The Bond Dissociation Energy of Peroxides Revisited

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Abstract

When dealing with organic peroxides in both laboratory and industrial applications, the relative strengths of the O-O bond is of vital importance, both from a safety and mechanistic perspective. Although it is well known that such oxidizing agents are highly reactive, reliable O-O bond dissociation energies (BDE) have only recently been established. In an earlier report, we suggested a median O-O BDE value of *ca*.45 kcal/mol for a variety of well-known peroxides based upon G2 *ab initio* calculations. In the present report we have calculated the O-O BDE of twenty peroxides of varying structure at the more accurate CBS-APNO level. We have also compared these bond energies to the corresponding BDEs calculated with several DFT functionals and shown that the M06-2X functional produces O-O bond energies that compare very favorably with G4 and CBS-APNO values.

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Introduction

The chemistry of peroxides continues to play an important role in the biochemistry of the human body, as well as in many industrial and laboratory processes.[1] One of the problems associated with an accurate chemical analysis of peroxides is the fact that in many cases they are either shock sensitive or difficult to isolate in high analytical purity or both. One particular aspect of peroxide chemistry that we addressed some time ago[2] is the bond dissociation energy (BDE) of the oxygen-oxygen bond in peroxides. At that time the relatively low generic O-O bond energy (*ca.* 34 kcal/mol) had typically been assumed for peroxides in general because they exhibit unusual chemical reactivity that has been ascribed to the highly reactive O-O bond. We reported relatively high level *ab initio* calculations suggesting a more realistic BDE of *ca.* 45 kcal/mol.[2] Historically, experimentally determined bond energies have always been better accepted that theoretically derived values. Perhaps an exception to that generalization is O-O BDE values that in many cases may be more accurately obtained by computational methods. In the present study we have calculated the O-O BDE of a series of important peroxides at the relatively high of accuracy using the G4 and CBS-APNO levels of theory.

Methodology

There are several general theoretical procedures available today to obtain thermodynamical data within “chemical accuracy” (ca. 1- 2 kcal/mol). The G4[3], CBS-QB3[4] and CBS-APNO[5] methods available in Gaussian 16[6] have been shown to calculate ΔH and ΔG values in very good agreement with experimental values that are typically reported to be accurate within one to two kcal/mol. For example, for gas phase deprotonation reactions, the mean absolute deviation of these three methods from experiment is 0.84 to 1.26 kcal/mol.[7] The root-mean-square deviation for ΔH and ΔG is 1.43 and 1.49 kcal/mol for the CBS-QB3 method; 1.06 and 1.14 kcal/mol for the CBS-APNO method; and 1.16 and 1.28 for the G4 method.[7] In a related benchmarking study on enthalpies of formation[8] of $C_xH_yO_z$ molecules these theoretical methods were rank ordered G4 > CBS-APNO > CBS-QB3 where the CBS-x methods on average predict Δ_fH^θ within ≈1.2 kcal/mol.[8] In general, CBS-APNO tends to underestimate the formation enthalpies of target molecules whereas CBS-QB3 and G4 have a tendency to overestimate them. In a related study on the formation enthalpies of radicals with molecular formula $C_xH_yO_z$ a similar order of accuracies was reported.[9,10] All molecular orbital calculations were carried out using the Gaussian 16 program system[6] utilizing gradient geometry optimization.[11] Zero point energies and thermal corrections to the enthalpy were obtained from vibrational frequency calculations (harmonic oscillator, rigid rotor approximation). Bond dissociation energies were calculated from enthalpy differences at 298 K. For those oxygen free radicals that pose difficulties in assigning an electronic state, the initial geometry was symmetrized to C_{2v} but then fully optimized without geometry constraints. The D_0 and bond dissociation enthalpies for the O-O bonds are computed at the G4, CBS-QB3 and CBS-APNO levels of theory. The bond dissociation energies (BDE) calculated with the B3LYP DFT functional.[12-15] utilized the 6-311+G(d,p) basis set while those calculated with the M06-2X DFT functional[16] utilized the 6-311+G(3df,2p) basis set. The calculated BDE values are compared with available experimental data in Table 1. The structures of the 22 peroxides described in Table 1 are provided in the text. In all cases the reported BDE assumes simple homolytic O-O bond cleavage. Total energies, enthalpies and geometric coordinates for individual species are provided either in the text or in the Supporting Information.

Results and Discussion

The accurate determination of O-O BDEs is no longer restricted to experimental techniques. In recent years, the application of computational methods, based on quantum chemistry, has afforded a wealth of BDE values whose accuracy is often comparable to or even better than data derived from experiment. This can be particularly valuable because of the hygroscopic nature of highly polar organic hydroperoxides that present purification difficulties. Chemical bonds of electronegative elements like oxygen typically have a relatively low BDE while the ubiquitous C-C bond is often stronger and has an average BDE of *ca.* 84 kcal/mol.

(a) Calculation of Peroxide O-O BDE at the CBS-APNO level.

Hydrogen peroxide is the simplest of all peroxides and is perhaps the most widely studied experimentally and as a result we have very accurate enthalpy, entropy and heat capacity data. Additionally, because of its small size, it was one of the first peroxides studied by theoretical means that have provided reliable structural and energetic data. This has allowed us to obtain very accurate bond dissociation energies[2]. The CBS-APNO BDE for HOOH is 50.17 kcal/mol and the experimental value is 50.30 kcal/mol reported in the Active Thermochemical Tables (ATcT).[17-20] Methyl hydroperoxide and dimethyl peroxide also fall into this small molecule category and this has also allowed us to obtain very accurate bond dissociation energies[2] (Figure 1). The calculated CBS-APNO BDE for these two relatively simple peroxides (44.64 and 39.27 kcal/mol, respectively) are also in excellent agreement with the experimental data as summarized in Table 1 (44.67 and 40.38 kcal/mol based on ATcT and the NIST Chemistry Webbook[21]).

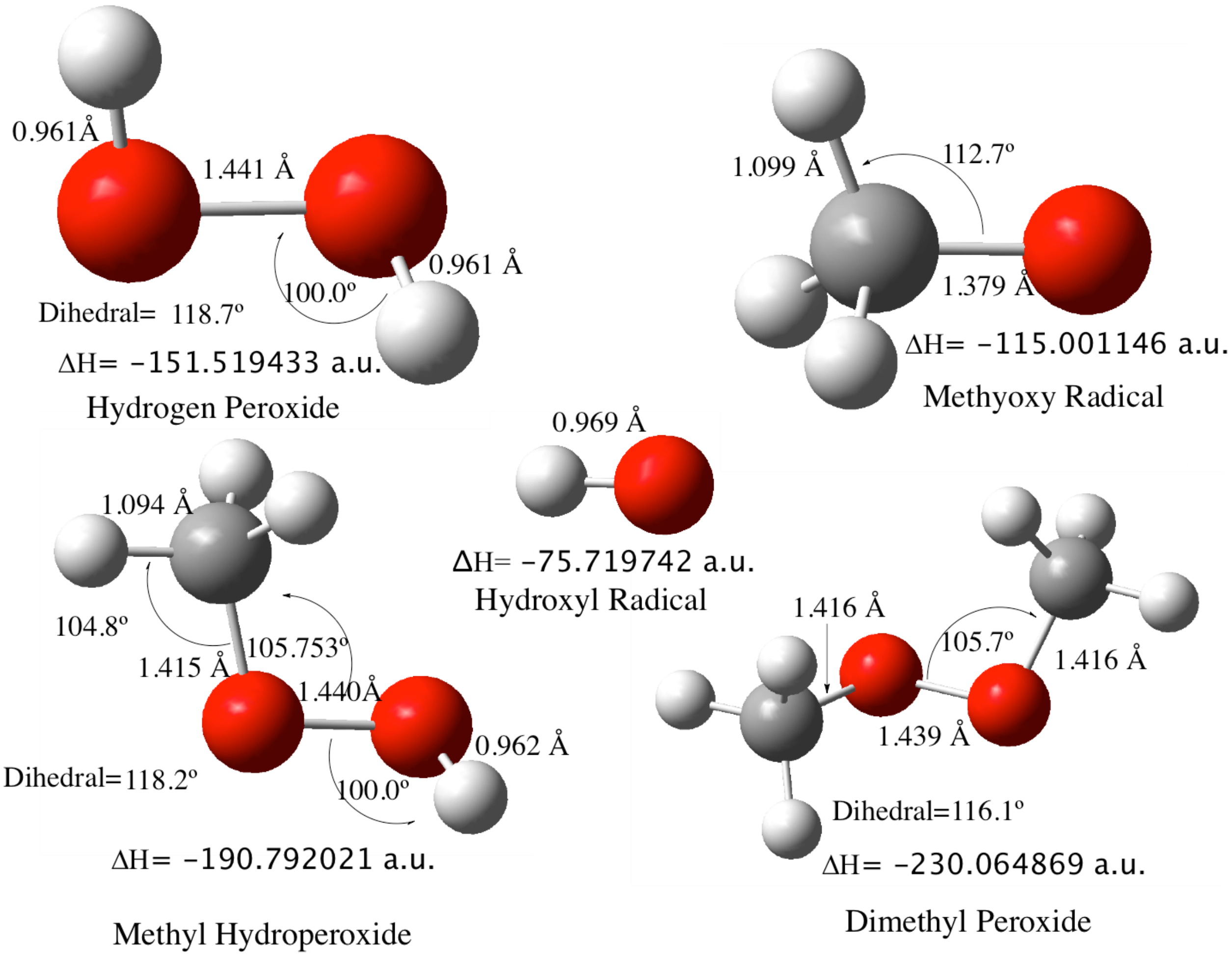


Figure 1. CBS-APNO enthalpies for hydrogen peroxide and methyl hydroperoxide.

Table 1. O-O Bond Dissociation Enthalpy (BDE at 298 K) for Selected Peroxides.

Peroxide	B3LYP[a]	M06-2X[b]	CBS-QB3	CBS-APNO	G4	Expt.
HO-OH	44.10	49.73	50.72	50.17	48.96	50.30[c,d]
MeO-OH	35.54	42.67	44.68	44.64	43.23	44.67[c]
MeO-OMe	26.95	40.91	38.52	39.27	37.58	40.38[c,e,f]
tert-BuO-OH	36.87	44.77	47.14	45.81	43.93	44.1[g] 44.6[e,h] 45.3[e,i]
di-*tert*-butyl peroxide	26.80	38.72		42.35	39.47	38.9[g] 41.8[j] 40.8[e,k] 40.5[e,h] 41.8[e,i]
CF_3OOCF_3	37.09	46.33	51.16	48.83	45.16	47.5[g] 40.6[l]
1-Phenylethyl-1-hydroperoxide	36.32	43.31		45.02		
Cumene hydroperoxide	34.01	45.02		45.01		
Hexafluoroacetone hydrate	33.64	46.59		46.32	42.24	
HC(C=O)O-OH	38.29	49.65	47.95	48.64		
FC(C=O)O-OH	30.91	46.61		44.28		
CH_3(C=O)O-OH	35.93	49.61	47.12	46.87	45.11	
Diacetyl peroxide	17.25	39.19		32.87		37.8[m]
CFH_2(C=O)O-OH	35.93	50.45		46.76		
CF_3(C=O)O-OH	36.62	50.82		47.32	44.09	
Ph(C=O)O-OH	35.71	49.21		46.19	43.38	
Benzoyl peroxide	19.96	41.10	34.84		31.34	
m-FPh(C=O)O-OH	35.86	49.90		49.04	43.38	
m-ClPh(C=O)O-OH	35.87	49.41			43.18	
PhO-OH			23.59	23.34		
PhO-OPh			2.59			
$(CH_3)_3OOTi(OCH_3)O_2C_2H_4$		57.68	59.83			

a. 6-311+G(d,p) basis set
b. 6-311+G(3df,2p) basis set
c. Reference 19
d. Reference 20
e. Reference 21
f. Reference 23
g. Reference 27
h. Reference 28
i. Reference 29
j. Reference 31
k. Reference 32
l. Reference 33
m. Reference 42

In our earlier report[2] we showed that the G2 and CBSQ methods performed remarkably well for predicting bond dissociation energies and gave values in excellent accord with experimentally determined O-O bond energies.[22] It is not only important to provide accurate BDE data but it is also of value to the experimentalist to have a means of comparing the relative O-O bond strengths of a wide range of different peroxides where the data is obtained with an internally consistent high level of calculation. One of the difficulties associated with an accurate assessment for the strength of the O-O bond is that simple homolytic cleavage of highly reactive O-O bonds are often complicated by extraneous factors such as secondary bonding interactions involving formation of a complex that precedes the actual O-O bond separation step. For example, homolytic O-O bond cleavage for certain diacyl peroxides can be accompanied by intramolecular Cope-like rearrangements that can scramble the peroxide oxygens.[23] Overall, the BDE values summarized in Table 1 concur with this assessment and the CBS-APNO values are in excellent accord with the rather limited experimental O-O bond energies.

Alkyl hydroperoxides are generic oxidants that are employed in a variety of oxidation processes. One of the most commonly used, *tert*-butyl hydroperoxide (*t*-BuOOH), is an organic peroxide that is normally supplied as a 69–70% aqueous solution (Figure 2). It is exemplified by its use in the Sharpless epoxidation reaction[24] and related metal catalyzed oxidations. This peroxide exhibits a CBS-APNO BDE of 45.81 kcal/mol. However, there have been relatively few experimental reports of the O-O BDE for this hydroperoxide despite its common usage. Simmie and coworkers[25] have reported an O-O BDE of 46.13 kcal/mol based upon formation enthalpy data and calculations. Green and coworkers[26] have reported BDE values of 46.4 and 46.8

kcal/mol from CBSQ and CBS-QB3 methods for *t*-BuOOH. Very low pressure pyrolysis experiments yielded a BDE of 44.1 kcal/mol for *t*-BuOOH.[27] Combining the heat of formation of *t*-BuOOH from NIST[21] and *t*-BuO from Blanksby and Ellison[28] and from Lineberger and coworkers[29] yields 44.6 and 45.3 kcal/mol for the *t*-BuO-OH BDE.

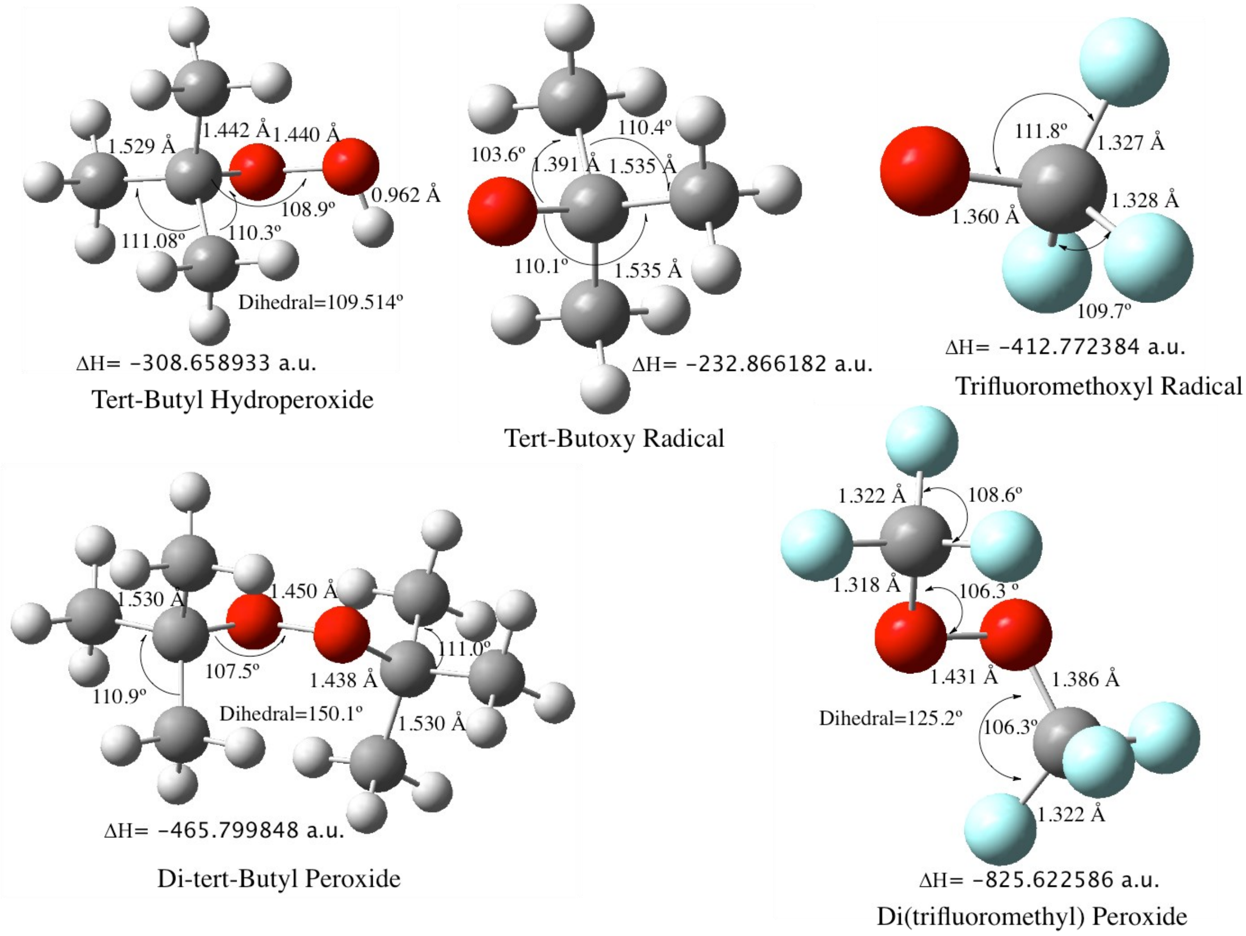
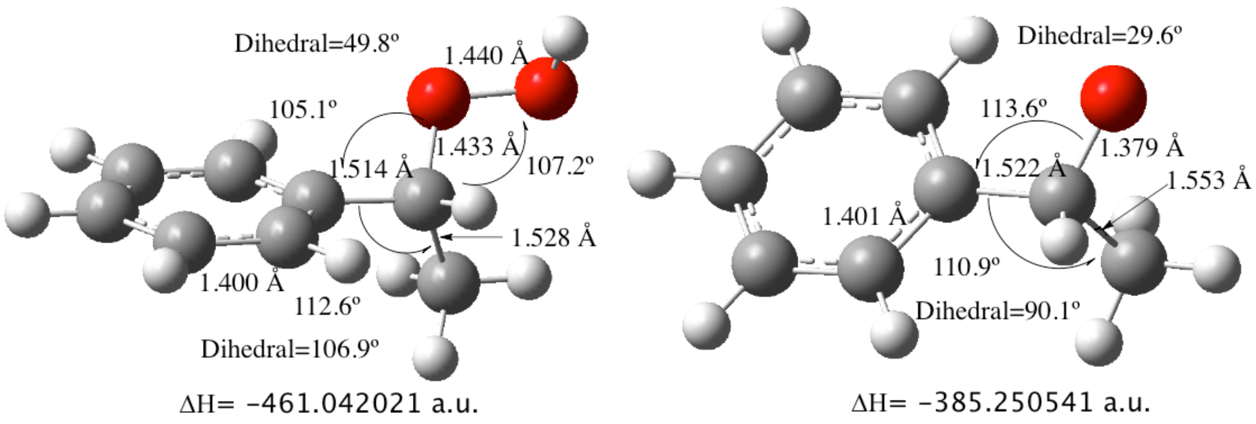


Figure 2. CBS-APNO enthalpies for *tert*-butyl hydroperoxide, di-*tert*-butyl peroxide and di(trifluoromethyl) peroxide.

A very commonly applied catalyst for free radical chain reactions is di-*tert*-butyl peroxide ($Me_3CO\text{-}OCMe_3$).[30] The best experimental BDE for di-*tert*-butyl peroxide are based upon a photoacoustic calorimetry study (42.9 kcal/mol) and a value derived from acidity and electron affinity data (41.2 kcal/mol).[31] Very low pressure pyrolysis[27] and collision induced dissociation experiments[32] gave BDE's of 38.9 and 40.8 kcal/mol.[27] Heats of formation of di-*tert*-butyl peroxide from NIST[21] and *t*-BuO from Blanksby and Ellison[28] and from Lineberger and coworkers[29] yield BDE's of 40.5 and 41.8 kcal/mol. The average of these values is in excellent accord with our CBS-APNO BDE of 42.35 kcal/mol. The somewhat lower O-O BDE for di-*tert*-butyl peroxide ($\Delta\mathrm{BDE} = 5.69$ kcal/mol) has been ascribed[31] to the stabilization of the *tert*-butylperoxyl radical by hyperconjugation. Such hyperconjugation effects for the CF_3 group are greatly reduced due to the inductive polarization of the C-F bond reducing the influence of the CF_3 group on the O-O BDE.

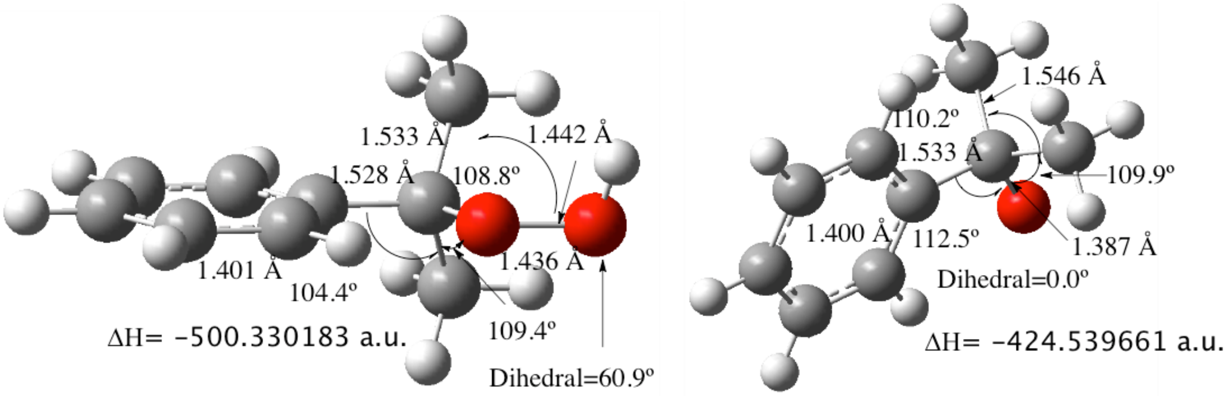
Trifluoromethoxy radical and di(trifluoromethyl) peroxide are relevant to the degradation of hydrofluorocarbons in the troposphere. Early measurements yielded O-O BDE's ranging from 40 – 50 kcal/mol.[33-35] A more recent pyrolysis study determined a BDE of 47.5 kcal/mol. A computational study obtained an O-O dissociation energy of 50.0 kcal/mol at the CBS-QB3 level of theory.[36] The present calculations with CBS-APNO give an O-O BDE of 48.83 kcal/mol for CF_3OOCF_3 in very good agreement with the recent pyrolysis study.

We also examined the O-O BDE 1-phenylethyl-1-hydroperoxide ($PhCH(CH_3)OOH$) and 1-methyl-1-phenylethyl-1-hydroperoxide that is more commonly referred to as cumene hydroperoxide ($PhC(CH_3)_2$-OOH). Cumene hydroperoxide is an intermediate in the cumene process for synthesizing phenol and acetone from benzene and propene. These two very commonly applied alkyl hydroperoxides both have essentially identical CBS-APNO O-O BDEs (45.02 and 45.01 kcal/mol).



1-Phenylethyl-1-hydroperoxide

1-Phenylethyloxy Radical

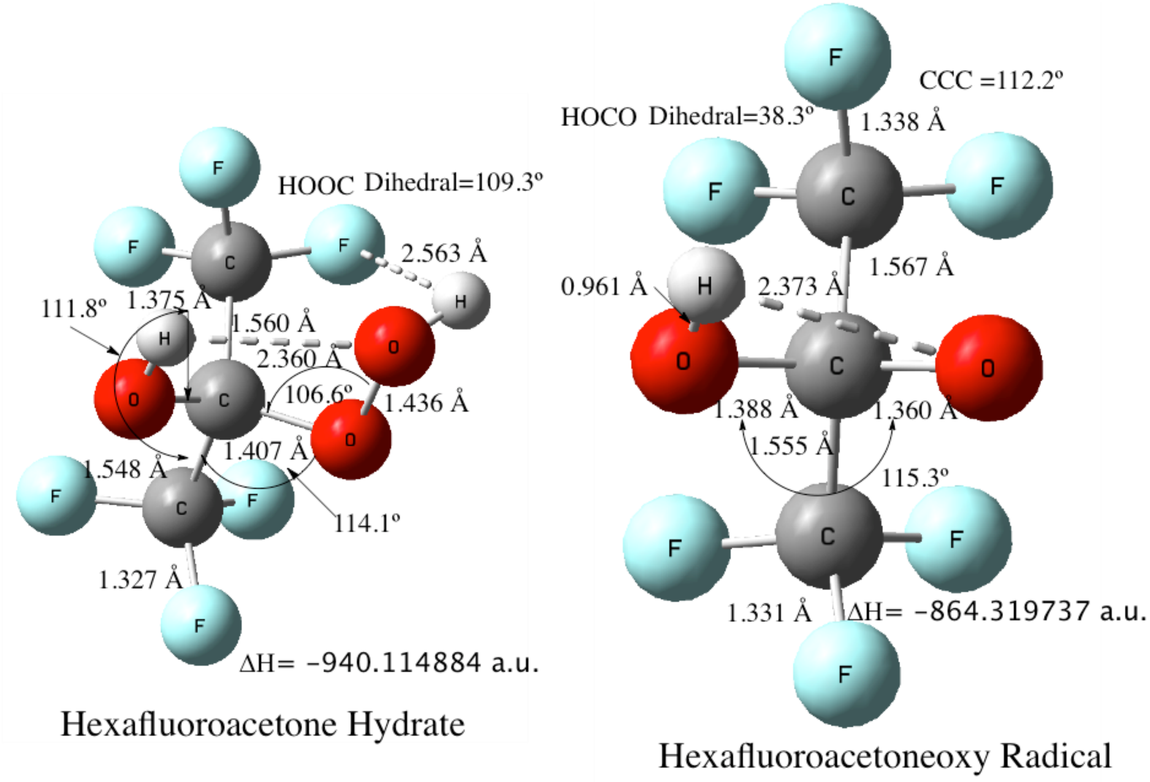


Cumene Hydroperoxide

Cumeneoxy Radical

Figure 3. CBS-APNO enthalpies for 1-phenyl-1-hydroperoxide and cumene hydroperoxide.

One of the more recent additions to this class of hydroperoxides that is used in many experimental applications is hexafluoroacetone perhydrate ($(CF_3)_2C(OH)OOH$). This highly reactive α-hydroxy hydroperoxide is derived from the addition of HOOH to hexafluoroacetone and the adduct has a sufficient lifetime to be a useful addition to the synthetic repertoire.[37] At the CBS-APNO level we calculate a BDE of 46.72 kcal/mol. Unfortunately, we cannot find an experimental BDE for this unusual hydroperoxide.



Hexafluoroacetone Hydrate

Hexafluoroacetoneoxy Radical

Figure 4. CBS-APNO enthalpies for hexafluoroacetone hydrate and its oxyradical.

The activation barrier for E-2-butene epoxidation with hexafluoroacetone perhydrate (14.31 kcal/mol) is essentially the same as that for peroxyacetic acid in that their $\Delta E^{\ddagger}$ differ by only a kcal/mol. Although this α-hydroxyperoxide undergoes oxygen atom transfer with about the same propensity as a peroxyacid, their oxidative mechanisms differ widely. We recently reported[38] a detailed mechanistic study on this and related alkyl peroxides with a comparison to peroxyacids in the epoxidation reaction. Oxygen atom transfer from a peroxyacid involves a 1,4-proton shift while the hydroperoxides proceed by a 1,2-hydrogen shift to the proximal oxygen. The reported O-O BDE for this hydroperoxide with the electron withdrawing CF_3 substituents at the G4 level (42.24 kcal/mol) is only 2.87 kcal/mol lower than that for peroxyacetic acid.

Determining the O-O BDE for a peroxyacid represents a special problem related to the electronic state of the radical species produced upon homolytic O-O bond cleavage (Figure 5). For example, in the simple case of peroxyformic acid, a formyloxy radical (H-C(C=O)O•) is produced in addition to the hydroxyl radical (HO•). After considerable discussion in the literature, it has now been firmly established that the ground state for the formyloxy radical is $^2A_1$ with the $^2B_2$ state lying only ≈1 kcal/mol above.[39-41] Thus, the assignment for these two states critically depends upon the method of calculation (Figure 5). In each case for these peroxyacids we symmetrized the starting geometry to C_{2V} in order to more easily classify the electronic states and then fully optimized the geometry without constraint. We have calculated an O-O BDE for peroxyformic acid to be 48.64 kcal/mol at the CBS-APNO level with the formyloxy radical at the $^2B_2$ electronic state (Figure 6). In our earlier work at the G2 level, we reported[2] a BDE of 48.41 kcal/mol that was also based upon a $^2B_2$ ground state for the formyloxy radical.

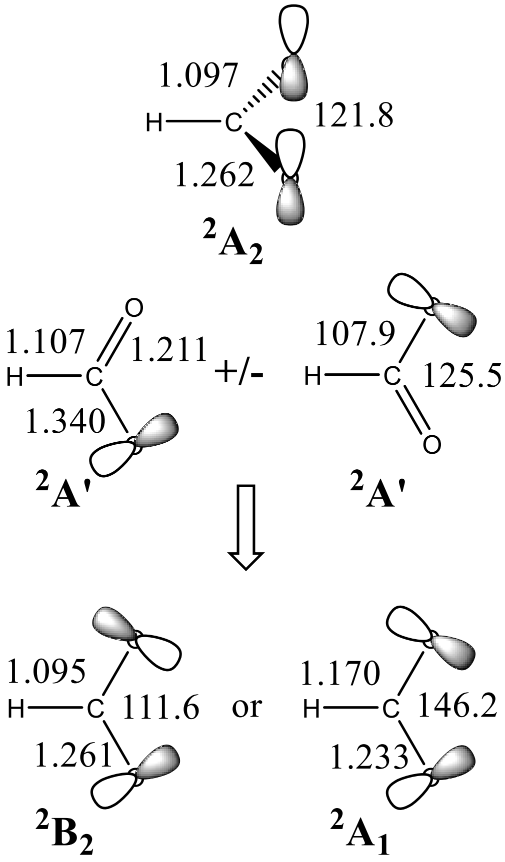
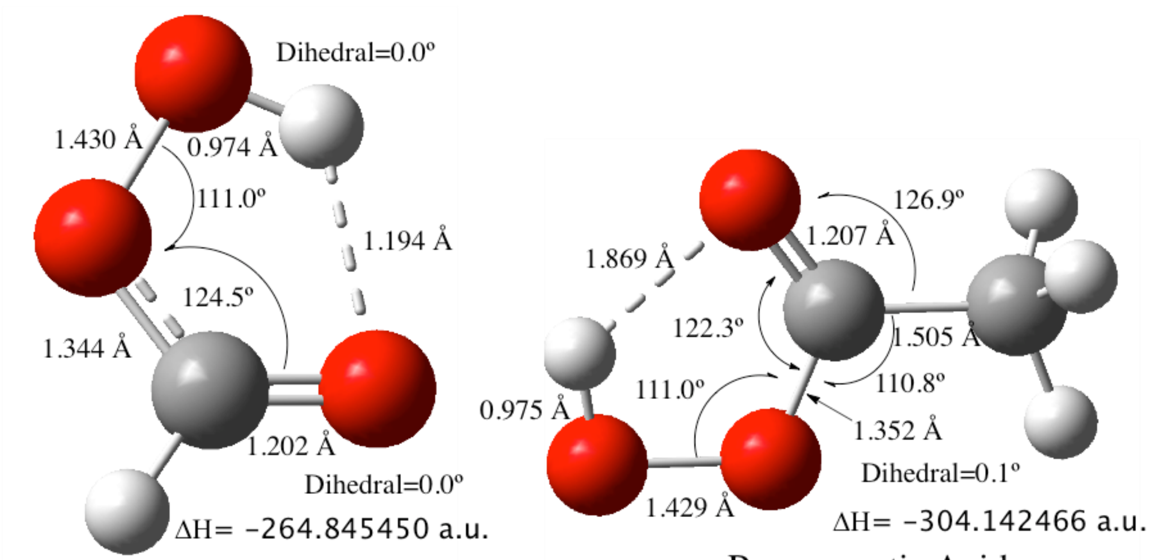
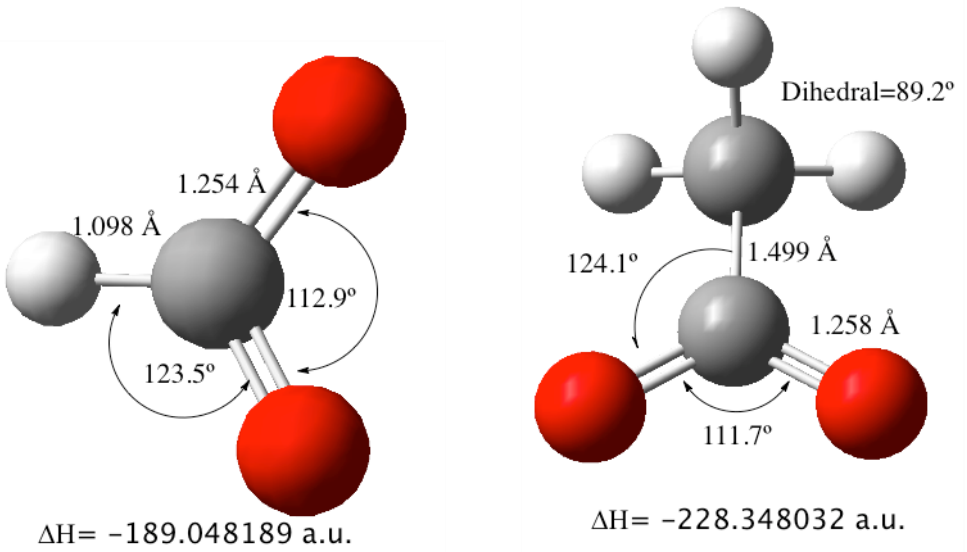


Figure 5. Lowest π state ($^2A_2$) and the two lowest σ states ($^2B_2$ and $^2A_1$) of formoxyloxyl radical (MP2/6-31G(d) geometries). The delocalized σ states can be described by two localized configuration resonance interactions (adapted with permission from *J. Am. Chem. Soc.* **1996**, *118*, 12758, copyright (1996) American Chemical Society).



Peroxyformic Acid

Peroxyacetic Acid

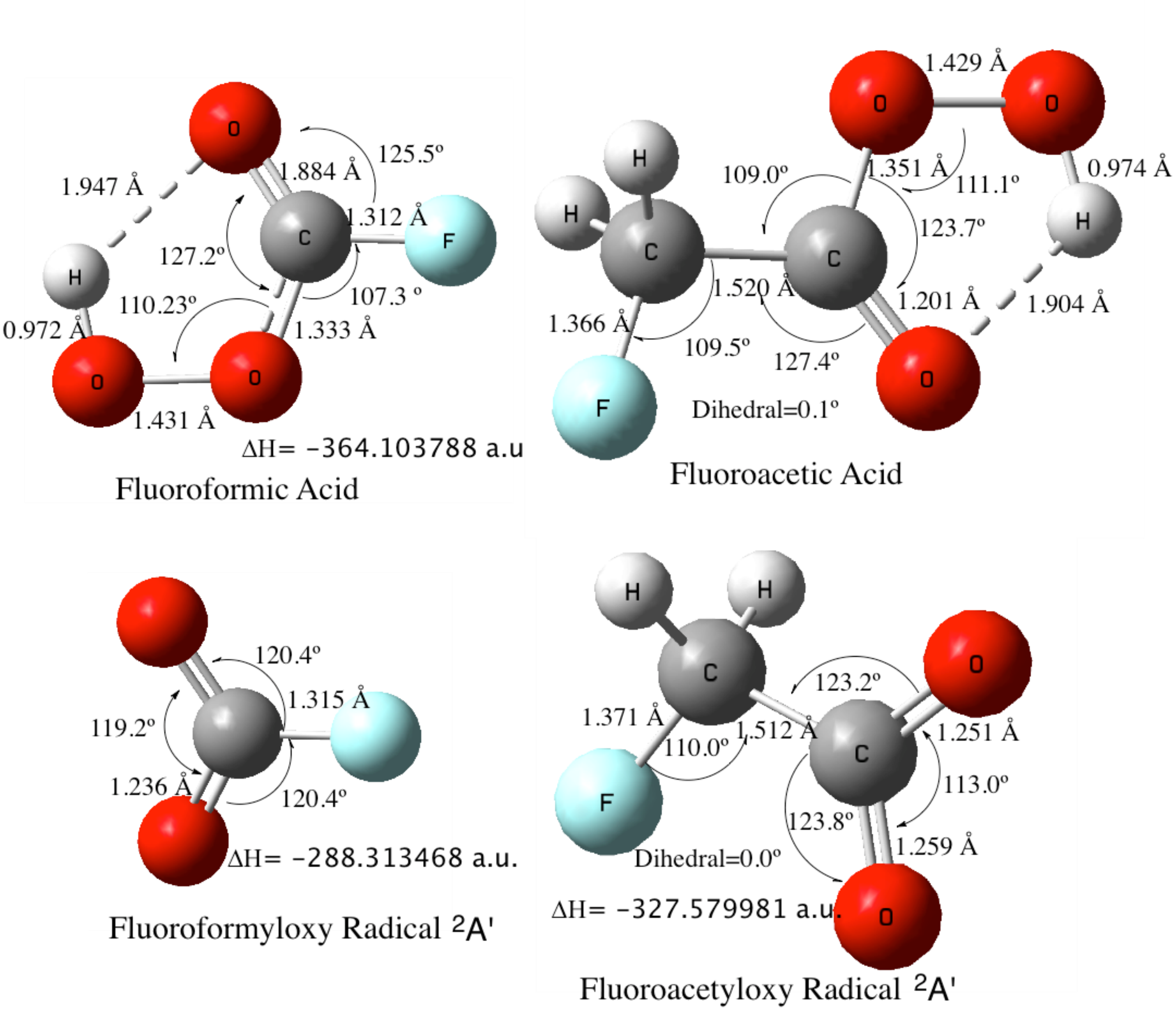


Formyloxy Radical $^2B_2$

Acetyloxy Radical $^2A''$

Figure 6. CBS-APNO enthalpies for peroxyformic acid and peroxyacetic acid.

While it is well known that electronegative elements such as fluorine can greatly influence the reactivity of a peroxyacid, it is less well established that these electronegative elements actually have little influence upon the magnitude of the O-O BDE in peroxy acids. Despite its lack of stability, we examined the O-O BDE for fluoroperoxyformic acid (FC(C=O)O-OH) simply to provide a comparison with trifluoroperoxyacetic acid. The electronic state for the fluoroperoxyformic radical is $^2A'$.



Fluoroformic Acid

Fluoroacetic Acid

Fluoroformyloxy Radical $^2A'$

Fluoroacetyloxy Radical $^2A'$

Figure 7. CBS-APNO enthalpies for fluoroformic acid and fluoroacetylacetic acid and their respective peroxoyl radicals.

Peroxyacetic acid is one of the more commonly employed peroxy acids in organic synthesis. Homolytic O-O bond cleavage produces the acetyloxy radical ((CH_3-

C(C=O)O•) that has an electronic state of $^2A''$ (Figure 6). Substitution of the peroxy acid moiety with a methyl group introduces additional problems with the potential for a number of σ and π radicals due to methyl group rotation in peroxyacetic acid. We have presented a thorough description of the number of different possible structures in our earlier report on peroxide O-O BDEs[2]. Fortunately, the energy differences between the most important structures are very small and consequently this does not affect our BDE assignment to a significant degree. The $^2A''$ electronic state for the acetyloxy radical results in an O-O BDE of 46.87 kcal/mol for peroxyacetic acid. While the CBS-APNO BDE for fluoroformic acid is 44.28 kcal/mol that is somewhat lower than that for trifluoroperoxyacetic acid which has a BDE of 47.32 kcal/mol and a $^2A''$ electronic state (Figure 8) with a somewhat greater BDE (ΔBDE=3.04 kcal/mol). The O-O bond energy is also a little lower than that for peroxyacetic acid (46.87 kcal/mol). We also reported[1] that the $\Delta E^\ddagger$ for epoxidation of E-2-butene with F(C=O)O-OH and CF_3(C=O)O-OH were nearly identical (6.41 vs 6.39 kcal/mol) suggesting that direct electron withdrawing effect of a single F atom is equivalent to the effect of a CF_3 group. Hence, it is not surprising that the BDE for fluoroacetic acid is also lower that that for its trifluoro analogue (BDE=46.76) and it oxy radical (FCH_2-C(C=O)O•) has a $^2A'$ electronic ground state.

Diacyl peroxides represent another case where it is difficult to arrive at an accurate O-O BDE. The lack of experimental data on diacyl peroxides presents a problem in finding a good reference point for comparison. For example, a value of 30±1 kcal/mol for the bond dissociation for diacetyl peroxide reported by Swarc[42] was based upon the assumption that its thermal decomposition was best described as a simple O-O bond cleavage as the first rate-limiting factor (Eq 1).

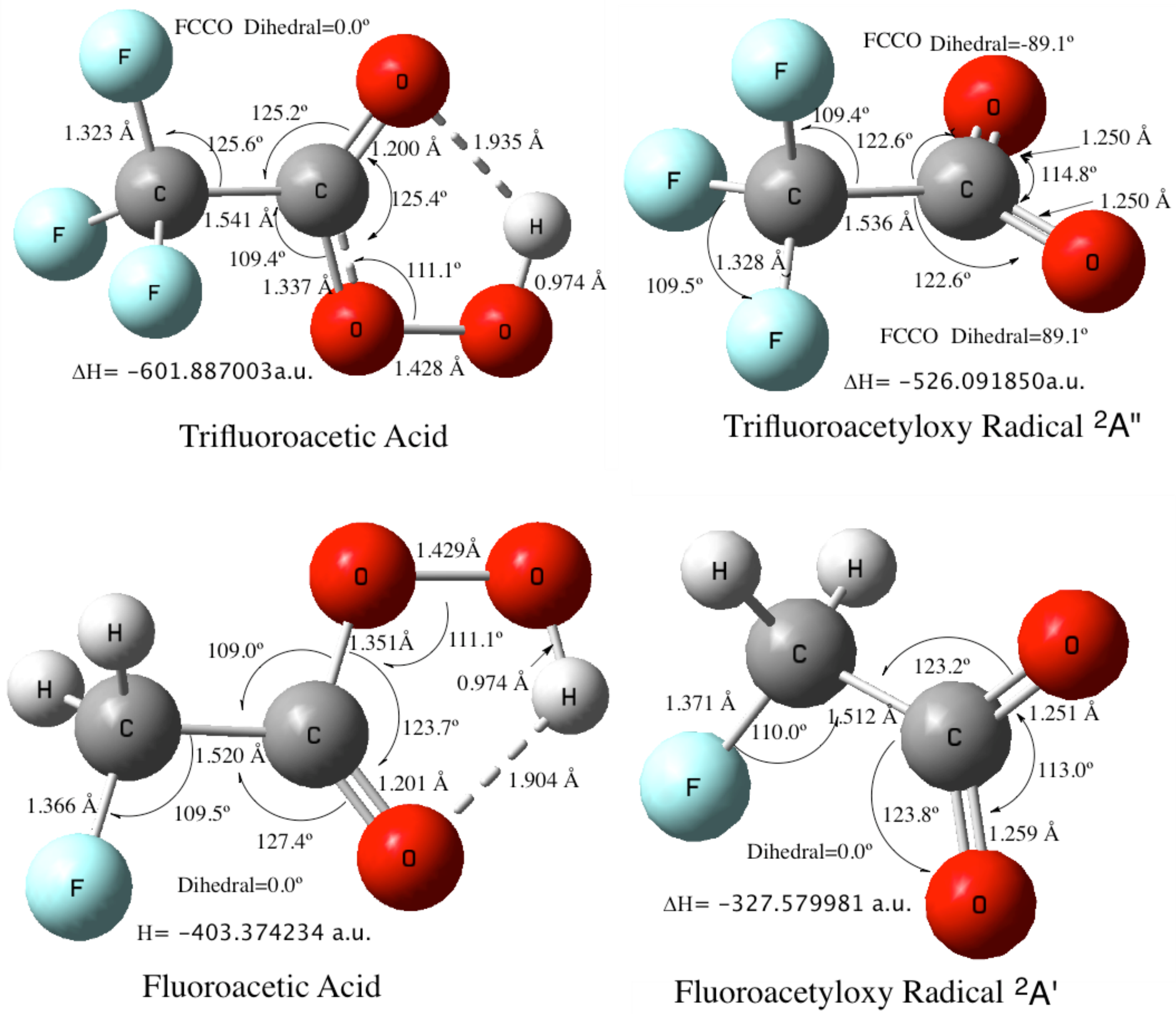


Figure 8. CBS-APNO enthalpies for fluoroperoxyacetic acid and trifluoroperoxyacetic acid and their respective peroxoyl radicals.

$$(CH_3CO_2)_2 \rightarrow 2\ CH_3CO_2 \rightarrow 2\ CH_3 + 2\ CO_2 \qquad \text{(Eq. 1)}$$

In addition, it was realized that O-O bond fission in diacetyl peroxide (Figure 9) could be further complicated by ^{18}O scrambling by both [3,3] and [1,3]-sigmatropic rearrangements. After considerable consideration of these several pathways, we predicted an O-O bond dissociation enthalpy of 36.9 kcal/mol at the G2 level.[2] At the CBS-APNO level we now predict a simple dissociation energy of 32.87 kcal/mol based upon the ^{2}A" state for the acetyloxy radical.

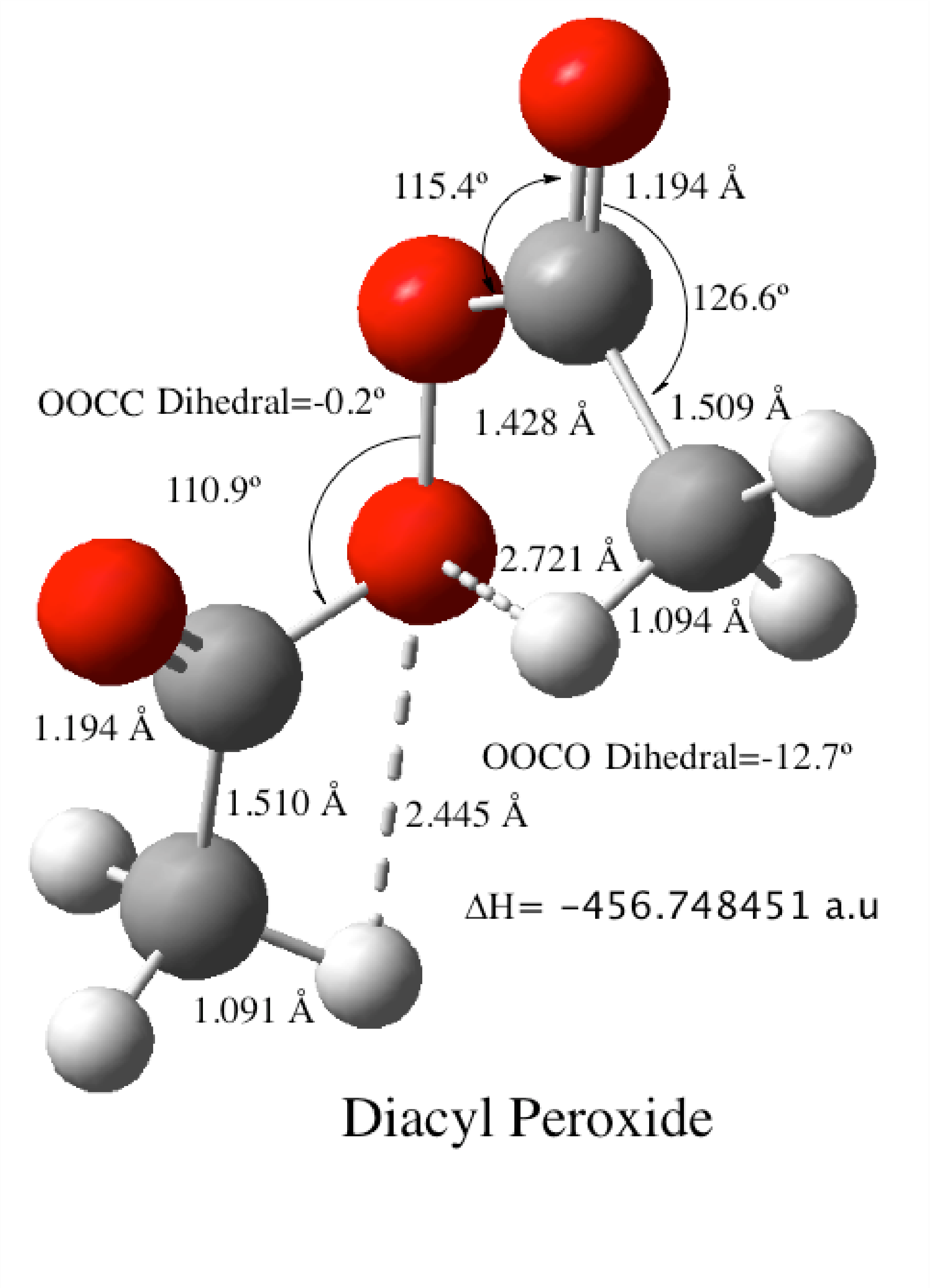
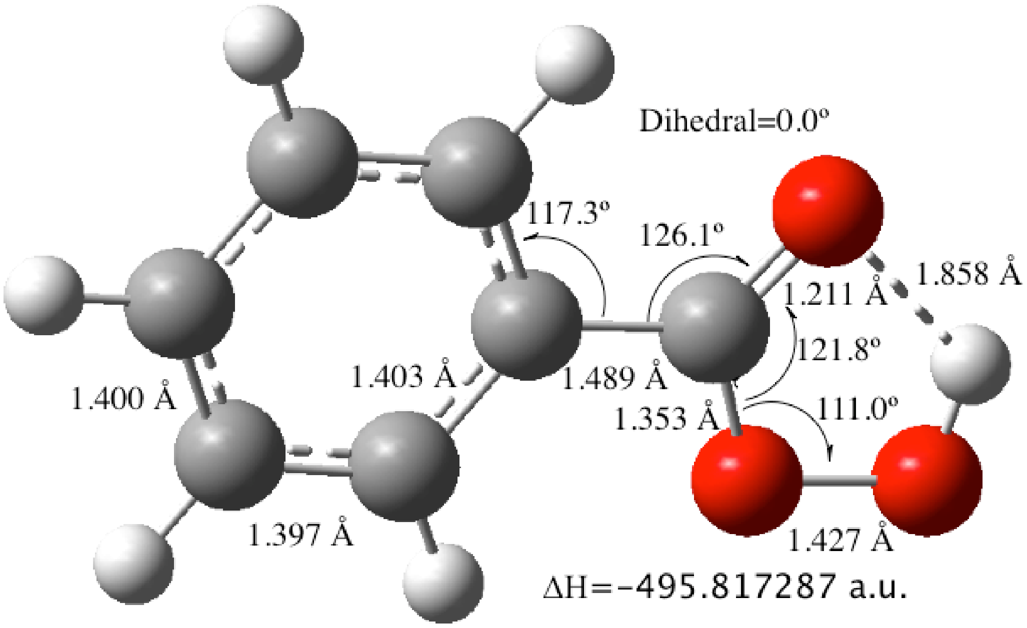
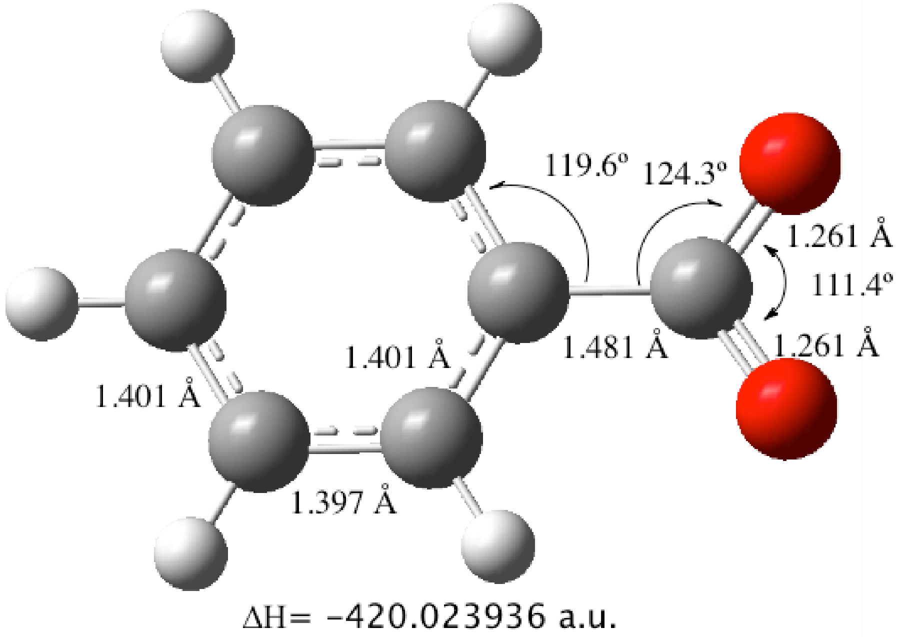


Figure 9. CBS-APNO enthalpies for diacyl peroxide.

Assigning a BDE value to any peroxide or peroxyacid that is directly bonded to a phenyl ring presents more serious problems. As noted above, direct bonding to a rotating alkyl group can introduce additional structures for the oxy radical. Even more problematic is the inclusion of an aromatic ring because the resulting benzoyloxy radical (Ph(C=O)O•) is often difficult to characterize. For example, peroxybenzoic acid upon O-O homolytic bond dissociation produces the benzoyloxy radical and hydroxyl radical. There is still some question as to whether the $^2A_2$ or $^2B_2$ benzoyloxy radical is the actual ground state.[43] We have assigned a $^2B_2$ ground electronic state after initially providing a C_{2V} starting geometry followed by complete geometry optimization at the CBS-APNO level. This leads to an O-O BDE of 46.19 kcal/mol for peroxybenzoic acid that is, within the accuracy of the calculations, essentially the same as peroxyacetic acid (46.87 kcal/mol).



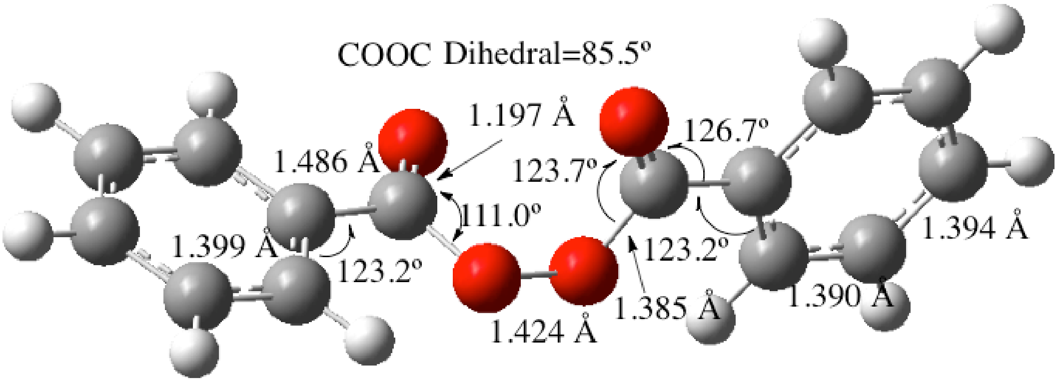
Peroxybenzoic Acid



Benzoyloxy Radical $^2B_2$

Figure 10. CBS-APNO enthalpies for peroxybenzoic acid and its benzoyloxy radical.

One of the most heavily used peroxides in industrial applications is benzoyl peroxide (BPO). Upon homolytic O-O bond cleavage the free radical initiator, benzoyloxy radical (Ph(C=O)O•), is produced and is applied to numerous free radical polymerization reactions. As discussed above dimeric peroxides pose special problems in establishing an accurate O-O BDE upon O-O bond dissociation due to the additional pathways possible including Cope-like rearrangements where the carbonyl oxygen can exchange with peroxide oxygens (*O=C-O-O-C=O* → O=C-O*-O*-C=O). A number of possible dissociative pathways have been discussed in detail including the loss of CO_2 to produce the very active phenyl radical.[44] Unfortunately the BPO molecule is sufficiently large that CBS-APNO calculations are not within our computational means. The QCISD step with a very large basis set simply did not allow us to complete the calculation. However, we were able to get a BDE at the G4 level (Figure 11) when we carried out a sequential one step process to get an O-O BDE of 34.34 kcal/mol. We also examined this important peroxide at the CBS-QB3 level and obtained a BDE of 34.84 kcal/mol.



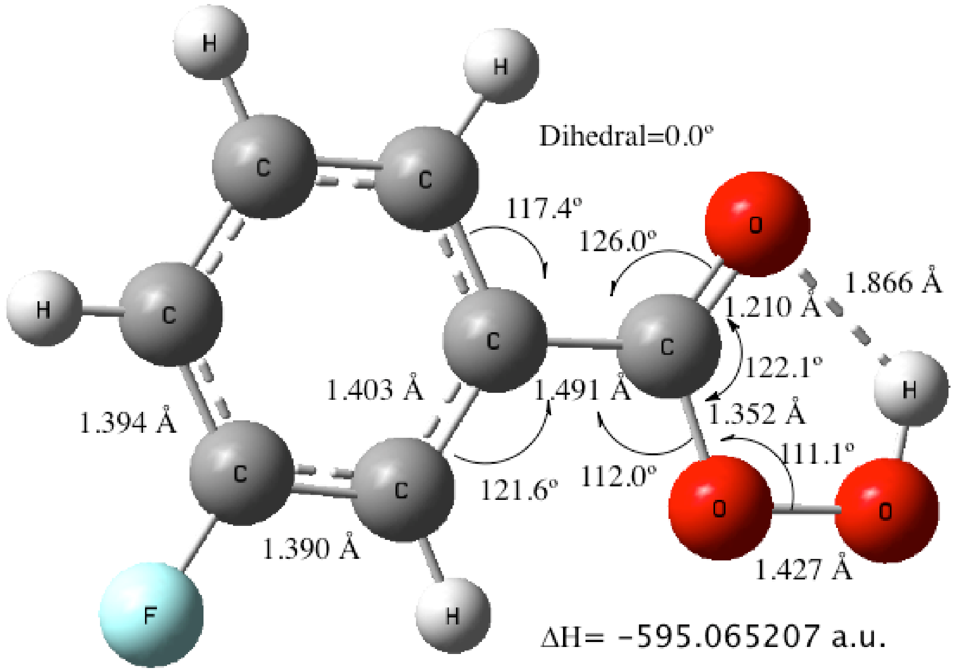
ΔH= −839.935284 a.u. (BPO G4)

ΔH= −419.942668 a.u. (Benzoyloxy Radical G4)

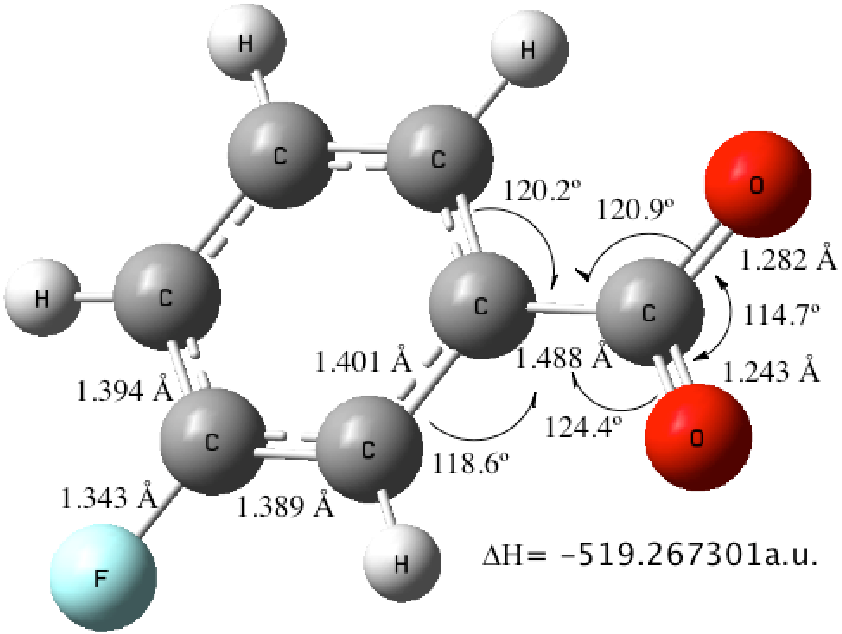
Benzoyl Peroxide

Figure 11. Benzoyl peroxide at the G4 level.

One of the most useful peroxy acids in a laboratory application is *meta*-chloroperoxybenzoic acid (mCPBA). Since the CBS-APNO method does not yet include second-row elements, we have initially included meta-fluoroperoxybenzoic acid (mFPBA). We calculate an O-O BDE of 49.05 kcal/mol for the $^2A'$ electronic state for the *meta*-fluorobenzoyloxy free radical (Figure 12). We have also been able to calculate the O-O BDE for mCPBA at the G4 level and report a BDE of 43.18. (Figure 13). As anticipated the G4 BDE for mFPBA is essentially the same with a BDE that is only 0.2 kcal/mol higher. It is also significant that the O-O BDE for mFPBA with the APNO and M06-2X methods differ by less than a kcal/mol. We will describe the BDE for mCPBA below where the M06-2X functional can be applied to provide very good BDEs for a variety of peroxides.

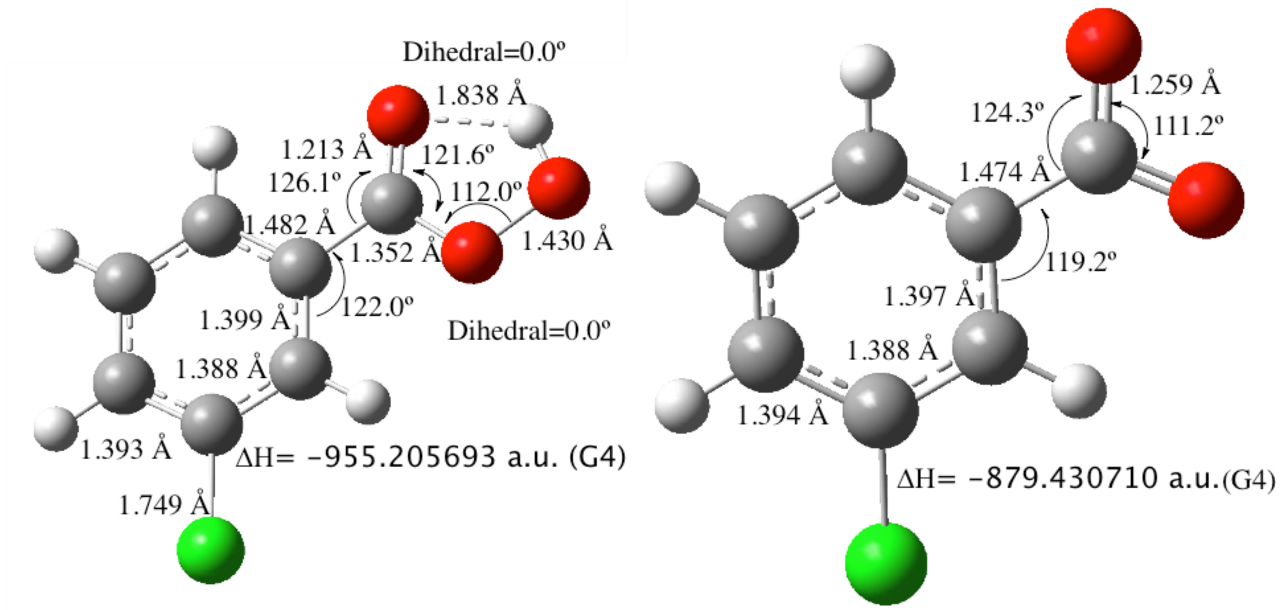


Fluoroperoxybenzoic Acid



Fluorobenzoyloxy Radical $^2A'$

Figure 12. CBS-APNO enthalpies for meta-fluoroperoxybenzoic acid and its fluorobenzoyloxy radical.



Meta-Chloroperbenzoic Acid Meta-Chloroperbenzoyloxy Radical $^2A'$

Figure 13. CBS-APNO enthalpies for meta-chloroperbenzoic acid and its chlorobenzoyloxy radical.

We have also included two peroxides that have O-O bonds adjacent to a multiple bond as an intellectual exercise to show how orbital interactions attending O-O bond dissociation can influence the stability of the σ and π electronic states of the developing oxygen delocalized free radicals to a point where such peroxides are not actually isolable. For example, phenyl hydroperoxide (PhCO-OH) upon O-O bond cleavage produces the phenoxy radical that needs to be treated with restricted open shell methods (e.g. ROCBS-QB3) that can offer a reasonable treatment of spin contamination (S2A=0.751). (Figure 14). However, this produces a very low BDE of 23.34 kcal/mol. In a similar fashion the BDE for diphenyl peroxide (PhO-OPh) we have estimated a BDE of 2.59 kcal/mol that obviously means that this highly reactive peroxide is not isolable.

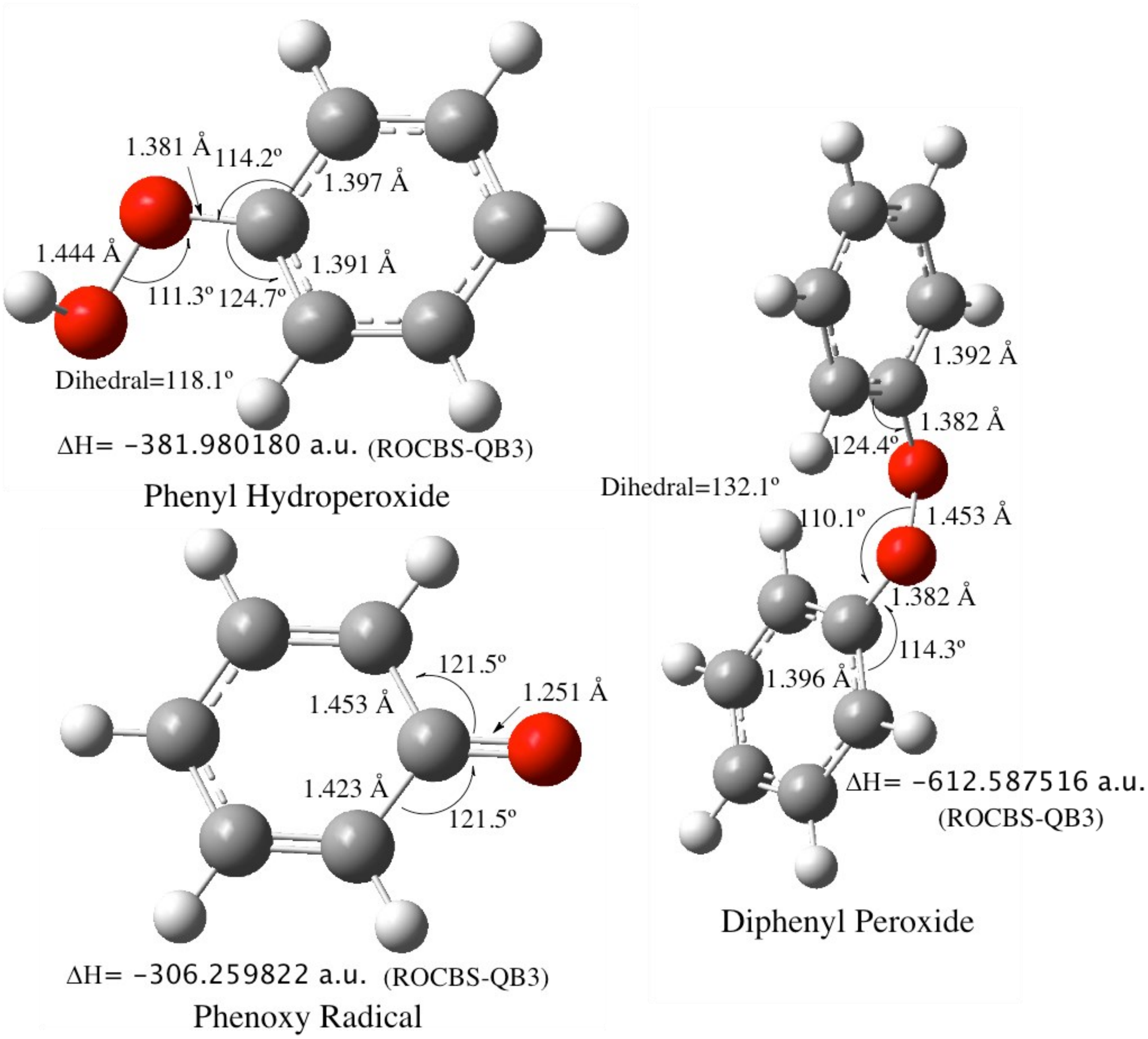


Figure 14. Phenyl hydroperoxide and diphenyl peroxide at the CBS-QB3 level.

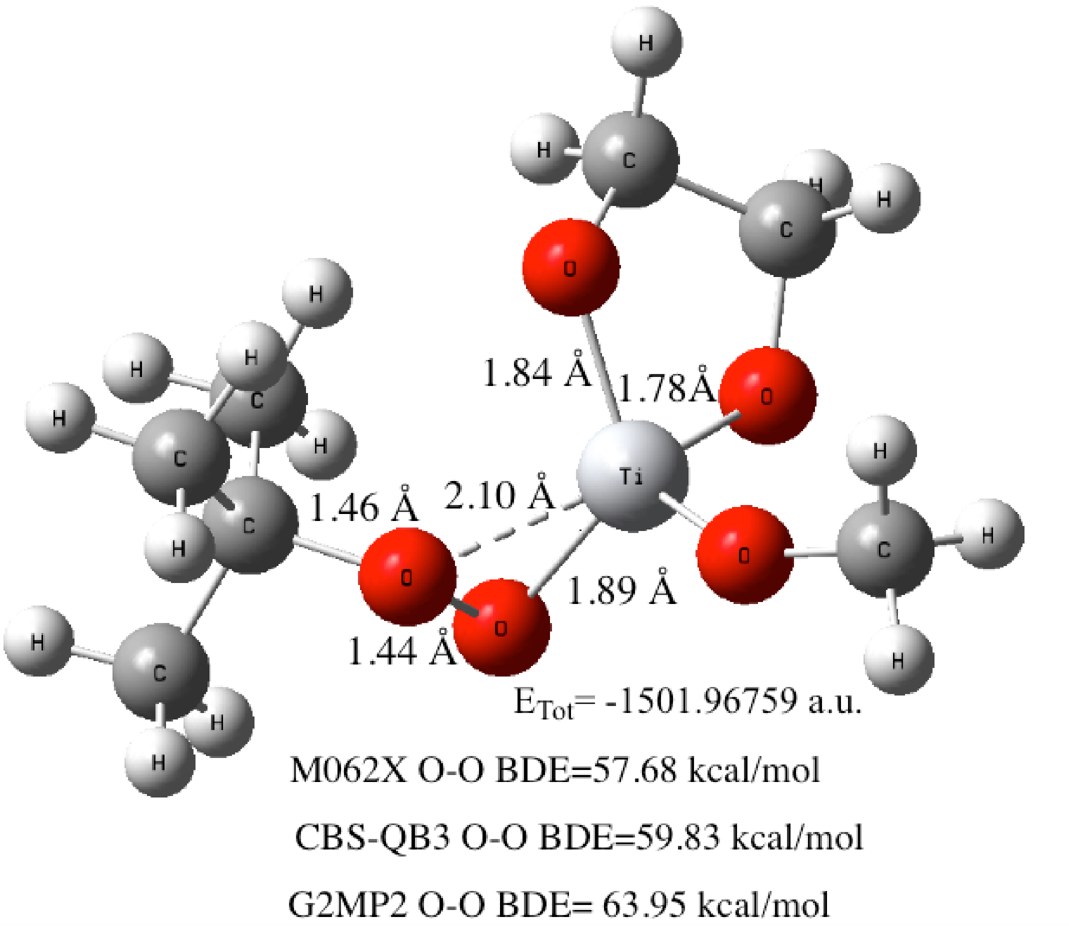
(b) Comparison of O-O BDEs calculated with CBS-APNO and DFT.

It has been known for some time that the B3LYP functional underestimates the O-O BDE of peroxides. However, we were still surprised to find that B3LYP/6-311+G(d,p) BDEs were consistently lower than the CBS-APNO values by an average of ≈ 11 kcal/mol (Table1). The use of the B3LYP functional is quite wide spread for a great many theoretical studies on oxidative reactions because this functional provides activation barriers in good accord with experimental kinetic data. As an example, we calculated the activation barriers for the epoxidation of E-2-butene with peroxyacetic acid at both the CBS-APNO and B3LYP/6-311+G(d,p) levels and find comparable free energies of activation ($\Delta G^{\ddagger}$=24.89 kcal/mol and 23.91 kcal/mol). We can offer no explanation for why the B3LYP functional performs so poorly for O-O BDE's but still provides respectable activation barriers for a process the involves O-O bond cleavage in the TS.

In a recent study we reported[38] that the M06-2X functional provides O-O BDEs in excellent agreement with CBS-APNO values. This, of course, was a pleasant surprise so we extended the current study to compare values with this functional to our CBS-APNO data. The CBS-APNO BDE values were only slightly higher for the alkyl hydroperoxides (average 0.35 kcal/mol) but somewhat lower for the peroxy acids (average 2.5 kcal/mol). With the M06-2X functional we did use a rather extended basis set (6-311+G(3df,2p)) but this still allows calculations on much larger molecules than is possible with the CBS-APNO method that is far more compute intensive. For example, we are not able to calculate molecules as large as benzoylperoxide (BPO) with CBS-APNO, but with the M06-2X functional we calculate the benzoyloxy radical ($^2B_2$) and find a BDE for BPO of 41.10 kcal/mol that is 21 kcal/mol greater than that calculated with the B3LYP functional. However, the O-O BDE at the CBS-QB3 and G4 levels that should be more reliable are considerably lower at 34.84 and 31.34 kcal/mol. The ωB97XD functional is often suggested for this type of oxidative reaction, However, we found that the O-O BDE in *tert*-butyl peroxide with the ωB97XD/6-311+G(3df,2p) level of theory gave a BDE that was 18 kcal/mol lower than with the corresponding M06-2X functional. To further confuse the situation, we also found that the ωB97XD BDE for peroxyacetic acid, 40.55 kcal/mol, is intermediate between the B3LYP and CBS-APNO values. This clearly suggests that O-O BDE are quite sensitive to the method of calculation but that the M06-2X functional still allows one to compute fairly accurate O-O BDEs for relatively large molecules. This is particularly important because we can also calculate BDEs on molecules with second row elements. With this method we can assign an O-O BDE to *meta*-chloroperoxybenzoic acid (mCPBA) of 49.41 kcal/mol. However, we do calculate a somewhat lower BDE at the G4 level (43.18 kcal/mol) where the corresponding carboxy free radical is at the $^2A'$ electronic state by both methods. We feel fairly confident about the assigned BDE for mCPBA because of the excellent agreement with that calculated for mFPBA. This peroxycarboxylic acid is one of the most commonly used peroxy acids in organic synthesis. It is a strong oxidizing agent that may cause fire upon contact with flammable material. Its use is primarily due to the fact that it is a solid that it is typically sold as 75 % peroxy acid that includes a mixture of *meta*-chlorobenzoic acid and H_2O to insure its safety and relative ease of handling. It is of particular value to the mechanistic organic chemist to have a reliable value of the O-O BDE of reactants in order to evaluate relative activation barriers. It is not surprising that that both *meta*-fluoro and *meta*-chloro peroxyacids have nearly identical O-O BDE.

The increasing importance of transition metal catalyzed epoxidations encouraged us to include a model Sharpless reaction catalyst.[24] This is particularly relevant because essentially nothing is known today about the O-O bond BDEs for such oxidizing agents.

The model titanium (IV) *tert*-butyl hydroperoxide (Figure 15) contains one methoxy group and an ethylene glycol moiety to model the chiral tartrate auxiliary in the Sharpless catalyst. This is particularly relevant because the peroxide moiety exists as an η^2 structure with the primary Ti-O bond having a distance of ca. 1.9 Å and a much weaker secondary Ti-O bond of ca. 2.1 Å. This η^2 bonding motif is shown in Figure 15 and raises questions about the enthalpy requirements for oxygen atom transfer.



E_{Tot}= -1501.96759 a.u.

M062X O-O BDE=57.68 kcal/mol

CBS-QB3 O-O BDE=59.83 kcal/mol

G2MP2 O-O BDE= 63.95 kcal/mol

Figure 15. Model titanium(IV) *tert*-butyl hydroperoxide complex at the M06-2X/6-311+G(3df,2p) level of theory.

Oxygen atom transfer involves breaking the primary Ti-O bond, as well as, the secondary Ti•••O bond. With the DFT M06-2X functional the O-O BDE = 57.68 kcal/mol and that represents a 12.78 kcal/mol increase with respect to *t*-BuOOH at the same level of theory. Since this represents a rather significant increase in BDE we also checked this result at the CBS-QB3 level and get a BDE of 59.38 kcal/mol that is 12.69 kcal/mol higher than *t*-BuOOH. The somewhat lower accuracy G2MP2 method overestimates the O-O BDE by 6 kcal/mol. Despite this atypically high O-O bond BDE this type of metal catalyzed oxygen atom transfer is very efficient and compares favorably with the other types of peroxide catalysts. It should be noted, however, that the mechanism for oxidation is very different for this type of peroxide. For example, peroxyacid epoxidation involves a 1,4- hydrogen shift to the adjacent C=O group while hydroperoxide oxidation involves a 1,2-hydrogen shift from the distal to the proximal oxygen in the TS.[38] In both cases it is the distal oxygen that is transferred. By contrast in the metal catalyzed epoxidation it is the proximal oxygen that is transferred as the distal oxygen transfers its primary bonding allegiance from the proximal oxygen to the adjacent metal in a 1,3-rearrangement. Thus, it is this concerted rearrangement where both Ti-O bonds are of comparable strength that helps to ameliorate the overall activation energy. Thus the net molecular event is the breaking of the O-O bond in concert with oxygen transfer to the substrate that provides a plausible explanation for why these metal-containing catalysts are so efficient.

Conclusions

The calculations at the CBS-APNO level do seem to provide O-O BDE values that are more accurate than those in our earlier report[6] and are on average slightly higher than those calculated at the G4 level. The average O-O BDE for the 17 peroxides in Table 1 at the CBS-APNO level is 45.3 kcal/mol. It is particularly relevant to this study that those same 17 peroxides have a calculated O-O BDE that is on average only 0.5 kcal/mol higher at the M06-2X level. For the 11 peroxides reported at the G4 level in Table 1 the average O-O BDE = 42.3 kcal/mol but the CBS-APNO BDE are on average 2.8 kcal/mol higher. The close agreement within all three methods strongly suggest that the DFT M06-2X functional provides a method to obtain quite accurate O-O bond energies on relatively large molecules. This will also include metal catalysts containing elements not yet included in composite methods such as the CBS-APNO or G4 protocols. One of the most interesting observations that we have made in this study is while the O-O BDE values for a wide variety of peroxides differ very little in magnitude, their activation barriers for oxygen atom transfer vary markedly.[38] This is particularly puzzling because all such oxidative reactions with peroxides involve O-O bond breaking in the rate-determining step.

ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the

ACS Publications website at DOI: 10.1021/acs.jpca.5b12086.

Total energies and Cartesian coordinates for all

structures are included. (PDF)

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Notes

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Funding

This work was supported in part by a grant from National Science Foundation (CHE1856437) to HBS.

Acknowledgements

SEAGrid (http:www.seagrid.org) is acknowledged for computational resources and services for selected results used in this publication. This work also used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number OCI-1053575.

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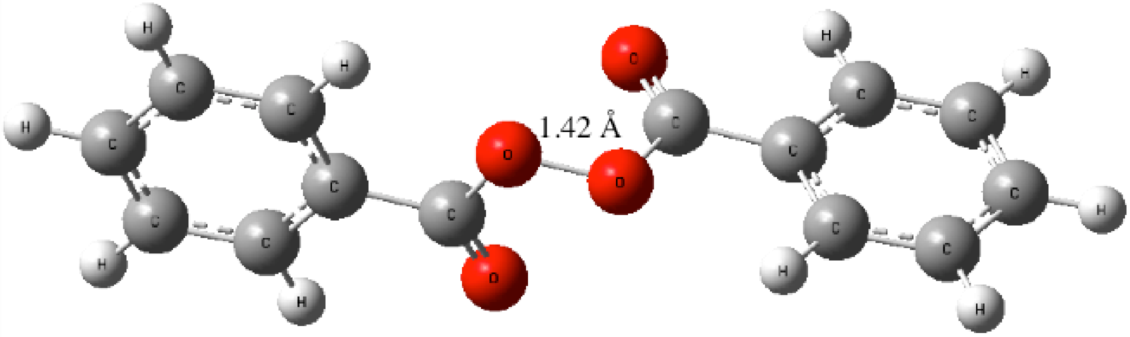

Benzoyl Peroxide O-O Bond Energy 31.34 Kcal/mol (G4)