+51.2)	−226.057 79 (+48.6)
HOH + $^1O_2$	−226.118 97 (−10.2)[b]	−226.146 10 (−6.8)[b]
	HOOOH + HOH → 2HOH + $^1O_2$	
HOOOH + HOH	−302.312 86 (0.0)	−302.356 08 (0.0)
(HOOOH)(HOH)	−302.330 41 (−11.0)	−302.373 49 (−10.9)
TS-2	−302.286 58 (+16.5)	−302.332 00 (+15.1)[c]
$(HOH)_2$ + $^1O_2$	−302.340 38 (−17.3)	−302.378 00 (−13.7)
2 HOH + $^1O_2$	−302.329 10 (−10.2)	−302.366 87 (−6.8)

[a] Relative energies (kcal/mol) are given in parentheses. [b] HOH (MP2/6-31++G*, $R(O-H) = 0.971$ Å, $\angle H-O-H = 105.4°$, $E = -76.21013$ au; MP4//MP2/6-31++G*, $E = -76.22078$ au). $^1O_2$ (MP2/6-31++G*, $R(O-O) = 1.274$ Å, $E = -149.90884$ au; MP4//MP2/6-31++G*, $E = -149.92532$ au). [c] The zero-point energy correction, calculated with the analytical second derivative at the 6-31++G* level (the geometry optimized at the same level) and corrected by an empirical factor of 0.893, lowers this value to 14.5 kcal/mol. The zero-point energy corrected value ΔE ($E_{TS-2} - E_{HOOOH-HOH}$) is 23.4 kcal/mol.

When a molecule of water was allowed to participate in the 1,3-hydrogen migration (reaction 2) the energy barrier was drastically lowered.[11] Only one, i.e., a six-centered cyclic transition state (TS-2), was found that is more stable than TS-1 by 33.5 kcal/mol ($\Delta E^‡ = 15.1$ kcal/mol) relative to the isolated reactants, and 26.0 kcal mol less stable than the HOOOH−H_2O complex.

The Mulliken population analysis showed that the migrating hydrogen behaves as a proton in these reactions (1 and 2). Apparently, the water molecule participates in the process as a bifunctional catalyst by accepting H_5 from HOOOH to a greater extent than transferring its H_7 to the polyoxide O_2 at the transition state.[12] As a consequence, the O_2-O_3 bond is considerably polarized. It is interesting to mention that the geometry of the hydrogen trioxide part of TS-2 resembles (apart from the dihedral angle $\angle H_1O_2O_3O_4$) that of the hydrotrioxide anion, $HOOO^-$. In this species, which has been proposed to be a key intermediate in the ozonation of saturated compounds,[13] the O_2-O_3 is even more polarized than in TS2 (see Table 2). The extraordinary long O_2-O_3 bond distance and the Mulliken charge distribution indicate that $HOOO^-$ is dissociating into HO^- and O_2.[14] Therefore, it seems unlikely that this loosely bound structure could exist as a distinguished molecular entity in water solutions of hydrogen trioxide (HOOOH + HOH → $HOOO^-$ + H_3O^+).[2]

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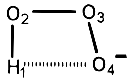
(10) (a) For a pioneering modern *ab initio* study of HOOOH, see: Cremer, D. *J. Chem. Phys.* **1978**, *69*, 4456. Cremer, D. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 1. (b) See also: Jackels, C. F.; Phillips, D. H. *J. Chem. Phys.* **1986**, *84*, 5013.

(11) For theoretical studies of the modification of potential energy surfaces by solvation, see for example: Bosch, E.; Lluch, J. M.; Bertran, J. *J. Am. Chem. Soc.* **1990**, *112*, 3868 and references cited therein. Bach, R. D.; Owensby, A. L.; Gonzalez, C.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1991**, *113*, 6001. Morokuma, K.; Muguruma, C. *J. Am. Chem. Soc.* **1994**, *116*, 10316.

(12) Optimization of HOOOH−HOH complex and transition state TS-2 with 6-31++G and 6-31++G* basis sets gave qualitatively similar results except for the distance O_2-O_3 which was considerably less polarized in the transition state, and the O_3-O_4 bond which was somewhat longer in TS-2 than in HOOOH. The energy (6-31++G) of TS-2 was 22.6 kcal/mol higher than that of the isolated reactants and 35.1 kcal/mol higher than that of the HOOOH−HOH complex. The corresponding 6-31++G*//6-31++G* values were much higher, i.e., 43.8 and 51.6 kcal/mol, respectively. (See supporting information.)

(13) Nangia, P. S.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105. Pryor, W. A.; Ohto, N.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 3614. Li, S.; Deslongchamps, P. *Tetrahedron Lett.* **1993**, *34*, 7759 and references therein.

Table 2. Equilibrium Geometries (Å, deg) and Energies (au) for Hydrotrioxide Anion, $HOOO^-$, at Various Levels of Theory



	6-31++G	6-31++G** [a]	MP2/ 6-31++G* [b]	MP4/ 6-31++G**
$R(H_1-O_2)$	0.957	0.949	0.982	0.979
$R(O_2-O_3)$	1.480	1.420	1.958	2.086
$R(O_3-O_4)$	1.494	1.402	1.304	1.341
$R(H_1 \cdots O_4)$	2.079	1.956	2.378	2.393
$\angle H_1O_2O_3$	100.1	97.6	79.7	73.4
$\angle O_2O_3O_4$	104.2	105.1	110.0	109.7
$\angle H_1O_2O_3O_4$	0	0	42.5	38.5
E	−224.89147	−224.95815	−225.54036 (−225.57438)[c]	−225.58858

[a] Reference 1. Total atomic charges (e), 6-31++G**: H_1, 0.33; O_2, −0.52; O_3, −0.01; O_4, −0.79 ($\mu = 2.33$ D). MP2/6-31++G*: H_1, 0.38; O_2, −0.96; O_3, 0.07; O_4, −0.49 ($\mu = 2.32$ D). MP4/6-31++G**: H_1, 0.27; O_2, −0.88; O_3, 0.05; O_4, −0.44. ($\mu = 3.03$ D). [b] Density Functional Theory (*Gaussian 94*): BLYP (6-31++G*), $R(H_1-O_2) = 0.985$ Å, $R(O_2-O_3) = 1.902$ Å, $R(O_3-O_4) = 1.337$ Å, $\angle H_1O_2O_3 = 87.9°$, $\angle O_2O_3O_4 = 112.4°$, $\angle H_1O_2O_3O_4 = 54.2°$, $E = -226.12493$ au; BVWN (6-31++G*), $R(H_1-O_2) = 0.979$ Å, $R(O_2-O_3) = 1.969$ Å, $R(O_3-O_4) = 1.331$ Å, $\angle H_1O_2O_3 = 86.9°$, $\angle O_2O_3O_4 = 113.6°$, $\angle H_1O_2O_3O_4 = 61.0°$, $E = -227.48334$ au. [c] MP4//MP2/6-31++G*.

It is also worth commenting briefly on the HOOOH−HOH complex. The binding energy in this complex is 1.5 kcal/mol smaller than that for the cyclic HOOOH dimer.[15] However, the entropic factors are obviously less favorable in the latter case (eight-membered intermolecularly hydrogen-bonded system). This, as well as a relatively good solubility of this polyoxide in less polar solvents, might indicate that HOOOH is more lipophilic than water (and most probably more lipophilic than hydrogen peroxide as well[16a]). Somewhat shorter $O-H\cdots O$ bonds in the $HOOOH-H_2O$ complex (1.85 and 2.19 Å), as compared to those in the $HOOH-H_2O$ complex (1.91 and 2.31 Å),[16] calculated at a comparable level of sophistication, can be rationalized on the basis of greater gas-phase acidity of HOOOH (352 kcal/mol) by 24.3 kcal/mol as compared to HOOH (376 kcal/mol).[17,18] By comparison, hydrogen peroxide is more acidic than water by 14.9 kcal/mol at the MP4//MP2/6-31++G* level of theory.

In summary, the participation of water drastically lowers the activation energy for the decomposition of HOOOH on a singlet potential energy surface. Experimental activation parameters are in good qualitative agreement with theory. Since the effect of solvation was approximated with only one molecule of water, it was reasonable to assume that the involvement of additional molecules of water would further lower the activation energy of this process. Attempts are, therefore, being made to evaluate the energetics of the potential energy surface of 1,3-proton transfer of hydrogen trioxide for such cases and the results of these studies will be reported in due course.[19] The stabilizing effect of dimethyl ether (B), a relatively strong oxygen base, on HOOOH, i.e., the formation of $B\cdots HOOOH\cdots B$ complexes, is also being explored.

Acknowledgment. This research was funded by the Ministry of Science and Technology of the Republic of Slovenia and (in part) the U.S.−Slovene Joint Fund (NSF No. 95-455). We wish to thank Črtomir Podlipnik for preliminary DFT calculations on the hydrotrioxide anion.

Supporting Information Available: Equilibrium energies and geometries of reactants, complexes, transition states (TS-2, TS-3) and products for the reaction $HOOOH + nHOH \rightarrow (n + 1)HOH + {}^1O_2$ at the 6-31++G and 6-31++G* (zero-point energies) ($n = 1$) and at the MP4SDTQ//6-31++G ($n = 2$) level of theory (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(14) The reaction $HOOO^- \rightarrow HO^- + {}^1O_2$ (reaction 1) was endothermic, both at the MP2/6-31++G* ($\Delta E = 26.7$ kcal/mol; HO^-: $R(H-O) = 0.979$ Å, $E = -75.58894$ a.u.) and the MP4/6-31++G** level of theory ($\Delta E = 32.5$ kcal/mol; ${}^1O_2$: $R(O-O) = 1.266$ Å, $E = -149.92538$ au; HO^-: $R(H-O) = 0.973$ Å, $E = -75.61136$ au). The decomposition of $HOOO^-$ to produce superoxide anion (O_2^-) and hydroxyl radical ($HO^\bullet$) was calculated to be slightly less endothermic than reaction 1 at the MP4/6-31++G** level of theory ($\Delta E = 30.9$ kcal/mol. UMP4/6-31++G**, O_2^-, $R(O-O) = 1.387$ Å, $E = -149.97998$ au; $HO^\bullet$: $R(H-O) = 0.976$ Å, $E = -75.55717$ au).

(15) Cyclic dimer $(HOOOH)_2$: $R(H_1-O_2) = 0.983$ Å, $R(O_2-O_3) = 1.462$ Å, $R(O_3-O_4) = 1.432$ Å, $R(O_4-H_5) = 0.989$ Å, $R(O_2\cdots H_5; H_5\cdots O_2) = 1.873$ Å, $\angle H_1-O_2-O_3 = 101.0°$, $\angle O_2-O_3-O_4 = 106.5°$, $\angle O_3-O_4-H_5 = 101.2°$, $\angle H_1-O_2-O_3-O_4 = 68.2°$, $\angle H_5-O_4-O_3-O_2 = 82.1°$. MP4//MP2/6-31++G*, $E = -452.29031$ au.

(16) (a) Mo, O.; Yanez, M.; Rozas, I.; Elguero, J. *Chem. Phys. Lett.* **1994**, *219*, 45. (b) Dobado, J. A.; Molina, J. M. *J. Phys. Chem.* **1994**, *98*, 1819.

(17) The gas-phase acidity was estimated as the energy (MP4//MP2/6-31++G*) difference between the energy minimum of the neutral molecule and that for the corresponding anion. HOOH: $R(H-O) = 0.978$ Å, $R(O-O) = 1.474$ Å, $\angle H-O-O = 99.0°$, $\angle H-O-O-H = 120.6°$. $E = -151.16751$ au. HOO^-: $R(H-O) = 0.973$ Å, $R(O-O) = 1.516$ Å, $\angle H-O-O = 97.6°$. $E = -150.56777$ au. HO^-: $R(H-O) = 0.979$ Å, $E = -75.59732$ au.

(18) Bierbaum et al. give the experimental $\Delta H°_{acid}(H_2O_2) = 374.8 \pm 0.7$ kcal/mol. Bierbaum, V. M.; Schmitt, R. J.; DePuy, C. H.; Mead, R. D.; Schulz, P. A.; Lineberger, W. C. *J. Am. Chem. Soc.* **1981**, *103*, 6262.

(19) Since the treatment of the 1,3-hydrogen migration in HOOOH in the presence of two molecules of H_2O at the MP2/6-31++G* level is beyond our present computational possibilities, we have obtained some preliminary results by calculating the geometries of the 1:2 complex HOOOH−2HOH and the corresponding transition state (TS-3) for the 1,3-hydrogen migration with the 6-31++G basis. The energy of TS-3 was found to be above that of the isolated reactants HOOOH + 2(HOH) by only 5.4 kcal/mol ($\Delta E_1^\ddagger$) and 13.4 kcal/mol ($\Delta E_2^\ddagger$) above the water dimer + HOOOH. However, the reaction from the cyclic hydrogen bonded (eight-membered ring) 1:2 complex HOOOH−2HOH would be much more difficult due to a much higher barrier ($\Delta E_3^\ddagger = 33.5$ kcal/mol). The corresponding MP4/6-31++G*//6-31++G values are 13.7 kcal/mol ($\Delta E_1^\ddagger$), 16.8 kcal/mol ($\Delta E_2^\ddagger$), and 35.5 kcal/mol ($\Delta E_3^\ddagger$). It is interesting to mention that while one molecule of water served as a bifunctional catalyst (as in TS-2), the second water molecule only stabilized the TS-3 by forming two intermolecular hydrogen bonds with the partially formed “hydrotrioxide anion” part of the TS-3. (See supporting information.)