indicates that 3pπ occupation and pπ–dπ backbonding play an important role for the stability of SO_3, which is in fact the only well-known molecule out of those considered by Rajca and Lee.

The present results further allow for a rationalization of the stability of BH_3, BF_3, and $AlCl_3$ with respect to their dimers. There is clearly no backbonding in BH_3, and dimerization to B_2H_6 is favored energetically (per BH_3) by 15 mh on the SCF level ($\approx$32 mh if correlation effects are included).[7] For a discussion of BF_3 and $AlCl_3$ let us start from an electronic structure where π backbonding is suppressed and consider dimerization and backbonding as competing mechanisms of stabilization. Dimerization leads to energy lowerings of 15 mh per BH_3 unit in B_2H_6 (abbreviated $^1/_2B_2H_6$), 35.2 mh ($^1/_2B_2F_6$), and 48.7 mh ($^1/_2Al_2Cl_6$), as listed in Table IV. The trend displayed is in accordance with increasing ionic character of bonding. Backbonding stabilizes BF_3 by 53.7 mh and $AlCl_3$ by 31.3 mh, as noted for δE^π found in Table IV. This shows that π backbonding dominates for BF_3 which forms no dimer in fact.

IV. Summary

We have proposed to measure the ionic character of a bond by the energy increase, δE^{val}, obtained in SCF calculations on deletion of unoccupied cation AOs. Applications to a series of diatomics showed the corresponding δE^{val} to cluster around 10 mh for typical ionic bonds such as in LiH to NaCl. Another group of values of δE^{val}, 35–68 mH, was found for hydrides, fluorides, and chlorides of Al. The remaining diatomics considered (HF, HCl, BH, ClF, BF, BCl, H_2, F_2, Cl_2) lead to markedly larger δE^{val} which exceed 140 mH. Only the weakly bound alkali dimers (Li_2, Na_2, K_2, NaLi) are special with relatively small δE^{val} around 35 mh.

Applications to systems where Y-conjugation is possible showed a large effect for NO_3^- (δE^π = 321 mh) and a relatively small one for BF_3, which is, however, sufficiently large to rationalize the stability of the monomer with respect to dimerization. PO_3^- and $P(CH_2)_3^-$ lead to $\delta E^\pi \approx$ 155 mh. This indicates that Y-conjugation not only provides modest stabilization but also shows that a purely ionic description of the π bond, e.g., Lewis-type structure **1c** $P^{2+}(O^-)_3$ (see Introduction), is inappropriate. Our results are in line with computed 3pπ(P) populations of 0.8, 0.56 (Mulliken, NAO) for PO_3^- and 0.89 (NAO) for $P(CH_2)_3^-$ as reported by Streitwieser et al.[6] Since σ bonds, e.g., in PO_3^-, are certainly polarized, their contribution to the positive charge on P also has to be taken into consideration. If one wants to characterize this state of affairs by resonance structures, then a mixture of **1b**, **1c**, and, to a lesser extent, **1d** appears most appropriate in our opinion.

Acknowledgment. This work has been supported by the "Fonds der Chemischen Industrie".

Chemistry of Hydrotrioxides. A Comparative ab Initio Study of the Equilibrium Structures of Monomeric and Dimeric Hydrotrioxides (CH_3OOOH, $H_3SiOOOH$) and Hydroperoxides (CH_3OOH, H_3SiOOH). Relative Bond Strengths in and the Gas-Phase Acidities of Hydrotrioxides and Hydroperoxides

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Abstract: Ab initio calculations have been carried out to predict the equilibrium structures of monomeric and dimeric CH_3OOOH, $H_3SiOOOH$, CH_3OOH, and H_3SiOOH. The calculated relatively strong binding energies for the intermolecularly hydrogen-bonded cyclic dimers of the hydrotrioxides and hydroperoxides investigated (BE = 6–8 kcal/mol) support the belief that self-association is the characteristic structural feature of these species. Ab initio calculations of the theoretical acidities, defined as the energy differences between the energy minima for the neutral molecules and those for the corresponding anions, reveal the following order of the gas-phase acidities: $H_3SiOOOH > CH_3OOOH > H_3SiOOH > CH_3OOH$. The investigation of relative bond strengths indicates that the RO–OOH bonds in the hydrotrioxides are weaker than the ROO–OH bonds, supporting the predictions from the previous thermochemical and kinetic studies that the split into RO• and •OOH radicals is the lowest energy radical decomposition pathway available for these polyoxides.

Alkyl hydroperoxides (ROOH) and alkyl hydrotrioxides (ROOOH) are key species in oxidation of organic compounds with oxygen and ozone.[1,2] Knowledge of their structure is thus essential for studying autoxidation, in the chemistry of combustion and flames, in atmospheric chemistry, and in biochemical oxidations. Yet relatively few data on the structure of these important compounds have been published. It has already been reported that self-association is one of the most characteristic physical properties of hydroperoxides.[3] It was suggested that, at least at moderate concentrations, cyclic dimeric and, to a lesser extent, trimeric entities predominate in solutions of inert solvents.[3,4] It has also been proposed that the rate of decomposition of hydrogen-bonded hydroperoxides to give radicals is faster than homolysis of the uncomplexed hydroperoxide.[5] However, until now there has been no direct spectroscopic evidence for the various possible self-associated species.

Even less is known about the structure of recently discovered hydrotrioxides (ROOOH).[6] In order to test the hypothesis of

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[1] *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983.

[2] Bailey, P. S. *Ozonation in Organic Chemistry*; Academic: New York, 1982; Vols. 1 and 2.

[3] Walling, C.; Heaton, L. *J. Am. Chem. Soc.* **1965**, *87*, 48.

[4] For a review, see: Richardson, W. H. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 5.

[5] Hiatt, R.; McCarrick, T. *J. Am. Chem. Soc.* **1975**, *97*, 5234. See also: Hiatt, R. In *Organic Peroxides*; Swern, D., Ed.; Wiley: New York, 1971; Vol. 2, Chapter 1. Howard, J. A. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 8.

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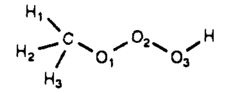
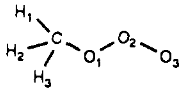
Table I. Equilibrium Geometries and Total Energies for Methyl Hydrotrioxide and Its Anion and Binding Energies for the Methyl Hydrotrioxide Dimer[a]

					$(CH_3OOOH)_2$		
bond lengths (Å) and angles (deg)	STO-3G	4-31G	6-31G	6-31++G	STO-3G	4-31G	6-31G
$C-O_1$	1.453	1.438	1.439	1.420	1.450	1.437	1.439
O_1-O_2	1.396	1.436	1.430	1.465	1.397	1.437	1.432
O_2-O_3	1.392	1.440	1.433	1.496	1.391	1.438	1.431
O_3-H_4	1.003	0.958	0.957		1.006	0.969	0.968
$H_4 \cdots O_1$					1.731	1.798	1.823
$\angle O_2-O_3-H_4$	102.4	103.4	103.9		102.4	102.9	103.4
$\angle O_1-O_2-O_3$	105.9	106.1	106.5	109.0	105.7	106.3	106.7
$\angle C-O_1-O_2$	106.5	107.7	108.1	108.2	107.8	108.8	109.1
$\angle H_1-C-O_1-O_2$	179.1	179.0	179.0	185.2	180.0	179.9	179.9
$\angle C-O_1-O_2-O_3$ (ψ_1)	87.8	85.8	86.0	69.2	83.2	83.4	83.6
$\angle O_1-O_2-O_3-H_4$ (ψ_2)	83.5	82.4	82.6		76.1	81.9	83.0
$\angle O_3-H_4 \cdots O_1$					166.3	164.6	163.2
$\angle O_2-O_1 \cdots H_4$					113.2	106.5	106.2
$\angle O_2-O_1 \cdots H_4-O_3$					7.8	37.2	37.3
STO-3G//STO-3G		-261.167 18				-522.348 30	(-8.75)[b]
4-31G//4-31G		-264.189 63				-528.403 38	(-15.1)[b]
6-31G//6-31G		-264.454 17				-528.930 99	(-14.2)[b]
6-31G**//6-31G		-264.569 44				-529.152 65	(-8.64)[b]
6-31++G//6-31G		-264.464 01		-263.893 01 (6-31++G//6-31++G)			

[a] Total energies in hartrees. [b] Binding energies in kilocalories per mole. The tetrahedral angle in the methyl group (109.47°) and the C–H bond length (1.0900 Å) were not optimized.

the possibility of self-association of hydrotrioxides,[6i] we have undertaken an extensive ab initio molecular orbital study of monomeric and dimeric methyl and silyl hydrotrioxides (CH_3OOOH, $H_3SiOOOH$), and, for comparison, the monomeric and dimeric methyl and silyl hydroperoxides (CH_3OOH, H_3SiOOH) as well. This is to the best of our knowledge the first theoretical study of alkyl hydrotrioxides and of the association of hydroperoxides and hydrotrioxides, respectively.

Since the acidity of hydroperoxides and hydrotrioxides is of fundamental importance to the understanding of several aspects of the chemistry of these classes of compounds, we have also calculated gas-phase acidities of the above-mentioned compounds.

Methods of Calculation

The calculations were carried out within the closed-shell LCAO–SCF approximation with the STO-3G, 4-31G, and 6-31G basis sets.[7] The geometry of CH_3OOH was also optimized with 6-31G**, which has polarization (d-type) functions on non-hydrogen atoms and p-type functions on hydrogen.[8] The electron correlation contribution was examined by the use of Møller–Plesset perturbation theory of the second order (MP2/6-31G**)[9] for the geometry optimization of CH_3OOH and H_3SiOOH, respectively.

The geometry optimization of anions were carried out with the use of the 6-31++G basis set, in which p-polarization functions are added to hydrogens and diffuse functions are added to all atoms (an sp set for heavy atoms and a single s for hydrogen).[10]

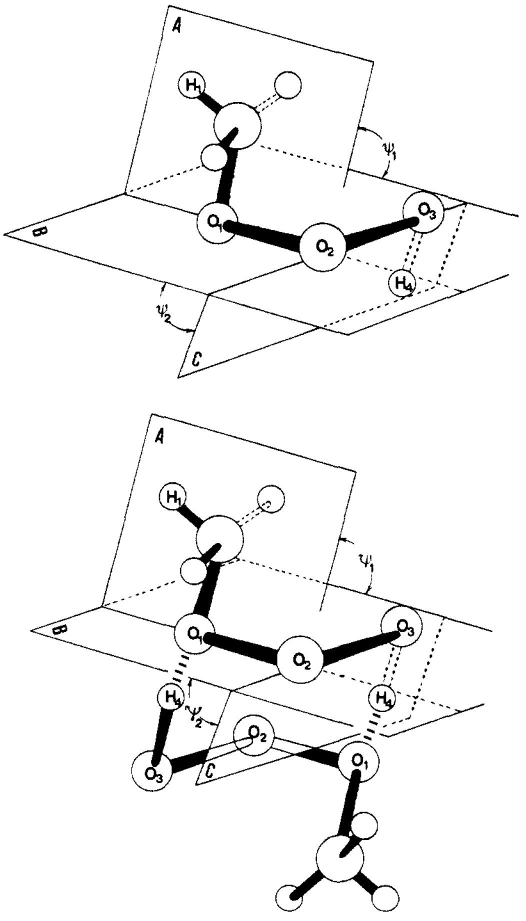


Figure 1. Geometrical representations (atomic numbering scheme) of monomeric and cyclic dimeric CH_3OOOH and $H_3SiOOOH$: C(Si), O_1, and O_2 are in plane A; O_1, O_2, and O_3 are in plane B; O_2, O_3, and H_4 are in plane C.

The procedure was to optimize all geometrical variables in monomeric and dimeric species (unless stated otherwise), subject only to the symmetry constraints in dimeric entities. Dimers were arranged in a cyclic configuration with the oxygen atom next to carbon acting as a proton acceptor.

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(6) (a) Stary, F. E.; Emge, D. E.; Murray, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 1880. (b) Kovač, F.; Plesničar, B. *J. Am. Chem. Soc.* **1979**, *101*, 2677. (c) Shafikov, N. Ya.; Sadykov, R. A.; Shereshovets, V. V.; Panasenko, A. A.; Komisarov, V. D. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1923. (d) Pryor, W. A.; Ohto, N.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 3614. (e) Zarth, M.; de Meijere, A. *Chem. Ber.* **1985**, *118*, 2429. (f) Kuramshin, E. M.; Kulak, L. G.; Zlotskii, S. S.; Rakhmankulov, D. L. *Zh. Org. Khim.* **1986**, *22*, 1986. (g) Corey, E. J.; Mehrotra, M. M.; Khan, A. U. *J. Am. Chem. Soc.* **1986**, *108*, 2472. (h) Posner, G. H.; Wetzburg, M.; Nelson, W. M.; Murr, B. L.; Seliger, H. H. *J. Am. Chem. Soc.* **1987**, *109*, 278. Posner, G. H.; Webb, K. S.; Nelson, W. M.; Kishimoto, T.; Seliger, H. H. *J. Org. Chem.* **1989**, *54*, 3252. (i) Plesničar, B.; Kovač, F.; Hodoščk, M.; Koller, J. *J. Chem. Soc., Chem. Commun.* **1985**, 515. Plesničar, B.; Kovač, F.; Schara, M. *J. Am. Chem. Soc.* **1988**, *110*, 214.

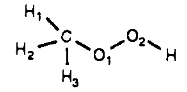
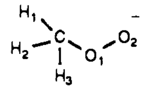
(7) (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. (b) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

(8) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217.

(9) Pople, J. A.; Krishan, H. B.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545, and references cited therein.

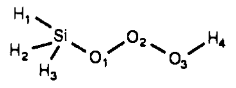
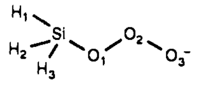
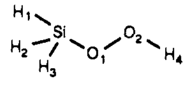
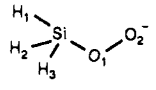
(10) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3263.

Table II. Equilibrium Geometries and Total Energies for Methyl Hydroperoperoxide and Its Anion and Binding Energies for the Methyl Hydroperoxide Dimer[a]

bond lengths (Å) and angles (deg)	 STO-3G	4-31G	6-31G	6-31G**	MP2/ 6-31G**	 6-31++G	(CH₃OOH)₂ STO-3G	4-31G	6-31G
$C-O_1$	1.451	1.428	1.429	1.396	1.420	1.408	1.447	1.426	1.427
O_1-O_2	1.396	1.463	1.458	1.403	1.466	1.525	1.401	1.462	1.457
O_2-H_4	1.002	0.956	0.955	0.946	0.969		1.004	0.965	0.964
$H_4\cdots O_1$							1.752	1.869	1.895
$\angle O_1-O_2-H_4$	101.6	101.1	101.5	101.2	101.6		99.7	100.4	100.8
$\angle C-O_1-O_2$	105.5	104.8	105.0	105.3	103.9	107.0	105.7	105.8	106.0
$\angle C-O_1-O_2-H_4$ (ψ)	108.9	179.7	179.6	179.6	121.7		127.8	179.1	180.0
$\angle H_1-C-O_1-O_2$	178.8	178.5	179.8	179.7	177.5	180.0	178.6	179.0	180.0
$\angle O_2-H_4\cdots O_1$							153.9	152.9	152.2
$\angle O_2-O_1\cdots H_4-O_2$							0.0	0.0	0.0
STO-3G//STO-3G			−187.35205					−374.71617	(−7.57)[b]
4-31G//4-31G			−189.53034					−379.07968	(−11.9)[b]
6-31G//6-31G			−189.72070					−379.45914	(−11.1)[b]
6-31G**//6-31G			−189.80317					−379.61781	(−7.20)[b]
6-31G**//6-31G**			−189.80629						
MP2/6-31G**//MP2/6-31G**			−190.33443						
6-31++G//6-31G			−189.72829			−189.13647 (6-31++G//6-31++G)			

[a] Total energies in hartrees. [b] Binding energies in kilocalories per mole. The tetrahedral angle in the methyl group (109.47°) and the C–H bond length (1.0900 Å) were not optimized.

Table III. Equilibrium Geometries and Total Energies for Silyl Hydrotrioxide, Silyl Hydroperoxide, and Their Anions and Binding Energies for Silyl Hydrotrioxide and Silyl Hydroperoxide Dimers[a]

bond lengths (Å) and angles (deg)	 6-31G	 6-31++G	(H₃SiOOOH)₂ 6-31G	 6-31G	6-31++G	MP2/ 6-31G**	 6-31++G	(H₃SiOOH)₂ 6-31G
$Si-O_1$	1.771	1.737	1.781	1.757	1.759	1.704	1.699	1.752
O_1-O_2	1.441	1.474	1.443	1.464	1.460	1.487	1.564	1.467
O_2-O_3	1.429	1.488	1.430					
O_3-H_4 (O_2-H_4)	0.958		0.974	0.954	0.954	0.970		0.968
$H_4\cdots O_1$			1.734					1.804
$\angle O_2-O_3-O_4$	103.9		103.3					
$\angle O_1-O_2-H_4$				101.5	101.9	98.1		100.4
$\angle O_1-O_2-O_3$	106.2	106.4	106.5					
$\angle Si-O_1-O_2$	109.6	112.6	109.7	105.8	106.7	99.1	103.1	106.3
$\angle H_1-Si-O_1-O_2$	180.2	160.8	180.1	180.0	179.9	176.8		180.0
$\angle Si-O_1-O_2-O_3$ (ψ_1)	84.1	34.6	88.4					
$\angle O_1-O_2-O_3-H_4$ (ψ_2)	79.3		80.9					
$\angle Si-O_1-O_2-H_4$				180.0	179.9	118.8		180.0
$\angle O_3-H_4\cdots O_1$			166.5					
$\angle(O_2-H_4\cdots O_1)$								154.9
$\angle O_2-O_1\cdots H_4-O_3$			44.9					
$\angle(O_2-O_1\cdots H_4-O_2)$								0.0
6-31G//6-31G	−515.49701		−1031.02181 (−17.5)[b]		−440.76547			−881.55341 (−14.1)[b]
6-31++G//6-31G	−515.507647				−440.77324			−881.57006 (−14.8)[b]
6-31++G// 6-31++G		−514.94465			−440.77327		−440.19116	
6-31G**//6-31G	−515.64679		−1031.30634 (−8.0)[b]		−440.88289			−881.77846 (−7.9)[b]
MP2/6-31G**// MP2/6-31G**					−441.37403			

[a] Total energies in hartrees. [b] Binding energies in kilocalories per mole. The optimized value $R(Si-H)$ of 1.480 Å, obtained for H_3SiOOH at the 6-31G//6-31G level, was used through all other calculations. The tetrahedral angle in the silyl group (109.47°) was not optimized.

The binding energies (BE) for dimers were obtained by substracting the sum of the monomer energies from the energy of the dimer.

Bond orders were calculated from force constants and bond lengths via eq 1, where k is the force constant (mdyn/Å) and R_e is the equilibrium bond length (Å).[11] Both these values were obtained at the 6-31G//6-31G level of theory.

$$\text{bond order} = 0.55747(k/R_e)^{1/2} \qquad (1)$$

Results and Discussion

A. Structures. The parameters of equilibrium geometries of both hydrotrioxides and hydroperoxides, as well as those of the corresponding cyclic dimers, are collected in Tables I–III. The schematic representations of the geometry of the monomeric and dimeric entities are shown in Figures 1 and 2.

CH_3OOOH and $H_3SiOOOH$. No experimental data are available for these or any other alkyl hydrotrioxide. These calculations are the first attempt to get insight into the geometry of this class of polyoxides.

It is interesting to note that 4-31G and 6-31G geometry parameters for CH_3OOOH as well as $H_3SiOOOH$ are in good qualitative agreement with the results of an ab initio study of hydrogen trioxide, HOOOH. Namely, Cremer calculated, by using 6-31G* basis set and by treating electron correlation via many-body Rayleigh–Schrödinger–Møller–Plesset perturbation theory (MP2), the following geometrical parameters: R(O–H)

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[11] Politzer, P.; Ranganathan, S. *Chem. Phys. Lett.* **1986**, *124*, 527. For a study of bond orders in some peroxides, see: Politzer, P.; Bar-Adon, R.; Miller, R. S. *J. Phys. Chem.* **1987**, *91*, 3191.

Table IV. Net Atomic Charges (e)[a]

atom	CH_3-O_1-O_2-O_3-H_4	$(CH_3OOOH)_2$	CH_3-O_1-O_1-H_4		$(CH_3OOH)_2$
	6-31G**/6-31G	6-31G**//6-31G	6-31G**//6-31G	MP2/6-31G**	6-31G**//6-31G
C	-0.015	-0.011	0.003	0.007	0.009
O_1	-0.339	-0.400 (-0.061)[b]	-0.377	-0.372	-0.433 (-0.056)[b]
O_2	-0.087	-0.082			
O_3 (O_2)	-0.335	-0.336	-0.375	-0.371	-0.379
H_4	0.372	0.428 (+0.056)[b]	0.369	0.371	0.415 (+0.046)[b]

	H_3Si-O_1-O_2-O_3-H_4	$(H_3SiOOOH)_2$	H_3Si-O_1-O_2-H_4		$(H_3SiOOH)_2$
	6-31G**//6-31G	6-31G**//6-31G	6-31G**//6-31G	MP2/6-31G**	6-31G**//6-31G
Si	1.009	1.022	1.021	1.010	1.030
O_1	-0.484	-0.556 (-0.072)[b]	-0.516	-0.492	-0.583 (-0.067)[b]
O_2	-0.079	-0.075			
O_3 (O_2)	-0.321	-0.358	-0.364	-0.362	-0.370
H_4	0.374	0.447 (+0.073)[b]	0.377	0.383	0.433 (+0.056)[b]

[a] The term net atomic charge is defined as $Z - n$(6-31G**//6-31G or MP2/6-31G**), where Z is the atomic number and n is the net electronic density of an atom. [b] The losses and gains of charge (e) after complexation.

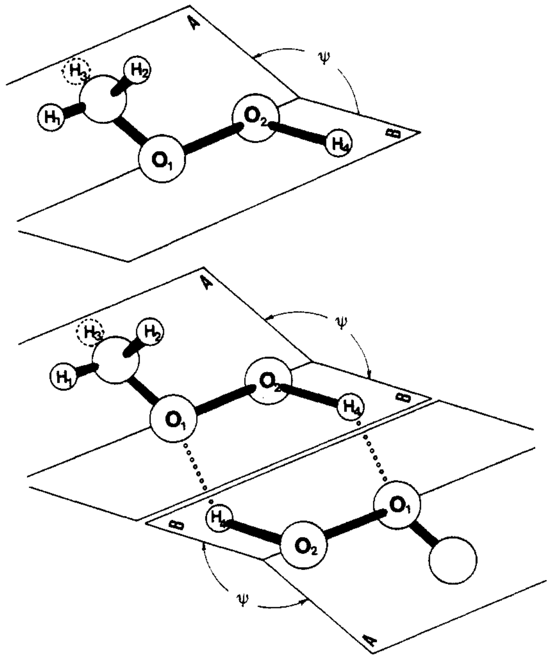

Figure 2. Geometrical representations (atomic numbering scheme) of monomeric and dimeric CH_3OOH and H_3SiOOH: C(Si), O_1, and O_2 are in plane A; O_1, O_2, and H_4 are in plane B.

= 0.972 Å, R(O–O) = 1.439 Å, ∠O–O–O = 106.3°, ∠O–O–H = 100.2°, ψ = 78.1°.[12] This is actually not surprising, since it is known from the previous studies that calculations with minimal and moderately sized extended basis sets can better reproduce the geometry and relative energies of peroxides than either DZ or DZ+P calculations due to a fortuitous cancelation of basis set and correlation errors. Thus, it seems unlikely that further refinement of the geometry of these hydrotrioxides at still higher levels of theory, prohibitively expensive for our purposes, including correlation effects would result in major changes of the geometry.

As expected, the minimal STO-3G basis set rather severely underestimates the O–O distance in CH_3OOOH also giving the wrong sequence of the distances (O–O < C–O instead of O–O > C–O).

The Mulliken population analysis with the use of 6-31G**//6-31G shows a considerable accumulation of charge on both terminal oxygen atoms, with only a little charge accumulated on the central oxygen (Table IV). The calculated net atomic charges on oxygen and hydrogen atoms are very similar to those calculated by Jackels et al. for HOOOH by using 6-31G**/CI (O_1, O_3, -0.31e; O_2, -0.07e; H, 0.35e).[13] The results of the population analysis thus support the belief that the middle oxygen atom is most probably the "electrophilic" center in hydrotrioxides. Namely, we have recently reported that hydrotrioxides of benzylic ethers and alcohols, as well as dimethylphenylsilane hydrotrioxides, oxidize substituted methyl phenyl sulfides to the corresponding sulfoxides as electrophilic oxidants (the Hammett ρ value, -1.7 ± 0.2, acetone-d_6 or methyl acetate at -78 °C).[14] A nucleophilic attack by the olefins on triethylsilane hydrotrioxide has also been reported.[6h]

The calculated electric dipole moment of CH_3OOOH (6-31G**//6-31G, μ = 1.38 D) is somewhat greater than that of $H_3SiOOOH$ (μ = 1.16 D). Both these values are in close agreement with the net moment of 1.26 D, calculated for HOOOH at the CI level.[13]

CH_3OOH and H_3SiOOH. Although there are some reports in the literature on the structure of some crystalline hydroperoxides,[15] no experimental structural data are available on any silyl hydroperoxide.

As in the case of CH_3OOOH, STO-3G underestimates the O–O distance in CH_3OOH compared to the experimentally obtained values for the O–O bond in hydroperoxides. Namely, it is usually found that the O–O bond in crystal structures of these peroxides is in the range 1.46–1.47 Å.[15] On the the other hand, the dihedral angle, ψ (109°), is relatively well reproduced at this level of theory. Namely, experiment predicts the value of 114° for the dihedral angle in CH_3OOH.[16,17] It is interesting to note that the experimental[18a] and theoretical value (at the Hartree–Fock level with uncontracted (11s6p2d/6s2p) basis set)[18b] for ψ in HOOH is 111°.

The 4-31G and 6-31G geometrical parameters for CH_3OOH are in good agreement with those of Bair and Goddard (R(C–O) = 1.446 Å, R(O–H) = 0.967 Å, R(O–O) = 1.452 Å, ∠C–O–O = 105.0°, ∠O–O–H = 99.6°, ψ = 126°),[19] except for the dihedral angle ψ. We were not able to find a local minimum at ψ = 110–130° at these levels of theory. The same results were obtained with 6-31G**. This basis set even underestimates the O–O distance considerably. However, with the use of MP2/6-31G**, the dihedral angle was reproduced reasonably well. It is interesting

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to note that the full structure optimization with this basis set resulted in some distortion of the methyl group ($\angle H_1$–C–O_1–O_2 = 177.5°). Namely, with decreased dihedral angle ψ, the distortion somewhat increases.[17]

Similar observations were made also in the case of H_3SiOOH. The dihedral angle ψ (118.8°), which is somewhat smaller in comparison to the calculated dihedral angle in CH_3OOH, was reproduced only at MP2/6-31G** level of theory. A distortion of the silyl group ($\angle H_1$–Si–O_1–O_2 = 176.8°) became also evident only at this level of sophistication.

Again, as in the case of the hydrotrioxides, the calculated electric dipole moment of CH_3OOH (MP2/6-31G**, μ = 1.81 D) is somewhat greater than that of H_3SiOOH (μ = 1.66 D).

Hydrogen-Bonded Complexes. Calculated dimeric structures of the hydrotrioxides and hydroperoxides under investigation were found to have a symmetric cyclic structure with two equivalent O–H···O distances (Tables I–III; Figures 1 and 2). Cyclic structure was found to be a local minimum on the potential surface and not a saddle point, as tested by an unsymmetric distortion into the equilibrium geometry of the cyclic dimer. Although it is apparent from the above discussion that high level treatment of correlation effect, not practical for the present study, would be necessary to describe the geometry of the dimers, the lack of such a treatment appears to be not a deciding factor in our study. Namely, Bair and Goddard reported, using generalized valence bond (GVB) and configuration interaction method, an extremely flat potential energy function for the C–O–O–H torsion (ΔE = 0.25 kcal/mol, ψ = 126–180°).[19]

Comparing the hydrogen bond distance O–H···O (R_{HB}) in dimeric hydrotrioxides and hydroperoxide species, we see that in the former the R_{HB} are shorter than in the latter at all levels of theory investigated. At the same time, the hydrogen bonds are nearly linear in the hydrotrioxide dimers with the binding energies being more negative as compared to the corresponding values for the hydroperoxide dimers.[20,21] It should be pointed out that 6-31G**//6-31G binding energy for CH_3OOH is in good agreement with the enthalpy for self-association of $(CH_3)_3COOH$; i.e., $-\Delta H$ = 6.0 ± 0.4 kcal/mol, as determined by IR[3,22a] and NMR[22b] spectroscopic methods. The direct comparison of the computed binding energies with experimentally obtained enthalpies is, strictly speaking, possible only after their conversion to ΔH^{298}. Due to the size of the largest basis set (6-31G**) and the size of the systems under investigation (which make the calculations of the zero-point vibrational energies very time consuming), ΔH^{298} was calculated only in the case of CH_3OOH.[23,24] After a basis set superposition error (BSSE) correction of 0.56 kcal/mol,[25,26] the computed binding energy of −7.20 kcal/mol (6-31G**//6-31G) is translated into an enthalpy of dimerization of −4.74 kcal/mol. Due to neglect of electronic correlation energy in our calculations, it is difficult to place any definitive uncertainties on the hydrogen-bonding energies from these sources of error. However, a recent study of basis set and correlation effects in neutral hydrogen-bonded dimers of NH_3, H_2O, and HF indicates that electron correlation was important in shortening and stabilizing the hydrogen bonds in these dimers.[27] Thus, it seems safe to predict that ΔH^{298} for CH_3OOH dimerization, calculated at the 6-31G**//6-31G level of the theory, is almost certainly too small.

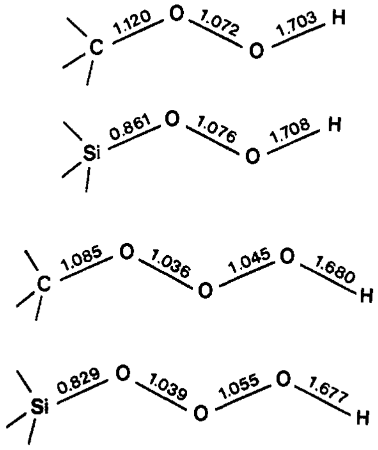

Figure 3. Bond orders in CH_3OOH, H_3SiOOH, CH_3OOOH, and $H_3SiOOOH$.

The overall trends in the Mulliken charges, when going from the monomeric to dimeric entities, are consistent with those expected of the intermolecularly hydrogen-bonded associates. The acceptor oxygen atom gains charge, while the hydrogen atom loses it. It is indicative to note that these gains and loses of charge are greater in the case of the association of the hydrotrioxides at all levels of calculations (Table IV).

B. Bond Orders. In order to get some insight into relative bond strengths in these species, we have calculated bond orders for various bonds. Namely, it has recently been demonstrated that bond orders, calculated from force constants and bond lengths by eq 1, correlate well with experimentally obtained bond dissociation energies (BDE), especially within a given family of bonds.[11] Thus, the ab initio GAUSSIAN 86 program was used at the 6-31G level to compute the bond force constants. The results are summarized in Figure 3.

As seen from Figure 3, the O–O bonds in the two hydroperoxides have nearly the same bond orders. The same holds for the O–H bonds in these two species. Thus, it seems safe to predict that BDE of the O–O and O–H bonds in H_3SiOOH, for which there are no experimental data available, must be very similar to those in CH_3OOH (BDE: CH_3O–OH, 44 kcal/mol; CH_3O-O–H, 88–89 kcal/mol).[28]

It has already been shown on thermochemical grounds that the split into RO• and •OOH radicals in hydrotrioxides is the lowest energy and the fastest radical decomposition pathway available (BDE: CH_3O–OOH, 23 kcal/mol; CH_3OO–OH, 29 kcal/mol).[28] The calculated bond orders of the respected O–O bonds in both

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(20) Dimerization energy–decomposition study of hydrogen-bonded dimers of H_3SiOOH and $H_3SiOOOH$, performed by the method of Morokuma[21] at the 6-31G//6-31G level of theory, revealed that each of these two associates is strongly ES in nature, with a small but significant contribution from CT. $(H_3SiOOH)_2$: BE = −14.1, ES = −23.5, EX = 18.0, PL = −3.1, CT = −5.5, MIX = −0.1 kcal/mol. $(H_3SiOOOH)_2$: BE = −17.5, ES = −29.4, EX = 24.2, PL = −4.3, CT = −6.8, MIX = −1.2 kcal/mol.

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(23) For conversion of the computed binding energy to enthalpy, the following equation was used $\Delta H^{298} = \Delta E_e^\circ + \Delta E_v^\circ + \Delta(\Delta E_v)^{298} + \Delta E_r^{298} + \Delta E_t^{298} + \Delta PV$ where ΔE_e° is the computed electronic energy change (BE), ΔE_v° is the change in zero-point vibrational energy, and $\Delta(\Delta E_v)^{298}$ is the change in the vibrational energy difference between 298 and 0 K. The last three terms are for changes in the rotational and translational degrees of freedom and the work term. Within the harmonic approximmation, ΔE_v° and $\Delta(\Delta E_v)^{298}$ were calculated to be 2.30 and 2.49 kcal/mol, respectively, at the 6-31G**//6-31G level. In keeping with the previous observations, both values were reduced by 10% to bring them in closer agreement with experimental values (the neglect of anharmonic effects).[24] The rotational, translational, and the work terms were treated classically ($-{}^3/{}_2RT$ for ΔE_r^{298}, $-{}^3/{}_2RT$ for ΔE_t^{298}, and $-RT$ for ΔPV), and they sum to −2.37 kcal/mol at 298 K.

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Table V. Calculated Acidities

compound	ΔE_{eq}
CH_3OOH	371.4 (16.10)
H_3SiOOH	365.3 (15.84)
CH_3OOOH	358.3 (15.54)
$H_3SiOOOH$	353.3 (15.32)

[a] ΔE_{eq}, the difference in energy between the energy minimum of the neutral molecule (RHF, 6-31++G//6-31G) and that for their anion (RHF, 6-31++G//6-31++G), in kilocalories per mole and electronvoltes in parentheses. The difference between 6-31++G//6-31G and 6-31++G//6-31++G minimum energies was found to be negligible in the only case investigated (H_3SiOOH; see Table III).

hydrotrioxides unambiguously confirm these predictions.

The induced decomposition, i.e., the abstraction of the hydrogen atom by various reactive radicals, $Z^\bullet$ present in the system (eq 2), is a very common decomposition pathway for hydroperoxides.[5]

$$\mathrm{ROOH + Z^\bullet \rightarrow ROO^\bullet + HZ} \qquad (2)$$

Since the O–H bonds in the hydrotrioxides investigated are, according to the bond strength–bond order correlation,[11] consistently weaker than the O–H bonds in the corresponding hydroperoxides, an even higher reactivity of hydrotrioxides in this type of reactions (eq 3), producing alkyltrioxyl radicals, is expected.

$$\mathrm{ROOOH + Z^\bullet \rightarrow ROOO^\bullet + HZ}$$

C. Gas-Phase Acidities. Since hydroperoxides are rather unstable compounds at room temperature (therefore, it is difficult or in most cases impossible to prepare them in high purity), the acidity of only a few of the members of this class of compounds has been measured experimentally.[29] There are to the best of our knowledge no reports in the literature on the acidity of any silicon analogues. On the other hand, hydrotrioxides are too unstable, even at low temperatures, for their acidity to be measured.

The theoretical acidity was estimated as the energy difference between the energy minimum for the neutral molecules and that for the corresponding anions. Since it has already been reported that diffuse functions are essential for the correct calculation of the energy of anions,[30] we have used the 6-31G++G basis set for this purpose. Summary of theoretical acidities of the hydroperoxides and hydrotrioxides is presented in Table V.

Although the use of such calculations has the disadvantage that they do not reproduce the acidity with sufficient accuracy unless the highest level calculations including extensive corrections for electron correlation is used, we nevertheless believe that the observed order of acidity, i.e., $H_3SiOOOH > CH_3OOOH > H_3SiOOH > CH_3OOH$, correctly reproduces the relative acidities of these species. Namely, this order of acidity is in accordance with the observation that silanols are stronger acids than the corresponding alcohols. For example, pK_a values of triethylsilanol and *tert*-butyl alcohol are 13.6 and 17, respectively.[31] At the same time, hydroperoxides are more acidic than alcohols ($(CH_3)_3COOH$, pK_a = 12.8).[29]

Conclusions

The calculations reported are, except for CH_3OOH, the first ab initio studies of the equiliium structures of H_3SiOOH, CH_3OOOH, and $H_3SiOOOH$ and their anions. At the same time, this is the first theoretical study of the cyclic dimers of these species.

The structural parameters for the hydroperoxides investigated are very similar to those reported previously for CH_3OOH with the GVB + CI method. The dihedral angle in CH_3OOH (ψ = 121.7°) and H_3SiOOH (ψ 118.8°) was reproduced satisfactorily only by taking into account the electron correlation contributions from the 6-31G** basis set and the Møller–Plesset perturbation theory through second order (MP2).

On the other hand, the structure of both hydrotrioxides (including both dihedral angles, ψ_1, and ψ_2), calculated with the 6-31G basis set, was found to be very close to that of HOOOH, for which data are available from previous theoretical studies at higher levels of theory. This is most probably due to the fact that, in trioxides, the rotational potential is much steeper compared to that in peroxides, and thus less sensitive to basis set effect. Therefore, reasonable answers are obtained even with a relatively smaller basis set.

The relatively strong binding energies (BE = 6–8 kcal/mol), calculated for the intermolecularly hydrogen-bonded cyclic dimers of the hydroperoxides and hydrotrioxides investigated at the 6-31G**//6-31G level of sophistication, correlate very well with those obtained experimentally for self-association of $(CH_3)_3COOH$, structurally most similar hydroperoxide, for which such data are available ($-\Delta H = 6.0 \pm 0.4$ kcal/mol). It is thus reasonable to assume that self-association is most probably the main structural feature of hydroperoxides and hydrotrioxides as well.

The order of theoretical acidities, i.e., $H_3SiOOOH > CH_3OOOH > H_3SiOOH > CH_3OOH$, is in accordance with the expectation that an increased number of oxygen atoms in the members of the homologous series of this class of compounds should increase their acidity. The calculations revealed that $H_3SiOOOH$ and CH_3OOOH give up a proton more readily than the corresponding hydroperoxides by about 12–13 kcal/mol.

The RO–OOH bonds in the hydrotrioxides are weaker than the ROO–OH bonds, thus supporting the observations from previous thermochemical and kinetic studies that the split into $RO^\bullet$ and $^\bullet OOH$ radicals is the lowest energy radical decomposition pathway available for these polyoxides. At the same time, somewhat weaker O–H bonds in the hydrotrioxides, as compared to the corresponding hydroperoxides, render these polyoxides even more susceptible to induced decomposition.

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