

Oxygen–oxygen bond dissociation enthalpies of di-*tert*-butyl peroxide and di-trifluoromethyl peroxide

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Abstract

The oxygen–oxygen bond dissociation enthalpies in di-*tert*-butyl peroxide ($\text{Me}_3\text{CO}-\text{OCMe}_3$) and di-trifluoromethyl peroxide ($\text{F}_3\text{CO}-\text{OCF}_3$) were determined using MP2, the hybrid functional B3LYP, and the CBS-QB3 method. Comparison of the performances of these methods, with particular emphasis on extrapolation procedures to infinite basis-set, showed that only CBS-QB3 is suitable for the accurate calculation of O–O bond dissociation enthalpies. The CBS-QB3 calculations led to $DH^\circ(\text{Me}_3\text{CO}-\text{OCMe}_3)=176.8 \text{ kJ mol}^{-1}$ and to $DH^\circ(\text{F}_3\text{CO}-\text{OCF}_3)=209.4 \text{ kJ mol}^{-1}$. These results were compared with the available experimental data and the prediction for di-*tert*-butyl peroxide supports literature values that were derived by photoacoustic calorimetry and through a combination of electron affinity and acidity data. The structural analysis of the compounds and their radicals revealed that the lower O–O bond dissociation enthalpy in di-*tert*-butyl peroxide is mainly related to the stabilization of the *tert*-butyl peroxy radical by hyperconjugation.

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1. Introduction

Free radicals play a crucial role in many chemical transformations. The knowledge of the energetics of these species and the processes underlying their formation, reactivity, and fate is very important. A thermodynamic parameter that conveys valuable information about the feasibility of those processes, and also about the nature of chemical bonding, is the gas-phase bond dissociation enthalpy (BDE). The accurate determination of BDEs is no longer restricted to experimental techniques. In recent years, the application of computational methods, based on quantum chemistry, afforded a wealth of BDE values whose accuracy is often comparable to data derived from experiment [1].

High-level computational methods have been used to derive key values which are not easily amenable to

experiment and also to discuss discrepancies in experimentally obtained BDEs [2,3]. In the present paper, we will address an example of the latter, namely the oxygen–oxygen bond dissociation enthalpy in di-*tert*-butyl peroxide.

Di-*tert*-butyl peroxide is often used as an initiator in radical chain reactions, due to the labile nature of the O–O bond [4]. There are two literature values for the oxygen–oxygen gas-phase BDE $DH^\circ(\text{Me}_3\text{CO}-\text{OCMe}_3)$, both relying on the determination of the activation energy for the O–O bond homolysis of that compound, viz. $159.0 \pm 2.1 \text{ kJ mol}^{-1}$ [5] and $162.8 \pm 2.1 \text{ kJ mol}^{-1}$ [6]. However, these ‘low’ values were questioned by a photoacoustic calorimetry (PAC) study, where $DH^\circ(\text{Me}_3\text{CO}-\text{OCMe}_3)=179.6 \pm 4.5 \text{ kJ mol}^{-1}$ was recommended, and also by a value derived from acidity and electron affinity data ($172.5 \pm 6.6 \text{ kJ mol}^{-1}$) [7,8].

Somehow related to the O–O BDE in di-*tert*-butyl peroxide, is the O–O BDE in di-trifluoromethyl peroxide, CF_3OOCF_3 . As pointed out by Mulder [6,9], the ratio of the rate constants for the bond homolysis reactions at a given temperature suggest that the activation energy for the fluoro compound is 37 kJ mol^{-1} higher than for di-*tert*-butyl peroxide. Therefore, the above PAC value implies that $DH^\circ(\text{F}_3\text{CO}-\text{OCF}_3)$ can be as high as ca. 215 kJ mol^{-1} ,

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i.e. close to the O–O BDE in hydrogen peroxide, $210.4 \pm 0.5 \text{ kJ mol}^{-1}$ [10].

Hoping to shed some light into this matter, we have applied several theoretical methods to estimate the gas-phase O–O bond dissociation enthalpies of di-*tert*-butyl peroxide and di-trifluoromethyl peroxide. Particular emphasis was placed on the extrapolation of the calculated bond dissociation enthalpies to infinite basis-set.

2. Computational procedures

In this work, the bond dissociation enthalpies were calculated from bond homolysis reactions (reaction 1) and isodesmic and isogyric reactions (reaction 2), which take advantage of error cancellation ($R = \text{Me}_3\text{C}$ or F_3C).



The procedure used to calculate the gas-phase bond dissociation enthalpies from these reactions can be summarized by the following steps: (1) the optimized geometries, at the theory levels described below, were determined for all the species involved; (2) a frequency calculation at the same theory level was performed for each compound to estimate the zero point energy (ZPE) and thermal corrections to 298 K (all the data presented in this study refers to this temperature), and also to confirm that the stationary points found were minimum energy structures; (3) the electronic energy, from the optimization calculation or from a single-point energy calculation at a higher theory level, and the thermal correction to the enthalpy were added to obtain the enthalpies of the reaction species; (4) reaction enthalpies, $\Delta_r H^\circ$, were then computed from these data. In the case of the bond homolysis reaction 1, the reaction enthalpy corresponds to the BDE. For the isodesmic and isogyric reaction 2, the reaction enthalpy is related to the BDE through Eq. (3), where the experimental value of $210.4 \pm 0.5 \text{ kJ mol}^{-1}$ was used for $DH^\circ(\text{HO} - \text{OH})$ [10].

$$DH^\circ(\text{RO} - \text{OR}) = \Delta_r H^\circ(2) + DH^\circ(\text{HO} - \text{OH}) \quad (3)$$

Different theoretical approaches were used, including density-functional theory (DFT) with the B3LYP hybrid functional [11,12], second-order Møller–Plesset perturbation theory (MP2) [13], and the complete basis set method CBS-QB3 [14–16]. For hydrogen peroxide, coupled cluster calculations with single and double excitations (CCSD) [17] and perturbative inclusion of triples (CCSD(T)) [18] were also carried out. One particularly relevant aspect concerning the theoretical prediction of BDEs is basis-set dependence. It seems reasonable to assume that the performance of a given theoretical approach should be assessed by using converged and reliable geometries and energy extrapolation to infinite basis-set [19]. For this purpose, the present calculations were carried

out with the hierarchical series of correlation-consistent polarized valence basis-sets of Dunning et al. [20–24], cc-pVXZ [with $X = \text{D}(2)$, $\text{T}(3)$ and $\text{Q}(4)$], and aug-cc-pVXZ [with $X = \text{T}(3)$ and $\text{Q}(4)$]. The importance of extrapolation procedures for estimating homolytic bond dissociation energies using DFT was recently investigated [25].

Geometry optimizations and frequency calculations were carried out at the B3LYP/cc-pVDZ and B3LYP/cc-pVTZ levels. It has been verified, for a series of open shell molecules, that B3LYP/cc-pVTZ geometries are quite reliable, and that the deviations from experimental information are similar, or even smaller, than those corresponding to CCSD/cc-pVTZ optimizations [26]. Since recent studies have shown that structures and harmonic vibrational frequencies are nearly converged at the triple ζ level [19], when ($X = 4,5$) only B3LYP/cc-pVTZ single-point energy calculations with the optimized geometries were performed.

Extrapolation of B3LYP energies to infinite basis set was carried out using the power-law expression [27]

$$E_X = E_\infty + A_3 X^{-3} + A_5 X^{-5} \quad (4)$$

Ab initio energies were extrapolated by using the dual level ($X - 1, X = (2,3)$) scheme of Truhlar [28]. All the calculations were performed using the Gaussian 03 package of programs [29].

The performance of the different theoretical approaches for estimating O–O bond dissociation enthalpies was initially assessed by carrying out calculations for hydrogen peroxide, for which reliable experimental data exists [10]. The predicted BDEs are gathered in Table 1.

The results in Table 1 show a clear dependence of the BDEs on the basis set. Although a good agreement with experiment is obtained with DFT calculations when $X = 2$, the computed $DH^\circ(\text{HO} - \text{OH})$ decreases with increasing basis set and the extrapolated value ($192.8 \text{ kJ mol}^{-1}$) is some 18 kJ mol^{-1} below experiment (Fig. 1). However, this behavior is not always observed. As shown in Fig. 1, the computed value of another bond dissociation enthalpy in the same molecule, $DH^\circ(\text{HOO} - \text{H})$ [25], increases with the basis set (the extrapolated B3LYP result is also below the experimental value, $367.4 \pm 2.1 \text{ kJ mol}^{-1}$ [30]). We also report calculations using the restricted open-shell method (RO)B3LYP for this test case. Although improvements are observed, (RO)B3LYP and B3LYP calculations exhibit a similar behaviour and significant deviations of extrapolated results from experiment are still noted.

MP2 BDEs increase with the basis set and the extrapolated results are $\sim 30 \text{ kJ mol}^{-1}$ above experiment. The values also indicate that MP2 results based on the frozen core (fc) approximation, where inner-shells are excluded from the correlation calculation, are similar to MP2(full). Our best estimates for $DH^\circ(\text{HO} - \text{OH})$ are based on CCSD(T)(full) and CBS-QB3 calculations. The extrapolated CCSD(T)(full) result ($217.2 \text{ kJ mol}^{-1}$) is 7 kJ mol^{-1} above experiment, whereas the CBS-QB3 prediction ($214.8 \text{ kJ mol}^{-1}$) is in

Table 1
Oxygen–oxygen gas-phase bond dissociation enthalpies of hydrogen peroxide

Method	$DH^\circ(\text{HO-OH})/(\text{kJ mol}^{-1})$				Extrapolated ^a
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	
B3LYP	208.2	200.2	196.8	194.5	192.8
(RO)B3LYP	215.8	210.0	207.1	204.9	203.4
MP2(fc)	197.3	221.9	227.4		239.2
MP2(fc) ^b	195.9	220.9	226.6		238.3
CCSD(fc) ^b	163.4	177.7	181.3		186.5
MP2(full) ^b	196.7	224.2	228.7		243.3
CCSD(full) ^b	164.0	180.8	183.0		191.1
CCSD(T)(full) ^b	178.9	202.7	206.3		217.2
CBS-QB3					214.8
Experimental ^c					210.4 ± 0.5

^a B3LYP extrapolation was based on the following scheme: $E_X = E_\infty + A_3X^{-3} + A_5X^{-5}$ [27]; ab initio energies were extrapolated by using the Truhlar (2,3) dual extrapolation procedure [28].

^b Single-point energy calculation. Geometry optimized at B3LYP/cc-pVTZ.

^c Ref. [10].

good agreement with experiment ($210.4 \pm 0.5 \text{ kJ mol}^{-1}$). Consequently, the results for $DH^\circ(\text{HO-OH})$ indicate that CBS-QB3 is a reliable procedure for estimating O–O BDEs. Moreover, they stress the importance of carrying out extrapolation to infinite basis set for assessing the reliability of BDEs predicted by DFT calculations.

3. Results and discussion

3.1. Bond dissociation enthalpies

The computed O–O BDEs of di-*tert*-butyl peroxide and di-trifluoromethyl peroxide, together with experimental information, are summarized in Table 2.

DFT calculations clearly underestimate $DH^\circ(\text{Me}_3\text{O-OMe}_3)$. In keeping with the tendency observed for hydrogen peroxide, deviations from experimental data increase when the basis set is improved. The disagreement between infinite basis set extrapolated DFT results and experiment is significant for both bond-homolysis (reaction 1) and isodesmic-isogyric processes (reaction 2). MP2 calculations overestimate $DH^\circ(\text{Me}_3\text{O-OMe}_3)$ and the extrapolated value ($198.7 \text{ kJ mol}^{-1}$) is at least 19 kJ mol^{-1} above experiment. The CBS-QB3 results based on reactions 1 and 2, 181.2 and $176.8 \text{ kJ mol}^{-1}$, respectively, are quite similar and in excellent agreement with the ‘high’ experimental value ($179.6 \pm 4.5 \text{ kJ mol}^{-1}$) mentioned in the Introduction. Moreover, since the

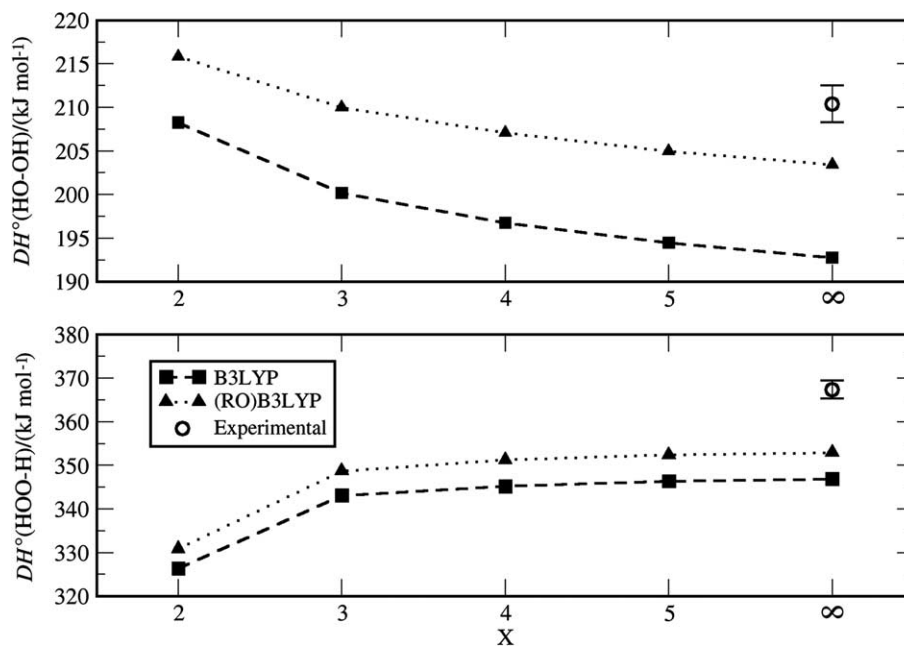


Fig. 1. Computed O–O and O–H bond dissociation enthalpies in H_2O_2 with different basis sets and extrapolation to infinite basis set. Results are based on B3LYP and (RO)B3LYP calculations.

Table 2

Oxygen–oxygen gas-phase bond dissociation enthalpies of di-*tert*-butyl peroxide ($\text{Me}_3\text{O}-\text{OCMe}_3$) and di-trifluoromethyl peroxide ($\text{F}_3\text{CO}-\text{OCF}_3$)

Method	$DH^\circ(\text{O}-\text{O}) / \text{kJ mol}^{-1}$			
	$\text{Me}_3\text{O}-\text{OCMe}_3$		$\text{F}_3\text{CO}-\text{OCF}_3$	
	(1) ^a	(2) ^b	(1) ^a	(2) ^b
B3LYP/cc-pVDZ	137.3	139.4	167.6	169.7
B3LYP/cc-pVTZ	120.8	131.0	162.7	172.9
B3LYP/cc-pVQZ//B3LYP/cc-pVTZ	115.4	129.1	160.3	173.9
Extrapolated ^c	111.0	127.7	158.1	174.7
MP2(fc)/cc-pVDZ	196.1	209.2	197.6	210.6
MP2(fc)/cc-pVTZ//MP2(fc)/cc-pVDZ	212.2	200.8	221.4	210.0
Extrapolated ^d	227.6	198.7	237.9	209.1
CBS-QB3	181.2	176.8	213.8	209.4
Experimental		159.0 ± 2.1^e		198.7 ± 2.1^f
		162.8 ± 2.1^f		
		179.6 ± 4.5^g		
		172.5 ± 6.6^h		

^a Derived from the enthalpy of the bond homolysis reaction 1.^b Derived from the enthalpy of the isodesmic and isogyric reaction 2.^c Extrapolated using the power law expression $E_X = E_\infty + A_3X^{-3} + A_5X^{-5}$ [27].^d Dual (2,3) extrapolation scheme of Truhlar [28].^e Ref. [5].^f Ref. [6].^g Ref. [7].^h Ref. [8].

photoacoustic calorimetry result relies also on some assumptions regarding solvation enthalpies, the agreement supports those assumptions.

In the case of di-trifluoromethyl peroxide the CBS-QB3 value for the O–O bond dissociation enthalpy, $209.4 \text{ kJ mol}^{-1}$, is some 10 kJ mol^{-1} higher than the one determined by Reints et al., $198.7 \pm 2.1 \text{ kJ mol}^{-1}$ [6]. However, the difference between the CBS-QB3 values for $DH^\circ(\text{F}_3\text{CO}-\text{OCF}_3)$ and $DH^\circ(\text{Me}_3\text{CO}-\text{OCMe}_3)$, 32.6 kJ mol^{-1} , is close to the difference between the respective O–O homolysis activation energies, in keeping with Mulder's prediction [9]. It is also worth noting that our values for $DH^\circ(\text{F}_3\text{CO}-\text{OCF}_3)$ ($209.4 \text{ kJ mol}^{-1}$) and $DH^\circ(\text{HO}-\text{OH})$ ($214.8 \text{ kJ mol}^{-1}$) are quite similar.

$DH^\circ(\text{F}_3\text{CO}-\text{OCF}_3)$ values predicted by B3LYP are also underestimated in comparison with the experimental value, which, according to the discussion above, is probably a low limit. Based on reactions 1 and 2, the extrapolated values are, respectively, 41 and 24 kJ mol^{-1} below the experimental value ($198.7 \pm 2.1 \text{ kJ mol}^{-1}$). MP2 results for $DH^\circ(\text{F}_3\text{CO}-\text{OCF}_3)$ are in much better agreement with experiment. For example, the extrapolated MP2 result based on reaction 2 ($209.1 \text{ kJ mol}^{-1}$) is only 10 kJ mol^{-1} above experiment and quite similar to the CBS-QB3 result ($209.4 \text{ kJ mol}^{-1}$).

In general, deviations from experimental values are smaller when the isodesmic and isogyric reaction 2 is used. However, as expected, the difference between predictions based on reactions 1 and 2 is significantly reduced when the most accurate theoretical method (CBS-QB3) is used.

3.2. Structure and bond dissociation enthalpy

The analysis of the structures of peroxides and radicals allows to understand why $DH^\circ(\text{F}_3\text{CO}-\text{OCF}_3)$ is significantly higher than $DH^\circ(\text{Me}_3\text{CO}-\text{OCMe}_3)$.

Hyperconjugation, resulting from the overlap between the half-occupied orbital in the oxygen atom and the neighbouring C–C bonds σ orbitals, stabilizes the *tert*-butoxyl radical, decreasing the $\text{Me}_3\text{CO}-\text{OCMe}_3$ bond

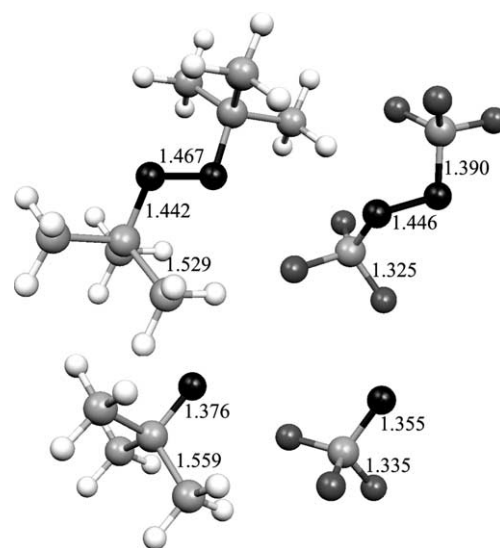


Fig. 2. B3LYP/cc-pVTZ optimized structures of di-*tert*-butyl peroxide (top-left), di-trifluoromethyl peroxide (top-right), *tert*-butoxyl radical (bottom-left), and trifluoromethoxyl radical (bottom-right). Bond distances in Å.

dissociation enthalpy. This hyperconjugation effect is reflected by the shortening of the C–O bond (from 1.442 to 1.376 Å) and the increase of the C–C bond (from 1.529 to 1.559 Å) upon radical formation (Fig. 2). For the fluorinated species the hyperconjugation effect is smaller, essentially due to the polarized nature of the C–F bond. This is in keeping with the fact that the O–O bond dissociation enthalpies of di-trifluoromethyl peroxide and hydrogen peroxide are similar, i.e. the presence of the CF₃ group does not have a significant influence on the O–O BDE.

4. Conclusions

We have investigated the performance of several theoretical methods for predicting O–O bond dissociation enthalpies. One relevant conclusion concerns the performance of DFT. Our results indicate that the B3LYP functional is unreliable for estimating O–O BDE for the present compounds. The dependence of the results on the basis set illustrates the interest of extrapolation schemes and the limitations of B3LYP and MP2 methods. Our best results are based on CBS-QB3 calculations. The CBS-QB3 result for the O–O BDEs in di-*tert*-butyl peroxide (176.8 kJ mol⁻¹) supports two independent experimental values, the first derived by photoacoustic calorimetry and the second through a combination of electron affinity and acidity data. A structural analysis of the compounds and their radicals revealed that the lower O–O bond dissociation enthalpy in di-*tert*-butyl peroxide is mainly due to a stabilization of the *tert*-butyl peroxy radical by hyperconjugation [31,32].

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