

Bond Dissociation Energy of Peroxides Revisited

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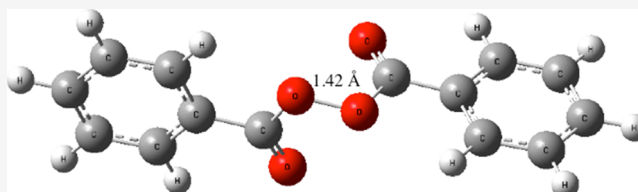


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ABSTRACT: When dealing with organic peroxides in both laboratory and industrial applications, the relative strengths of the O–O bond are of vital importance, both from a safety and mechanistic perspective. Although it is well known that such oxidizing agents are highly reactive, reliable O–O bond dissociation energies (BDEs) 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 structures at a 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.



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

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 ago² 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 than 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 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-APNO⁵ methods available in Gaussian 16⁶ have been shown to calculate ΔH and ΔG values in very good agreement with experimental values that are typically reported to be accurate within 1–2 kcal/mol. For example, for gas phase deprotonation reactions, the mean absolute deviation of these three

methods from experiments is 0.84–1.26 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, respectively.⁷ In a related benchmarking study on enthalpies of formation⁸ of $C_xH_yO_z$ molecules, these theoretical methods were ranked $G4 > CBS-APNO > CBS-QB3$, where the CBS-x methods on average predict enthalpies of formation 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 system⁶ 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). BDEs 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 BDEs calculated with the B3LYP DFT functional^{12–15} utilized the 6-311+G(d,p) basis

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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}
<i>tert</i> -BuO–OH	36.87	44.77	47.14	45.81	43.93	44.1 ^g 44.6 ^{e,h} 45.3 ^{e,i}
<i>di-tert</i> -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 ₃ OOCF 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	
<i>m</i> -FPh(C=O)O–OH	35.86	49.90		49.04	43.38	
<i>m</i> -ClPh(C=O)O–OH	35.87	49.41			43.18	
PhO–OH			23.59	23.34		
PhO–OPh			2.59			
(CH ₃) ₃ OOTi(OCH ₃) ₂ O ₂ C ₂ H ₄		57.68	59.83			

^a6-311+G(d,p) basis set. ^b6-311+G(3df,2p) basis set. ^cReference 19. ^dReference 20. ^eReference 21. ^fReference 23. ^gReference 27. ^hReference 28. ⁱReference 29. ^jReference 31. ^kReference 32. ^lReference 33. ^mReference 42.

set, whereas those calculated with the M06-2X DFT functional¹⁶ 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 experiments. This can be particularly valuable because of the hygroscopic nature of highly polar organic hydroperoxides that present purification difficulties. Chemical bonds of electronegative elements such as oxygen typically have a relatively low BDE, whereas the ubiquitous C–C bond is often stronger and has an average BDE of ca. 84 kcal/mol.

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 BDE.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 BDE² (Figure 1). The

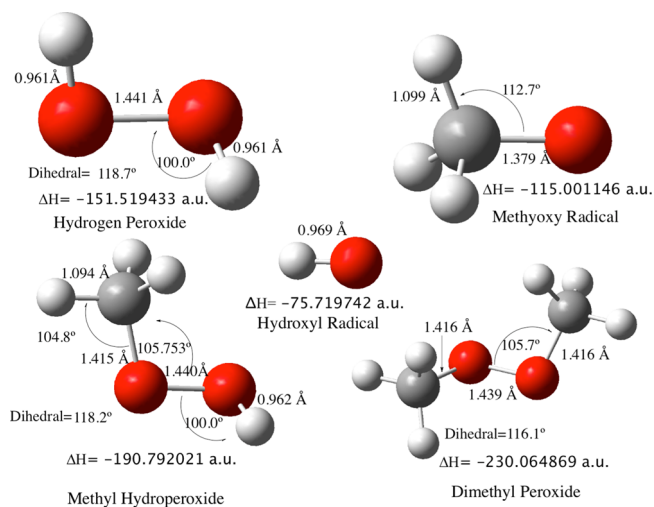


Figure 1. CBS-APNO enthalpies for hydrogen peroxide and methyl hydroperoxide.

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 Webbook²¹).

In our earlier report,² we showed that the G2 and CBSQ methods performed remarkably well for predicting BDE 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

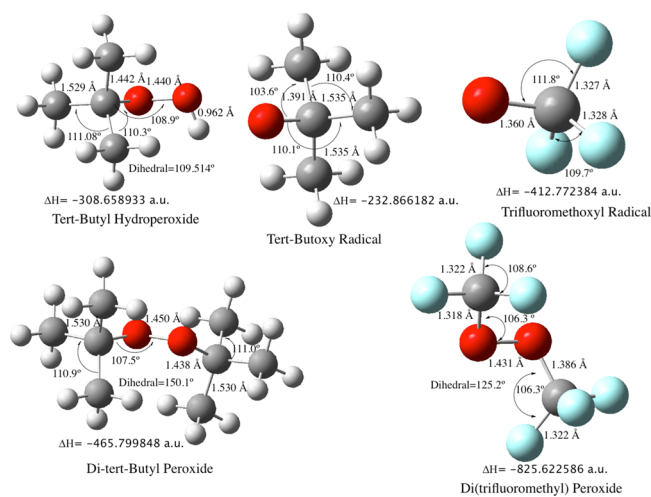


Figure 2. CBS-APNO enthalpies for *tert*-butyl hydroperoxide, di-*tert*-butyl peroxide, and di(trifluoromethyl) peroxide.

epoxidation reaction²⁴ 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 co-workers²⁵ have reported an O–O BDE of 46.13 kcal/mol based upon formation enthalpy data and calculations. Green and co-workers²⁶ 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 NIST²¹ and *t*-BuO from Blanksby and Ellison²⁸ and from Lineberger

and co-workers²⁹ yields 44.6 and 45.3 kcal/mol for the *t*-Bu-OH BDE.

A very commonly applied catalyst for free-radical chain reactions is di-*tert*-butyl peroxide ($\text{Me}_3\text{CO}-\text{OCMe}_3$).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 pyrolysis²⁷ and collision-induced dissociation experiments³² gave BDEs of 38.9 and 40.8 kcal/mol, respectively.²⁷ Heats of formation of di-*tert*-butyl peroxide from NIST²¹ and *t*-BuO from Blanksby and Ellison²⁸ and from Lineberger and co-workers²⁹ yield BDEs of 40.5 and 41.8 kcal/mol, respectively. 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 ($\Delta\text{BDE} = 5.69$ kcal/mol) has been ascribed³¹ to the stabilization of the *tert*-butylperoxyl radical by hyperconjugation. Such hyperconjugation effects for the CF_3 group are greatly reduced because of 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 values ranging from 40 to 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 , which is in very good agreement with the recent pyrolysis study.

We also examined the O–O BDE of 1-phenylethyl-1-hydroperoxide ($\text{PhCH}(\text{CH}_3)\text{OOH}$) and 1-methyl-1-phenylethyl-1-hydroperoxide that is more commonly referred to as cumene hydroperoxide ($\text{PhC}(\text{CH}_3)_2-\text{OOH}$), Figure 3.

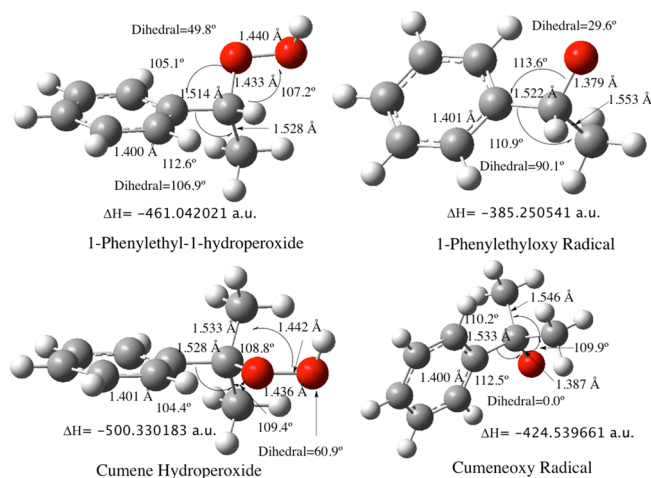


Figure 3. CBS-APNO enthalpies for 1-phenyl-1-hydroperoxide and cumene hydroperoxide.

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).

One of the more recent additions to this class of hydroperoxides that is used in many experimental applications is hexafluoroacetone perhydrate ($(\text{CF}_3)_2\text{C}(\text{OH})\text{OOH}$), Figure

4. This highly reactive α -hydroxy hydroperoxide is derived from the addition of HOOH to hexafluoroacetone and the

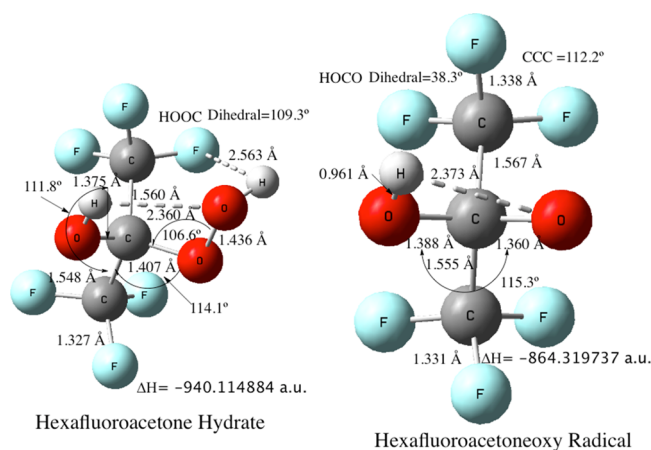


Figure 4. CBS-APNO enthalpies for hexafluoroacetone hydrate and its oxyradical.

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.

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 ΔE^\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 reported³⁸ 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, whereas 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 CF₃ 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 the O–O BDE for peroxyformic acid to be 48.64 kcal/mol at the CBS-APNO level with the formyloxy radical in the 2B_2 electronic state (Figure 6). In our earlier work at the G2 level, we reported¹ a BDE of 48.41 kcal/mol that was also based upon a 2B_2 ground state for the formyloxy radical.

Although 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

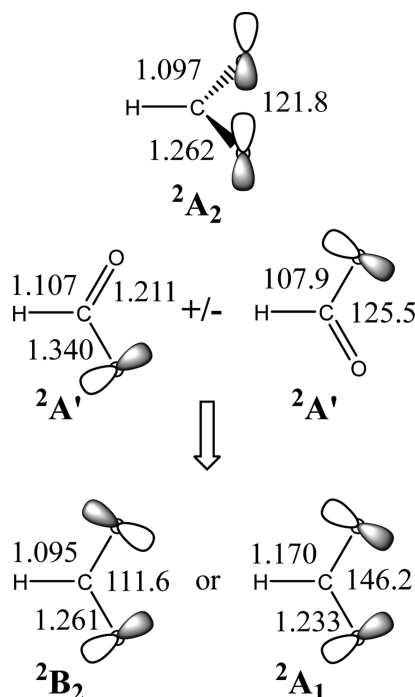


Figure 5. Lowest π state (2A_2) and the two lowest σ states (2B_2 and 2A_1) of formyloxy radical (MP2/6-31G(d) geometries). The delocalized σ states can be described by two localized configuration resonance interactions (adapted with permission from *J. Am. Chem. Soc.* 1996, 118, 12758, copyright (1996)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

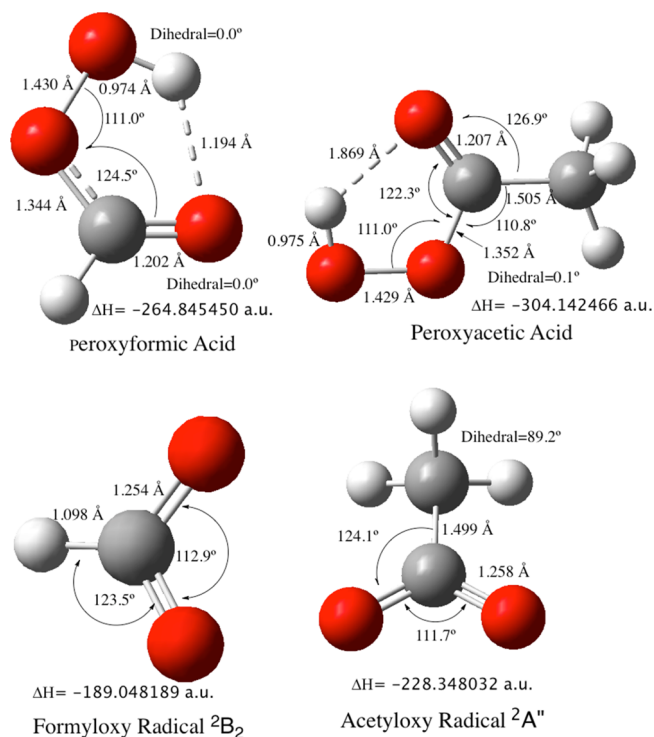


Figure 6. CBS-APNO enthalpies for peroxyformic acid and peroxyacetic acid.

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 trifluoroperoxy-

acetic acid, Figure 7. The electronic state for the fluoroperoxyformic radical is $^2A'$.

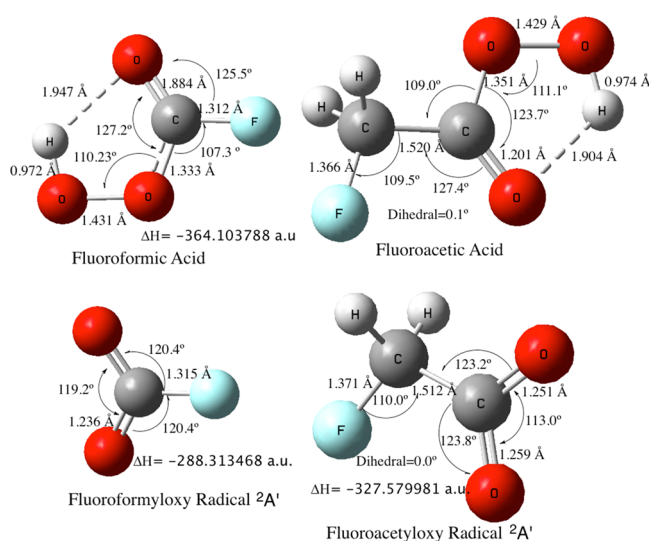


Figure 7. CBS-APNO enthalpies for fluoroformic acid and fluoroacetyloxy radical and their respective peroxy radicals.

Peroxyacetic acid is one of the more commonly employed peroxy acids in organic synthesis. Homolytic O–O bond cleavage produces the acetyloxy radical ($\text{CH}_3\text{-C}(\text{C}=\text{O})\text{O}^\bullet$) 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. Although 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 ($\Delta\text{BDE} = 3.04$ kcal/mol). The O–O bond energy is also a little lower than that for peroxyacetic acid (46.87 kcal/mol). We also reported¹ that the ΔE^\ddagger for epoxidation of *E*-2-butene with $\text{F}(\text{C}=\text{O})\text{O}-\text{OH}$ and $\text{CF}_3(\text{C}=\text{O})\text{O}-\text{OH}$ were nearly identical (6.41 vs 6.39 kcal/mol) suggesting that the 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 than that for its trifluoro analogue (BDE = 46.76) and its oxy radical ($\text{FCH}_2\text{-C}(\text{C}=\text{O})\text{O}^\bullet$) 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 Swarc⁴² 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).

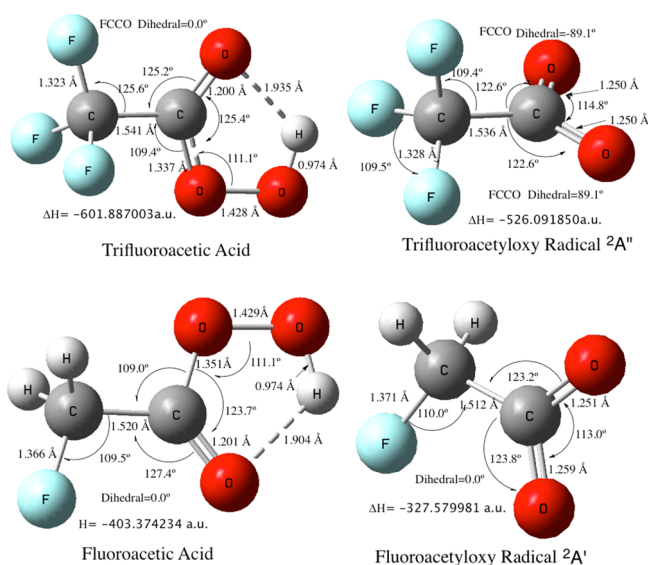
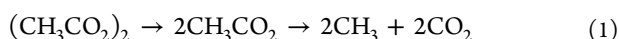


Figure 8. CBS-APNO enthalpies for trifluoroperoxyacetic acid and fluoroacetyloxy radical and their respective peroxy radicals.

In addition, it was realized that O–O bond fission in diacetyl peroxide (Figure 9) could be further complicated by ^{18}O

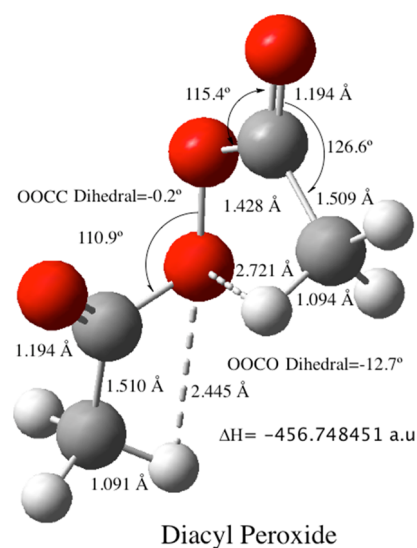


Figure 9. CBS-APNO enthalpies for diacetyl peroxide.

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 $^2A''$ state for the acetyloxy radical.

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 ($\text{Ph}(\text{C}=\text{O})\text{O}^\bullet$) 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, Figure 10. This leads to an O–O BDE of 46.19

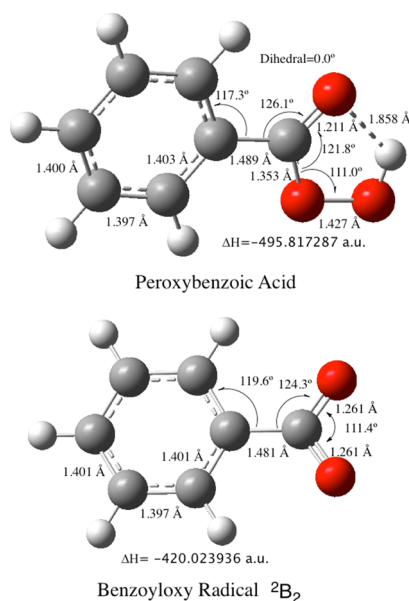


Figure 10. CBS-APNO enthalpies for peroxybenzoic acid and its benzoyloxy radical.

kcal/mol for peroxybenzoic acid that is, within the accuracy of the calculations, essentially the same as that for peroxyacetic acid (46.87 kcal/mol).

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 ($\text{Ph}(\text{C}=\text{O})\text{O}^*$), 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 ($^*\text{O}=\text{C}-\text{O}-\text{O}-\text{C}=\text{O}^* \rightarrow \text{O}=\text{C}-\text{O}^*-\text{O}^*-\text{C}=\text{O}$). 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.

One of the most useful peroxy acids in a laboratory application is *meta*-chloroperoxybenzoic acid (mCPBA). As 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

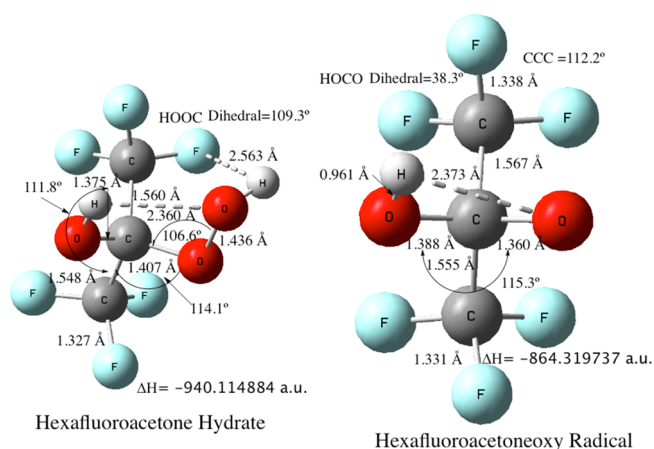


Figure 11. BPO at the G4 level.

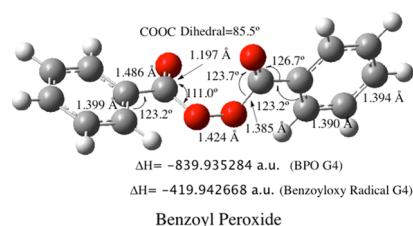


Figure 12. CBS-APNO enthalpies for *meta*-fluoroperoxybenzoic acid and its fluorobenzoyloxy radical.

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.

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 ($\text{PhCO}-\text{OH}$) 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

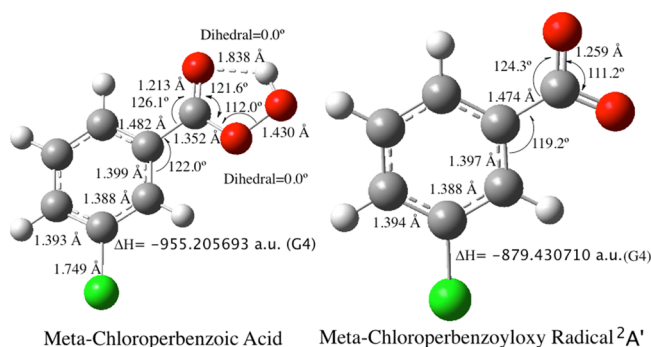


Figure 13. CBS-APNO enthalpies for *meta*-chloroperbenzoic acid and its chlorobenzoyloxy radical.

offer a reasonable treatment of spin contamination ($S2A = 0.751$) (Figure 14). However, this produces a very low BDE of

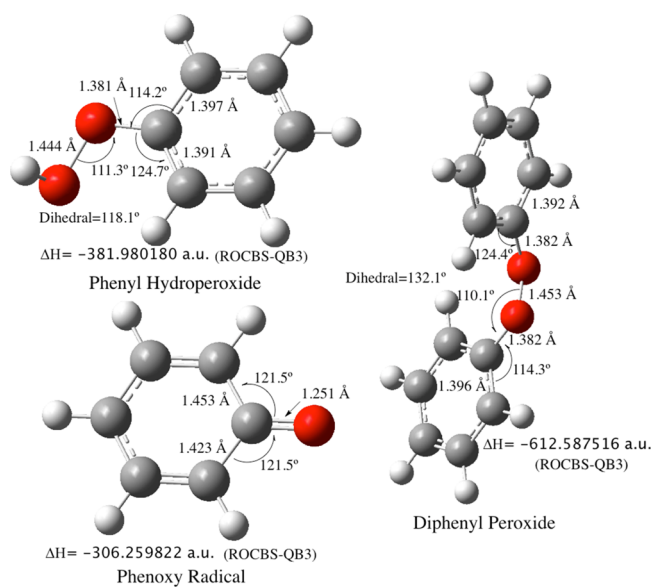


Figure 14. Phenyl hydroperoxide and diphenyl peroxide at the CBS-QB3 level.

23.34 kcal/mol. In a similar fashion, 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.

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 (Table 1). 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 ($\Delta G^\ddagger = 24.89$ and 23.91 kcal/mol, respectively). We can offer no explanation for why the B3LYP functional performs so poorly for O–O BDEs but still provides

respectable activation barriers for a process the involves O–O bond cleavage in the TS.

In a recent study, we reported³⁸ 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 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, respectively. The ω B97XD functional is often suggested for this type of oxidative reaction, However, we found that the O–O BDE in *tert*-butyl peroxide with the ω B97XD/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 ω B97XD BDE for peroxyacetic acid, 40.55 kcal/mol, is intermediate between the B3LYP and CBS-APNO values. This clearly suggests that O–O BDEs 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 value to *meta*-chloroperoxybenzoic acid (mCPBA) of 49.41 kcal/mol. However, we do calculate 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 peroxy-carboxylic 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 H₂O 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 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

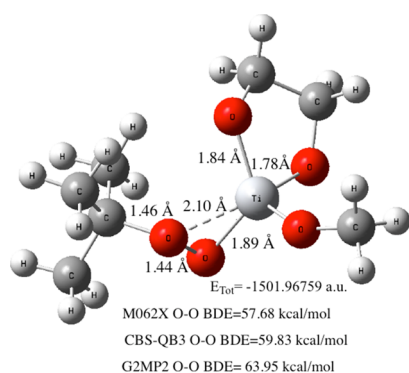


Figure 15. Model titanium(IV) *tert*-butyl hydroperoxide complex at the M06-2X/6-311+G(3df,2p) level of theory.

motif is shown in Figure 15 and raises questions about the enthalpy requirements for oxygen-atom transfer.

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. As this represents a rather significant increase in BDE, we also checked this result at the CBS-QB3 level and got a BDE of 59.38 kcal/mol that is 12.69 kcal/mol higher than that of *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, whereas 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 report² and are on average slightly higher than those calculated at the G4 level. The average O–O BDE value 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 value 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 BDEs are on average 2.8 kcal/mol higher. The close agreement within all three methods strongly suggests 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 that although 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 at <https://pubs.acs.org/doi/10.1021/acs.jpca.0c02859>.

Optimized Cartesian coordinates from CBS-APNO calculations (PDF)

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Notes

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