Hydrogen Polyoxides. *Ab Initio* Molecular Orbital Study

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Abstract: *Ab initio* molecular orbital theory with minimal STO-3G basis set is used to study conformations, stabilities, and possible modes of decomposition of H_2O_3 and H_2O_4. Both compounds are theoretically stable molecular species with respect to decomposition products. A zigzag skew chain is proposed. H_2O_4 can exist in various conformations of similar total energies. The possibility of intramolecular hydrogen bonds in this compound is indicated.

The compounds of the type XO_nX ($n = 3, 4$; X = H, R) are of theoretical interest because they represent further members of the homologous series beginning with water and hydrogen peroxide on one side and ethers and dialkyl peroxides on the other.

After a long controversy over the existence of polyoxides, infrared and mass spectroscopic evidence has been given for H_2O_3 and H_2O_4.[1] At present there is no experimental information about the structure of these interesting compounds. Most recently the isolation of di-*tert*-butyl trioxide has been reported,[2] and the existence of dialkyl tetroxides is also well documented.[3-5]

Our interest in polyoxides led us to undertake *ab initio* calculations on H_2O_3 and H_2O_4 in order to get some insight into the molecular geometry of these compounds. Minimal basis set STO-3G by Pople, *et al.*, has been used.[6] Standard geometries were employed[7] except for the cases where this was mentioned specifically (see Table I). The geometry of each molecular species was systematically varied (dihedral angle ϕ and OOH angle θ) until a minimum energy was obtained. Complete structure minimization was not undertaken due to computing expenses. Despite the usage of the minimal basis set, we assume that the results obtained are relevant because the calculations on three similar molecules have been made.

Table I. Geometries and Minimum Energies of Compounds under Investigation[a]

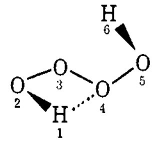
Compound		Θ^b	Ψ	Φ^b	E,[b] au
H_2O		99.9			−74.96588
H_2O_2		99.8		156.9	−148.75237
		98.8		180	−148.75264
H_2O_3		96	109.47	94.5	−222.55571
		96	109.47	180	−222.54849
H_2O_4		96	109.47	91	−296.34641
		96	109.47	180	−296.33919
	A	96	109.47	Tetrahedral angle between OOH groups	−296.34512
	B	96	109.47		−296.35422
$^1\Delta_g$ O_2					−147.55124

[a] Angles are defined in Figure 1. [b] Calculated values. Angles are in degrees.

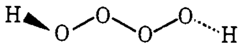
Results and Discussion

The results are presented in Table I. A zigzag skew chain (Figure 1) is the most possible structural feature of H_2O_3 and H_2O_4. The dihedral angle, Φ, which is of principal chemical interest in all peroxides, varies from 156.9° in H_2O_2 and 94.5° in H_2O_3 to 91° in H_2O_4. The consequences of the minimal basis set can most easily be seen from the calculated values of the dihedral angle in H_2O_2. These values are rather high compared with that recorded experimentally in the vapor phase (119.8°),[8] but are in good agreement with those reported previously.[9] It is also interesting to point out that calculations on H_2O_3 by using extended basis set[10] give the value of 90° for the dihedral angle in this compound which agrees well with our results.

The variation of the dihedral angle in going from H_2O_2 to H_2O_4 could probably be explained on the ground that electrostatic repulsion between OH bonds decreases with increasing number of oxygen atoms in the molecule. The above mentioned values were obtained by assuming all oxygen atoms to be in the same plane. In H_2O_4 there is still another possibility. The dihedral angle between the two OOH groups can be taken as tetrahedral (Figure 2, allowing thus two extreme possibilities: one conformation with hydrogen atoms directed one to another (A), and the other with hydrogen atoms in the opposite direction (B).



A, syn



B, anti

The form B (anti) is found to be more stable. Intramolecular hydrogen bonds between H_1 and O_4 and/or H_6 and O_3 are possible in conformation A. From these results it can be concluded that H_2O_4 can exist in various conformations of similar total energies.

Attempts have also been made to evaluate the two possible decomposition mechanisms of H_2O_3. The

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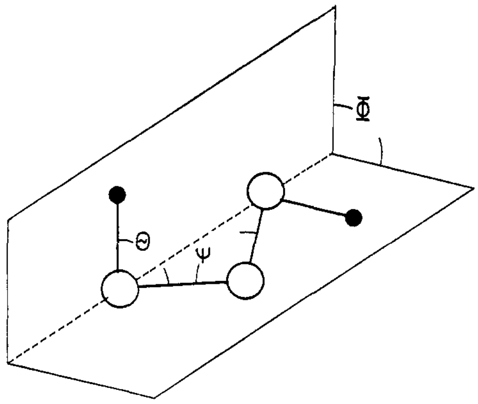

Figure 1. Skew chain structural model of H_2O_3.

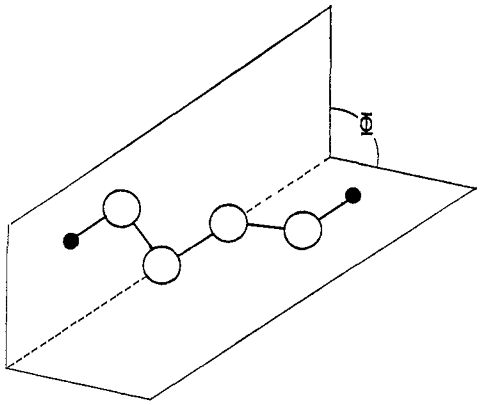

Figure 2. Skew chain structural model of H_2O_4 with dihedral angle between two OOH groups.

lowest theoretical energy for each molecule was used to calculate the energy of reaction 1. In spite of the

$$H_2O_3 \longrightarrow \begin{cases} H_2O + O_2{}^1\Delta_g & E_a = 0.03859 \text{ au} \\ H_2O_2 + \frac{1}{2}O_2{}^1\Delta_g & E_b = 0.02745 \text{ au} \end{cases} \qquad (1)$$

fact that complete geometrical optimization was not made it can be seen that the energy difference ($E_a - E_b$) between the two decomposition reactions is rather small. Different experimental conditions may favor one or the other.

The energy of the decomposition reaction of H_2O_4 (reaction 2) indicates that this compound is a stable

$$H_2O_4 \longrightarrow H_2O_2 + O_2{}^1\Delta_g \qquad E = 0.05034 \text{ au} \qquad (2)$$

molecular species with respect to decomposition into oxygen and hydrogen peroxide.

Although no calculations were made on organic polyoxides, we believe that the geometry of these compounds should be similar to that reported here. Namely, it was found that steric influence of substituents on stereochemistry of organic peroxides is very small at the interatomic distances and angles being considered.[11]

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Effect of Molecular Geometry on Spin–Orbit Coupling of Aromatic Amines in Solution. Diphenylamine, Iminobibenzyl, Acridan, and Carbazole[1a]

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Abstract: The fluorescence quantum yield, the phosphorescence quantum yield, and the lifetimes of a series of aromatic amines (diphenylamine, iminobibenzyl, acridan, and carbazole), whose molecular configurations gradually change from a distinctly nonplanar to a planar geometry, have been investigated at 298 and 77°K in EPA solution. From these data, the important deactivation parameters of the excited states have been derived. The intersystem crossing rate constants and the radiative phosphorescence rate constants decrease dramatically in going from diphenylamine to carbazole, while the radiative fluorescence rate constants change only slightly, leading to the conclusion that the excited state behavior of aromatic amines is dominated by the influence of molecular geometry on spin–orbit coupling.

Spin–orbit coupling in aromatic amines is enhanced relative to aromatic hydrocarbons, as evidenced by increased phosphorescence to fluorescence quantum yield ratios and shorter phosphorescence lifetimes.[2] These properties of aromatic amines are intermediate between those expected for aza-nitrogen heterocyclics with lowest $n\pi^*$ and lowest $\pi\pi^*$ triplet states.[3] It was

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(1) (a) Presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972. (b) Author to whom correspondence should be addressed at the Fachbereich Chemie, Universität Konstanz, Konstanz, Germany.

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