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An ab Initio Molecular Orbital Study of Polyoxides. 2. Fluorine and Alkyl Polyoxides (F_2O_3, F_2O_4, $(CH_3)_2O_3$, $(CF_3)_2O_3$)

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Abstract: Ab initio molecular orbital theory (STO-2G and STO-4G) is used to study equilibrium geometries, dipole moments, charge distribution, and molecular energetics of polyoxides of the type YO_nY (Y = F, CH_3, CF_3; n = 2, 3, 4). All compounds investigated have been found to possess a zigzag skew chain structure, and are stable molecular species with respect to decomposition products.

Ab initio calculations have been found to be a reliable tool for determination of equilibrium geometries and relative energies of molecules.[1,2]

We have recently reported the results of the ab initio study on hydrogen polyoxides.[2] Two recent reports, one on the theoretical[4] and the other on the experimental[5] aspect of the same subject, are in good agreement with our results.

We wish to present in this paper the results of our extended study on other polyoxides of the type YO_nY (Y = F, CH_3, CF_3). The existence of fluorine polyoxides is still a controversial issue.[6] On the other hand, two trioxides, i.e., CF_3OOOCF_3[7] and $(CH_3)_3COOOC(CH_3)_3$,[8] have recently been isolated and their spectroscopic data reported.

We have used in the present study the ab initio method to solve the Roothaan equation. Owing to the size of molecules, minimal STO-2G basis set was used to calculate molecular geometries of compounds under investigation.[9] The experience with this basis set (each Slater orbital is expanded into only two Gaussian ones) shows that such an expansion gives the same geometry parameters as STO-3G. Unless otherwise stated (see Tables I and II) complete structure minimization was undertaken subject only to the imposed symmetry (C_2 point-group symmetry for YO_4Y). Since a chain of six atoms in tetroxides would require three dihedral angles for complete specification, the problem was simplified by assuming dihedral angles $\angle Y_a\text{-}O_1\text{-}O_2\text{-}O_3$ and $\angle Y_b\text{-}O_4\text{-}O_3\text{-}O_2$ to be 180°. The dihedral angle $\angle Y_b\text{-}O_3\text{-}O_2\text{-}O_1$ in trioxides was taken to be 180°.[3] Tetrahedral arrangement of atoms in CH_3 and CF_3 groups was also assumed.

The calculation of dipole moments, charge distribution, and molecular energetics was performed with STO-4G basis set. Attempts to use the extended 4-31G (split-valence) basis set were frustrated (for larger molecules) by the limited capability of our computer facilities (CDC CYBER 72).

Results and Discussion

The results and experimental values, where available, are summarized in Tables I–III. A zigzag chain with a dihedral angle, Φ, is again the most characteristic feature of all polyoxides investigated. The equilibrium conformations have O–Y groups on the opposite sides of the O–O plane (anti-form). In polyoxides with Y = CH_3 or CF_3, a staggered conformation has been found to have the lowest energy.

The difficulties in obtaining satisfactory values for bond lengths, especially for F–O bonds, by using minimal basis set, have already been reported.[10] Particularly short O–O and particularly long F–O bonds are not accounted for by calculations at this level of approximation. It is interesting to note that bonds in F_2O_2 are also in serious error by using the extended 4-31G basis set (up to 0.2 Å).[4] However, good agreement with experiment has been obtained for the dihedral angle in F_2O_2 and for other compounds investigated.

The characteristic feature of charge distribution in fluorine compounds (Y = F) is dispersion of charge from oxygen atoms bonded to fluorine. All these oxygens bear a positive charge. The effect is most pronounced in the case of fluorine trioxide where oxygen bonded to fluorine, which is located out of the plane of the molecule, bears higher positive charge than the oxygen atom bonded to fluorine oriented in the plane. The alternating charges observed in these molecules were already encountered in theoretical studies on other fluorocarbons.[11,12]

In hydrogen polyoxides, the inner oxygen atoms bear relatively more positive charge compared to oxygens bonded to hydrogen atoms. A similar pattern is observed also in alkyl and fluorine substituted trioxides. Both groups, i.e., CH_3 and CF_3, are electron donating with the effect of the latter being more pronounced. All hydrogen atoms in alkyl polyoxides are positive and their net charges are approximately 0.06. In fluorine substituted alkyl compounds, all fluorine atoms are charged negatively (~ -0.13).

The calculated values for dipole moments of H_2O, H_2O_2, $(CH_3)_2O$, and F_2O are in fair agreement with experimental values. Exception is the calculated value for the dipole mo-

Table I. Equilibrium Geometries,[a] Dipole Moments, and Energies

Compd	r(X–O)	r(O–O)	Θ	ψ	Ω	Φ	μ, D	E, au
O_2		1.2187 (1.207)[b]						−148.611 31
F_2	1.2896 (1.435)[b]							−197.366 98
H_2O	0.9985 (0.957)[c]		98.48 (104.5)[c]				1.745 64 (1.846)	−75.498 93
F_2O	1.3585 (1.409)[d]		102.91 (103.3)[d]				0.196 58 (0.297)[e]	−271.713 01
H_2O_2	1.0096 (0.950)[f]	1.3822 (1.475)	101.69 (94.8)			100.65 (111.5)	1.800 68 (2.2)	−149.826 96
F_2O_2	1.3589 (1.575)[g]	1.3500 (1.217)	105.48 (109.5)			88.42 (87.5)	0.261 67 (1.44)	−346.051 80
H_2O_3	1.0094	1.4012	101.25	102.02	101.25	83.03	1.770 09	−224.166 63
F_2O_3	1.3564	1.4069	103.77	102.76	103.77	88.37	0.220 97	−420.383 85
H_2O_4	1.0094[h]	1.4012[h]	101.25[h]	102.02[h]		87.99	0.259 39	−298.503 45
F_2O_4	1.3564[h]	1.4069	103.77	102.76		88.12	0.037 03	−497.713 74

[a] Bond lengths and angles are in ångströms and degrees, respectively. [b] G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand, New York, N.Y., 1945. [c] K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.*, **36,** 2460 (1962). [d] Y. Morino and S. Saito, *J. Mol. Spectrosc.*, **19,** 435 (1966). [e] L. Pierce, R. H. Jackson, and D. Di Cianni, *J. Chem. Phys.*, **35,** 2240 (1961). [f] R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *ibid.*, **42,** 1931 (1965). [g] R. H. Jackson, *J. Chem. Soc.*, 4585 (1962). [h] Values taken from H_2O_3 and F_2O_3.

Table II. Equilibrium Geometries, Dipole Moments, and Energies

Compd	r(C–X)	r(C–O)	r(O–O)	Θ	ψ	Ω	Φ	μ, D	E, au
CH_3OCH_3	1.1006	1.4704 (1.41)[b]		108.53 (112)[b]				1.473 83 (1.30)[b]	−153.216 59
CF_3OCF_3	1.3552	1.4923		109.74				0.289 34	−742.158 75
CH_3OOCH_3	1.1006[c]	1.4704	1.3822	101.69			100.65	1.767 15	−227.544 93
CF_3OOCF_3	1.3552[c]	1.4923	1.3822	101.69			100.65	0.457 26	−816.4807
CH_3OOOCH_3	1.1006[c]	1.4/04	1.4012	101.25	102.02	101.25	83.03	1.853 59	−301.883 68
CF_3OOOCF_3	1.3552[c]	1.4923	1.4012	101.25	102.02	101.25	83.03	0.851 93	−890.814 32

[a] Bond lengths and angles are in ångströms and degrees, respectively. [b] U. Blukis, P. H. Kasai, and R. Myers, *J. Chem. Phys.*, **38,** 2753 (1963). [c] Values taken from CH_3OCH_3, CF_3OCF_3, H_2O_2, and H_2O_3, respectively.

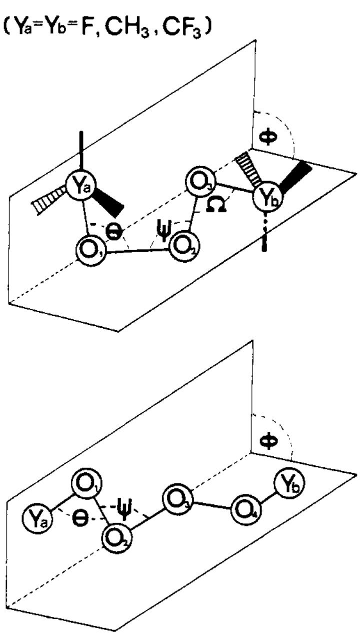

Figure 1. Skew chain structural models of trioxides and tetroxides.

ment of F_2O_2, which is considerably underestimated. The observed ordering (correctly reproduced for the known values) is $\mu(H_2O_2) > \mu(H_2O_3) > \mu(H_2O) > \mu(H_2O_4)$ and $\mu(F_2O_2) > \mu(F_2O_3) > \mu(F_2O) > \mu(F_2O_4)$.

On the other hand, the calculated values for dipole moments of alkyl trioxides are the highest among the investigated compounds. The observed ordering is as follows: $\mu(CH_3OOOCH_3) > \mu(CH_3OOCH_3) > \mu(CH_3OCH_3)$ and $\mu(CF_3OOOCF_3) > \mu(CF_3OOCF_3) > \mu(CF_3OCF_3)$. Although the qualitative interpretation of the observed order of dipole moments in these compounds is rather speculative, we believe that considerable closing of the bond angle (Θ) in going from dialkyl ether to alkyl polyoxides might be sufficient to account for this pattern.

The calculation of the decomposition energetics of fluorine and alkyl polyoxides indicates that these compounds are stable molecular species with respect to decomposition products. We believe that these results are relevant since a comparison of energies (STO-4G) of related systems has been made.

$$F_2O_3 \begin{array}{l} \rightarrow F_2O + O_2\ {}^1\Delta_g; \quad \Delta E = 0.059\ 53\ \text{au} \\ \rightarrow F_2O_2 + \tfrac{1}{2}O_2\ {}^1\Delta_g; \quad \Delta E = 0.026\ 40\ \text{au} \end{array}$$

$$F_2O_4 \longrightarrow F_2O_2 + O_2\ {}^1\Delta_g; \quad \Delta E = 0.050\ 63\ \text{au}$$

$$CH_3O_3CH_3 \begin{array}{l} \rightarrow CH_3OCH_3 + O_2\ {}^1\Delta_g; \Delta E = 0.061\ 78\ \text{au} \\ \rightarrow CH_3O_2CH_3 + \tfrac{1}{2}O_2\ {}^1\Delta_g; \Delta E = 0.033\ 10\ \text{au} \end{array}$$

$$CF_3O_3CF_3 \begin{array}{l} \rightarrow CF_3OCF_3 + O_2\ {}^1\Delta_g; \Delta E = 0.044\ 26\ \text{au} \\ \rightarrow CF_3O_2CF_3 + \tfrac{1}{2}O_2\ {}^1\Delta_g; \Delta E = 0.024\ 60\ \text{au} \end{array}$$

Table III. The Net Atomic Charges (× 10^{-3} e)[a]

Compd	Y_a	O_1	O_2	O_3	O_4	Y_b
H_2O	−169.12	−338.25				−169.12
F_2O	−17.90	35.81				−17.90
H_2O_2	190.87	−190.87	−190.87			190.87
F_2O_2	−16.81	16.81	16.81			−16.81
H_2O_3	204.72	−167.58	−50.25	−191.14		204.25
F_2O_3	−12.20	28.47	−14.81	3.58		−5.03
H_2O_4	290.95	−178.30	−31.64	−31.64	−178.30	290.95
F_2O_4	−3.02	7.39	−4.35	−4.35	7.39	−3.02
$(CH_3)_2O$	(C) −78.89	−232.44				(C) −74.40
$(CF_3)_2O$	(C) 544.79	−257.84				(C) 546.84
$(CH_3)_2O_2$	(C) −80.01	−137.45	−141.20			(C) −84.64
$(CF_3)_2O_2$	(C) 546.37	−134.59	−140.02			(C) 543.98
$(CH_3)_2O_3$	(C) −81.10	−122.54	−61.53	−143.07		(C) −80.51
$(CF_3)_2O_3$	(C) 547.29	−122.23	−42.66	−146.28		(C) 549.17

[a] The term net atomic charge is defined as $Z - n$(STO-4G), where Z is the atomic number, and n is the net electron density of an atom.

As in the case of hydrogen trioxides, the calculations show a slight preference of the decomposition to the corresponding fluorine oxide or dialkyl ether, respectively. An apparent calculated greater stability of alkyl trioxide compared to fluorine substituted compound (Y = CF_3) is not in accord with experimental observations. This may be due to the fact that the decomposition path cannot be followed; the initial and the final state were considered only.

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The Octant Rule. 5. On the Nature of the Third Nodal Surface. An Understanding of "Anti-Octant" and Front Octant Effects by a CNDO/S Study of Rotatory Strengths of the Carbonyl n → π* Transition[1]

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Abstract: The Del Bene–Jaffé parameterization of the CNDO SCF-LCAO-MO method is shown to reproduce well the rotatory strengths of the n → π* transition in ketones without the use of configuration interaction. Rotatory strengths for a series of methylcyclohexanones and *cis*- and *trans*-decalones are calculated, and computational support for the "primary zigzag" hypothesis of Kirk and Klyne is provided. The nature of the third surface, dividing front and back octants, is explored with a series of flexible model compounds in which a single dissymmetric methyl group is moved through space, and the signed rotatory strength computed as a function of position. The computed regions of sign change account for many of the supposed "anti-octant" effects observed.

For more than 15 years, the octant rule of Moffitt et al.[3] has been the subject of considerable interest by both experimentalists and theorists. In its simplest form, the rule states that the space surrounding the carbonyl chromophore in an optically active ketone is divided into eight regions by (i) the two symmetry planes of the isolated (C_{2v}) chromophore, and (ii) by a third plane perpendicular to and bisecting the C═O bond. If these three planes are taken to define a Cartesian coordinate system, then the *sign* of the contribution made by an alkyl substituent to the observed circular dichroism (CD) of the n → π* transition varies as the *sign* of the product $X \cdot Y \cdot Z$ of the atomic coordinates. Atoms having counterparts sym-