AB INITIO STUDY OF SOME PEROXIDES.
HOOH, CH_3OOH AND, CH_3OOCH_3

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Abstract: The geometries of HOOH, CH_3OOH, and CH_3OOCH_3 were optimized with different basis sets (3-21G, 6-31G$^{*(**)}$ and D95**) at different levels of theory (HF, MP2, MP4, and CI). HF/3-21G optimizations result in planar trans conformations for all three peroxides. HF/6-31G** calculations predict skew conformations for HOOH and CH_3OOH, but a planar trans structure for CH_3OOCH_3. For the larger basis set the calculated bond lengths, especially the O-O bonds, are too short. Optimizations for HOOH including electron correlation at the MP2, MP3, MP4, CI, and CCD level improve the agreement for bond lengths and the OOH angle, but result in dihedral angles which are too large by 3 - 8°. In the case of CH_3OOCH_3, similar calculations at the MP2 and CI level predict planar trans structures instead of the experimentally observed skew conformation. On the other hand, MP4 single point calculations at MP2 optimized parameters result in a correct skew structure. For all three peroxides a computationally "economic" method, i.e., single point calculations at MP2 or MP4 level with HF/3-21G optimized parameters, result in close agreement between calculated and experimental structures.

Introduction

The peroxides considered in this study are small molecules, but their structures, nevertheless, appear to be tough problems for experimentalists and theoreticians and thus present a particular challenge to structural chemistry. Naturally, among these peroxides, hydrogen peroxide has attracted the largest attention over the past decades.[1-19] Two experimental values for the equilibrium dihedral angle θ_e have been reported in the literature, θ_e = 111.5° determined by Hunt et al.[3] from infrared data using a semi-rigid model and θ_e = 119.1(18)° derived by Khachkuruzov et al.[7] from microwave data using a rigid model. This discrepancy has recently been resolved by J.Koput[20] by fitting infrared and microwave transitions simultaneously to a large amplitude Hamiltonian which accounts for vibration-torsion-rotation interaction. This analysis (θ_e = 111.8°) confirms the result of Hunt et al.

In extensive ab initio calculations on hydrogen peroxide (PO) Cremer studied the effect of basis sets and electron correlation on the equilibrium structure and on the barriers for the trans and cis conformation.[16] According to these calculations the barriers do not depend strongly on correlation effects, whereas the optimized geometries, especially the O-O bond length and the dihedral angle, are affected considerably: O-O = 1.390 Å and θ_e = 111.2° at HF level (with Duijneveldt's 11s6p2d/6s2p unrestricted basis) versus O-O = 1.451 Å and θ_e = 119.3°

at MP2 level with a rescaled version of the (4s3p1d/2s1p) basis set of Dunning and Winter. Since Cremer considered Khachkuruzov's value for θ_e (119.1°) as correct, he concluded that an electron correlation treatment at the MP2 level is essential and in combination with the above basis set sufficient for an accurate calculation of the H_2O_2 structure. Koput's recent experimental study demonstrates however, that Khachkuruzov's value for θ_e and thus Cremer's MP2 result are erraneous and that the HF value (111.2°) reproduces the experiment much closer. On the other hand, the HF approximation predicts the O-O bond too short, whereas the MP2 value is close to the r_o^* value of Koput (1.464(11) Å).

GVB calculations including CI[17] lead to results which are almost identical to Cremer's MP2 values (O-O = 1.464 Å, θ_e = 119.1°). Carpenter and Weinhold[19] demonstrated that additional polarization functions are required for a correct description of the dihedral angle. With a basis set including triple polarization, 6-311G(3d,2p), the experimental geometry of Koput is reproduced very closely at the MP2 level, resulting in θ_e = 111.8° and O-O = 1.450 Å.

Methylhydroperoxide (MPO) was studied by MW spectroscopy and the analysis which was based on a large-amplitude Hamiltonian, resulted in an O-O bond length of 1.443 Å and a COOH dihedral angle θ_e = 114°.[21] To our knowledge no HF calculation for this peroxide has been published. The GVB-CI value[17] for the O-O bond (1.452 Å) is in close agreement with the experiment, but the predicted dihedral angle of 126° is too large by about 10°, just as in the case of HOOH, when the same method is applied.

For dimethylperoxide (DMPO) experiments as well as theoretical calculations produced rather controversial results for the dihedral angle. An electron diffraction study[22] based on a large-amplitude model resulted in an O-O bond length of 1.457(12) Å and in a dihedral angle of 119(4)°. This is in qualitative agreement with vibrational spectra[23] which predict a skew conformation of C_2 symmetry, but is in contrast to earlier PES investigations[24,25], which interprete the splitting of oxygen lone pair ionization energies in terms of a planar or nearly planar trans conformation (C_{2h} symmetry). Microwave spectra for DMPO have been recorded in four different laboratories[26-29], but so far the very dense spectrum caused by large amplitude torsions around the O-C and O-O bonds could not be assigned. HF calculations by Gase and Boggs with a 4-21G basis set including polarization functions on oxygen only reproduce the electron diffraction value for θ_e (115.5°) very well, but predict the O-O bond too short (1.411 Å). GVB-CI calculations[17] lead to perfect agreement for the O-O bond, but result in a planar trans conformation with θ_e = 180°. At the time when these calculations were published (1982), the result of the electron diffraction study[22] was not yet known and the conformer obtained by the GVB-CI method was considered to be confirmed by the interpretation of the PES spectra.[24,25] The vibrational spectra[23] which definitely exclude a planar trans structure (C_{2h} symmetry), were not considered to contradict this result.

This short historical review demonstrates that ab initio calculations for these simple peroxides are not straightforward. The calculations of Carpenter and Weinhold show that both, O-O bond length and dihedral angle in PO can be reproduced correctly only by a suitable combination of basis set and level of theory.

In the present investigation we report calculations for MPO and DMPO applying different basis sets and various levels of theory with the aim to find the appro-

priate method for reproducing the experimental geometries. Although the PO problem
has been solved by Carpenter and Weinhold, we also include additional calculations
for this smallest peroxide to determine more systematically the effects of basis
sets and level of theory on the individual geometric parameters.

Computational methods

All calculations were performed with the GAUSSIAN 82 program system[31] on a BASF
7/88 and on a CONVEX C-1 XP computer at the University of Tübingen. Standard basis
sets, 3-21G, 6-31G$^{*(*)}$ and the Dunning-Huzinaga (9s5p,4s,2p) basis set[32] augmen-
ted by d-shells on oxygen and carbon and p-shells on hydrogen (D95**), were used.
To avoid convergence problems due to the flat torsional potential, geometric para-
meters in the case of MPO and DMPO were optimized at fixed dihedral angles and the
energy minima were determined by interpolation. Electron correlation was taken
into account at the MP2, MP4(SDTQ) or CI level with either direct optimization
of the geometry or by single point calculations at the corresponding HF optimized
structures. This latter method will be referred to as "economic" procedure.

Hydrogen Peroxide

The most simple calculations at the HF level with a 3-21G basis set results in
close agreement for the bond lengths and the OOH angle, but predicts a planar
trans conformation with $\theta_e = 180^0$ (see Table 1). If the basis set is increased and
polarization functions are included (6-31G** or D95**), the predicted conformations
are skew with dihedral angles only slightly larger (2 - 5^0) than the experimental
value. The calculated bond lengths, however, are too short by ca. 0.07 Å for the
0-0 and 0.02 Å for the O-H bond and the bond angle is too large by ca. 3^0 (Table
1). Cremer[16] demonstrated that the experimental dihedral angle of 111.8^0 can be
reproduced almost exactly (111.2^0) at the HF level by further increasing the ba-
sis set, but all basis sets which include polarization functions underestimate
the bond lengths, especially the 0-0 bond, and overestimate the bond angle as long
as electron correlation is neglected. This observation suggests, that simulta-
neous agreement for all geometric parameters can only be achieved at a higher
level of theory. At the MP2 level the bond lengths and OOH bond angle are repro-
duced very closely, but the dihedral angle is too large by about 6 - 8^0. The Dun-
ning D95** basis set leads to a slightly better agreement for this parameter and
was therefore chosen for further calculations at still higher levels of theory
(Table 1). Higher approximations for electron correlation (MP3, MP4, CISD and
CCD) affect the 0-0 bond length by up to 0.03 Å and θ_e by ca. 6^0, but these chan-
ges are not systematic, and furthermore, the experimental dihedral angle is not
reproduced correctly by just increasing the level of theory for this standard
basis set. Carpenter and Weinhold[19] showed that simultaneous agreement for all
geometric parameters requires only a low approximation for electron correlation
(MP2) but large basis sets with additional polarization functions (6-311G(3d,2p)).

As was pointed out above, HF calculations with a small basis set (3-21G) repro-
duce geometric parameters, except for the dihedral angle, quite well. This might
suggest that an economic procedure for obtaining a reasonable overall structure
consists of correlated single point calculations for various dihedral angles at
the corresponding HF/3-21G optimized geometries. This treatment results in energy
minima for the dihedral angles between 115-120^0, depending on the basis set (D95**
or 6-31G**) used in the single point calculation. The approximation for electron
correlation (MP2 or MP4) has almost no effect for a given basis set. The result
for the D95** basis set and MP4 approximation is given in Table 1.

Table 1: H_2O_2.
      Fully optimized geometries with different basis sets and at various
      levels of theory (bond lengths in Å, angles in °).

	0-0	0-H	OOH	θ_e	E_{tot} [a]
HF/3-21G	1.473	0.970	99.5	180	-149.945820
HF/6-31G**[b]	1.396	0.946	102.3	116.2	-150.776965
HF/D95**	1.391	0.947	102.8	113.8	-150.820105
MP2/6-31G**	1.468	0.969	98.6	120.3	-151.152040
MP2/D95**	1.465	0.970	99.1	117.7	-151.218783
MP3/D95**	1.448	0.966	100.3	114.5	-151.191792
MP4SDTQ/D95**	1.471	0.970	99.3	116.3	-151.214285
CISD/D95**	1.437	0.962	100.7	114.5	-151.174038
CCD/D95**[c]	1.451	0.968	100.2	114.8	-151.201651
GVB-CI[d]	1.464	0.967	99.9	119.1	-151.0216
MP2/6-311G(3d,2p)[e]	1.450	0.962	99.5	111.1	
MP4SDTQ/D95**//HF/3-21G[f]	1.467	0.972	100.9	115.0	-151.214129
Experiment[g]	1.464	0.965	99.4	111.8	

[a]: Total energies in Hartree.
[b]: ** denote d-shell on oxygen and p-shell on hydrogen.
[c]: Coupled cluster calculation with double substitution from the HF determinant.
[d]: Ref. 17.
[e]: Ref. 19, no E_{tot} reported.
[f]: MP4 single point calculation at the HF/3-21G optimized geometry.
[g]: Ref. 20.

Methylhydroperoxide

The microwave spectrum of the parent isotopic species of this compound does not
allow the determination of the complete structure. In the analysis, which is based
on a large-amplitude Hamiltonian, the skeletal parameters and barriers were ad-
justed to the rotational transitions.[21] We are unable to estimate error limits
for these parameters, but believe them to be definitely smaller than 0.02 Å for
0-0 and 0-C bond lengths and smaller than 2° and 5° for bond angles and dihedral
angle, respectively.

The HF calculations with a small basis set (3-21G) again predict bond lengths and
bond angles in reasonable agreement with the experiment but result in a trans pla-
nar instead of skew conformation (Table 2). Parameters for the CH_3 group were op-
timized but they are not given in Table 2 because they are not considered rele-
vant for the present discussion. The larger basis set which includes polarization
functions (6-31G**) results in a skew structure with θ_e = 118.°, i.e., slightly
larger than the experimental value, and in bond lengths which are too short. These
HF results for MPO parallel the observations made above for PO. The "economic"
procedure, i.e., correlated single point calculations with a 6-31G** at the HF

/3-21G geometries result in energy minima at 122° and 119° for θ_e at the MP2 and MP-4 level, respectively. All parameters except for the dihedral angle are close to the GVB-CI results reported by Bair and Goddard.[17] Since in the case of PO direct geometry optimizations at the MP2 or MP4 level lead to similar results as the GVB-CI method[17], no such calculations were performed for MPO. The treatment, which is most successful for PO, i.e., large basis sets with triple polarization and geometry optimization at the MP2 level[19], would probably further improve the agreement with experiment. Considering the still preliminary experimental values for geometric parameters and trans barrier and their unknown error limits, such expensive calculations, however, do not appear to be justified at this stage. All calculations, except HF/3-21G predict the trans barrier V_{trans} in close agreement with the experiment.

Table 2: CH_3OOH.
Calculated skeletal geometries with different basis sets and at various levels of theory (bond lengths in Å, angles in ^{o}).

	O-O	O-C	O-H	OOC	OOH	θ_e	V^a_{trans}	E^b_{tot}
HF/3-21G	1.468	1.445	0.971	103.9	99.9	180	-	-188.763113
HF/6-31G**	1.393	1.399	0.946	107.4	102.4	118	0.35	-189.807566
MP4/6-31G*// HF/3-21G	1.464	1.448	0.972	105.1	100.8	119	0.36	-190.326665
MP2/6-31G**// HF/6-31G**	1.394	1.399	0.946	107.3	102.2	115	0.32	-190.321146
GVB-CI^c	1.452	1.446	0.967	105.0	99.6	126	0.23	-190.0302
Experiment^d	1.443	1.437	0.967	105.7	99.6	114	0.25	

^{a}: V_{trans} in kcal/mole.
^{b}: Total energies in Hartree.
^{c}: Ref. 17.
^{d}: Ref. 21.

Dimethylperoxide

The same strategy which was used for MPO was also applied to DMPO. Again, HF/3-21G calculations reproduce bond lengths and OOC angle very well and predict a planar trans configuration. In contrast to PO and MPO, however, also large basis sets (6-31G** or D95**) lead to energy minima at θ_e = 180° at the HF level. The geometric parameters for the 6-31G** basis set only are given in Table 3. It is surprising that the HF method with a small basis set including polarization functions on oxygen atoms only, which was used by Gase and Boggs[30], predicts a skew conformation with a correct dihedral angle. In these calculations the shortening of the skeletal bond lengths is not as pronounced as for the 6-31G** basis set, but the O-O bond is too short by about 0.04 Å. The "economic" procedure leads to energy minima at θ = 123° or 116° and to trans barriers of 0.06 or 0.22 Kcal/mole, depending on whether the MP2 or MP4 method is applied. This latter method

reproduces all experimental geometric parameters and the trans barrier very close-
ly. If the 6-31G** optimized parameters are used in the correlated single point
calculations the dihedral angle is 122°, but the agreement for bond lengths be-
comes worse. Equivalent calculations with the D95** basis set (MP4/D95**//HF/D95**)
produce a flat single minimum potential, i.e., the wrong conformation. This ob-
servation differs from that made for PO, where D95** basis sets gave slightly
better values for the dihedral angle.

Table 3: CH_3OOCH_3.
          Calculated skeletal geometries with different basis sets and
          at various levels of theory (bond lengths in Å, angles in °).

	O-O	O-C	OOC	θ_e	V_{trans}^a	E_{tot}^b
HF/3-21G	1.464	1.445	104.3	180	-	-227.580306
HF/6-31G**	1.399	1.397	106.0	180	-	-228.838203
HF/4-21G[c]	1.411	1.422	105.4	115.5	0.52	-228.368522
MP4SDTQ/6-31G*// HF/3-21G	1.462	1.448	105.1	116	0.22	-229.503770
MP4SDQ/6-31G**// HF/6-31G**	1.393	1.399	107.3	122	0.13	-229.533131
MP2/6-31G*	1.478	1.419	103.2	180	-	-229.465520
CISD/6-31G*	1.450	1.417	104.2	180	-	-229.405618
GVB-CI[d]	1.450	1.444	104.1	180	-	-229.0391
MP4SDTQ/6-31G*// MP2/6-31G*	1.471	1.421	104.3	121	0.10	-229.505476
Experiment[e]	1.457	1.420	105.2	119	0.25	
(error limits)	(12)	(7)	(5)	(4)	(+25/-15)	

[a]: V_{trans} in kcal/mole.
[b]: Total energies in Hartree.
[c]: Ref. 30.
[d]: Ref. 17.
[e]: Ref. 22, error limits for the last digit.

We have performed additional calculations for DMPO to test whether the experimen-
tal geometry can be reproduced also with other computational procedures. Direct
optimizations at the MP2 level with the 6-31G** basis set results in a very flat
single minimum potential curve corresponding to a trans planar equilibrium struc-
ture. This result is difficult to rationalize, because the bond lengths and OOC
bond angle obtained by this method are close to the HF/3-21G values, which led
to a skew conformation at the MP2 level (see "economic" calculations). Such a
single minimum potential is also found by optimization at the CI level. The qua-
litatively wrong predictions of these two correlated treatments, i.e., a planar
instead of skew conformation, parallel the result of Bair and Goddard obtained
by the GVB-CI calculations.[17] All optimizations including electron correlation

effects predict skeletal bond lengths and the OOC angle much closer to the ex-
periment compared to corresponding HF optimizations, but predictions concerning
the conformation (planar instead of skew) are still erraneous. Inclusion of elec-
tron correlation leads only to flattening of the potential curves relative to the
HF potentials. A skew conformation again is found by single point MP4 calcula-
tions with the MP2 optimized parameters (θ_e = 121^0, V_{trans} = 0.10 Kcal/mole).

Discussion

In general, the quality of ab initio calculations should increase with increasing
level of theory. It is well known[33] that calculations at the HF level with small
double zeta basis sets (e.g. 3-21G) reproduce bond lengths in many cases reaso-
nably well and bond angles to within a few degrees. Larger basis sets with pola-
rization functions (e.g. 6-31G*) result in bond lengths which are too short, but
improve the agreement for bond angles, especially at atoms including lone pairs.
If electron correlation is taken into account, bond lengths increase again, thus
improving the agreement with experiment, whereas the bond angles are hardly af-
fected. All these changes in geometric parameters with increasing level of theory
are in general small, a few hundreds of an Ångstrom and less than about 4^0, and
these changes are predictable.

These general trends also apply to the peroxides considered in this study, except
for the dihedral angle, which depends much more strongly on the computational
procedure. The difference between a planar configuration and a skew configuration
with a dihedral angle of about 120^0 is not just quantitative but is a qualita-
tive difference. PO and MPO show similar behaviour. HF calculations with small
basis sets without polarization functions lead to planar configurations and lar-
ger basis sets including polarization functions predict skew conformers with bond
lengths which are too short. As is demonstrated for PO[19], inclusion of electron
correlation at the MP2 level and further extended basis sets reproduce all geo-
metric parameters correctly. Thereby, inclusion of additional polarization func-
tions seems to be more important than increase of level of correlation treatment.
For both compounds reasonable agreement with the experiment can be achieved with
the computationally more "economic" procedure outlined above. DMPO, however, be-
haves differently insofar, as the HF/6-31G** optimization predicts a qualitative-
ly wrong planar conformation. Furthermore, optimization at the MP2 and CI level
also results in energy minima at θ_e = 180^0. Possibly, additional polarization
functions would produce a skew conformer, but this effect was not further in-
vestigated. Using the standard 6-31G* basis set, very elaborate calculations are
required (MP4/6-31G*//MP2/6-31G*) to achieve agreement with the experiment. On
the other hand, such agreement is also obtained with the "economic" method. Tne
result of Gase and Boggs[30], which reproduces the correct conformation at the HF
level, appears to be a fortituous exception. The total energy of the ab initio
calculation can not be used as a criterion for the quality of the calculation,
as far as the geometric structure is concerned.

Since the computational procedure, which results in closest agreement for all
geometric parameters with the experimental values depends on the specific mole-
cule, and since changes in the dihedral angles at various levels of theory are
not predictable, ab initio calculations in such cases are highly "empirical".
Their quality can only be judged by comparison with the experiment and thus de-
pends on the quality of the experiment. This is clearly demonstrated by earlier
studies of PO and MPO. Calculations, which resulted in dihedral angles of about
119^0 for PO[16,17] and of 180^0 for DMPO[17], were considered to be correct because

they reproduced the experimental data which were chosen for comparison. In both cases, however, the chosen data were erraneous. The choice of other experimental data for comparison, i.e., Hunt's value[3] for θ_e in PO instead of Khachkuruzov's value[7], and the interpretation of vibrational spectra[23] instead of PES[24,25] for DMPO, would have led to different judgement of the quality of these calculations.

Conclusion

"Any valid use of ab initio procedures in chemistry has therefore to be on a pure-ly empirical basis, limited to situations where specific tests have shown the procedure in question to give satisfactory results." (M.J.S.Dewar, 1985)[34]

Acknowledgement

References:

1. J.T. Hougen, Canad. J. Phys. _62_, 1392 (1984), and references therein.
2. R.L. Redington, W.B. Olson, and P.C. Cross, J. Chem. Phys _36_, 1311 (1962).
3. R.H. Hunt, R.A. Leacock, C.W. Peters, and K.T. Hecht, J. Chem. Phys. _42_, 1931 (1965).
4. W.R. Busing and H.A. Levy, J. Chem. Phys. _42_, 3054 (1965).
5. W.C. Oelfke and W. Gordy, J. Chem. Phys. _51_, 5336 (1969).
6. C.S. Ewig and D.O. Harris, J. Chem. Phys. _52_, 6268 (1970).
7. G.A. Khachkuruzov and I. Przhevalskii, Opt. Spectrosc. _36_, 172 (1974); _44_ 112 (1978).
8. P.A. Giguere and T.K.K. Srinivasan, J. Mol. Spectrosc. _66_, 168 (1977).
9. D. Cremer and D. Christen, J. Mol. Spectrosc. _74_, 480 (1979).
10. P. Helminger, W.C. Bowman, and F. C. De Lucia, J. Mol. Spectrosc. _85_, 120 (1981).
11. W.C. Bowman, F. C. De Lucia, and P. Helminger, J. Mol. Spectrosc. _87_, 571 (1981).
12. W.H. Fink and L.C. Allen, J. Chem. Phys. _46_, 2261 (1967).
13. A. Veillard, Chem. Phys. Lett. _4_, 51 (1969).
14. T.H. Dunning, Jr., and N.H. Winter, J. Chem. Phys. _63_, 1847 (1975).
15. P. Botschwina, W. Heyer, and A.M. Semkow, Chem. Phys. _15_, 25 (1976).
16. D. Cremer, J. Chem. Phys. _69_, 4440 (1978).
17. R.A. Bair and W. A. Goddard III., J. Am. Chem. Soc. _104_, 2719 (1982).
18. R. Block and L. Jansen, J. Chem. Phys. _82_, 3322 (1985).
19. J.E. Carpenter and F. Weinhold, J. Chem. Phys. _90_, 6405 (1986).
20. J. Koput, J. Mol. Spectrosc. _115_, 438 (1986).
21. M. Tyblewski, R. Meyer, and A. Bauder, 8th Colloquium on High Resolution Mo-lecular Spectroscopy, Tours, France (1983).
22. B. Haas and H. Oberhammer, J. Am. Chem. Soc. _106_, 6146 (1984). This dihedral angle and its error limit refer to a quadratic-quartic potential function.
23. K.O. Christe, Spectrochim. Acta, Part A _27_, 463 (1971).
24. K. Kimura and K. Osafune, Bull. Chem. Soc. Jpn _48_, 2421 (1975).
25. P. Rademacher and W. Elling, Liebigs Ann. Chem. _1979_, 1473.
26. W.H. Flygare, Documentation of Microwave Data, University of Ulm.
27. D. Sutter, private communication.
28. A. Bauder, private communication.

29. D. Christen and H. Oberhammer, unpublished results.

30. W. Gase and J.E. Boggs, J. Mol. Struct. <u>116</u>, 207 (1984).

31. J. S. Binkley, M. Frisch, D.J. DeFrees, K. Raghavachari, R. A. Whiteside, H.B. Schlegel, G. Flueter, and J.A. Pople, Carnegie-Mellon Publication Unit, PA (1983).

32. T.H. Dunning, J. Chem. Phys. <u>53</u>, 2832 (1970).

33. W.J. Hehre, L. Radom, P.v.R. Schleyer, and J.A. Pople, Ab initio Molecular Orbital Theory, John Wiley (1986).

34. M.J.S. Dewar, J. Chem. Phys. <u>89</u>, 2145 (1985).