Quantum Chemical Studies on the Thermochemistry of Alkyl and Peroxyl Radicals

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Received: April 12, 1999; In Final Form: June 30, 1999

Homolytic bond dissociation enthalpies (BDEs) for C−H bonds in substituted methanes, C−O bonds in peroxyl radicals, and for O−H bonds in hydroperoxides have been calculated using density functional theory at the B3LYP/6-31G(d,p) and B3LYP/6-311+G(2df,2p) levels of theory, and using ab initio theory at the G2MS level. Ionization energies (IEs) of substituted methyl radicals and electron affinities (EAs) of peroxyl radicals have been calculated using the same methods. It is found that the B3LYP method is not generally reliable for prediction of absolute BDEs. However, this method works well for prediction of substituent effects on BDEs and for prediction of IEs and EAs. The deviations from experimental values are generally within 2−3 kcal/mol. The accuracy of the G2MS method is in general slightly better, and it is also capable of predicting accurate absolute BDEs. The stability of alkyl radicals is largely affected by substituents. This gives rise to large substituent effects on the C−H BDE in substituted methanes and the C−O BDE in peroxyl radicals. However, in the latter case the relative stabilization of the peroxyl radical is also of great importance for determining the BDE. In particular, electron-donating substituents have large stabilizing effects on peroxyl radicals. The substituent effects on the O−H bond in hydroperoxides are relatively small and largely determined by internal hydrogen bonding. There are relatively large substituent effects on the IE of alkyl radicals and the EA of peroxyl radicals. For some of the alkyl radicals with electron-withdrawing substituents, the ionization process leads to a considerable rearrangement of the nuclear configuration. In particular, three-membered ring systems are in several instances favored energetically over primary carbocations.

Introduction

Chemical reactions involving alkyl and peroxyl radicals play an integral part both in combustion and atmospheric degradation of organic material.[1,2] Recent studies have also indicated that alkyl and peroxyl radicals are formed during oxidation of proteins in biological systems.[3−6]

Most alkyl and peroxyl radicals are relatively unstable and short-lived species, which are difficult to characterize by experimental methods. Consequently, the thermochemistry of these compounds is largely unknown. In particular, there is only limited data on substituent effects on chemical reactions involving peroxyl radicals.

In recent years, quantum chemical calculations have become an increasingly used tool for determination of gas phase thermochemistry. In particular, the development of the G2[7] and CBS[8] approaches has furnished the theoretical chemists with efficient techniques for calculating thermochemical data with chemical accuracy. Unfortunately, these approaches involve the use of high-level ab initio methods, which limits the sizes of systems that can be studied. Density functional theory (DFT) methods have recently evolved as an important complement to advanced ab initio methods. They allow considerably larger systems to be studied with only a limited loss in accuracy.

In the present study, we have employed both DFT and high-level ab initio methods to analyze the substituent effects on a number of chemical reactions and processes involving alkyl and peroxyl radicals. The computed thermochemical data is critically evaluated against available experimental values and earlier computational results. The observed substituent effects on the reaction energetics are analyzed and discussed in relation to the effects the substituents have on the electronic structures of the participating molecular species.

Methods and Procedures

Optimized geometries and harmonic frequencies for all neutral molecules have been computed at the B3LYP/6-31G(d,p) level of theory. The B3LYP[9] functional is a modification of the three-parameter exchange-correlation functional of Becke.[10] In addition to the gradient-corrected exchange and correlation functionals of Becke[11] and Lee et al.,[12] respectively, it includes a part of the Hartree−Fock exchange energy. This functional has been shown to provide reliable geometries, frequencies, and bond energies.[13,14] Since it is well-known that diffuse functions are necessary for accurate description of anions,[15] the 6-31+G(d,p) basis set was used for the calculations on the peroxyl anions. To facilitate calculation of electron affinities, this basis set was also used for the peroxyl radicals.

DFT methods are generally not as basis set dependent as ab initio methods. However, Bauschlicher and Partridge have shown that the accuracy of thermochemical calculations can sometimes improve considerably by going from a medium sized to a large basis set.[14] For comparison, we have, therefore, performed single-point energy calculations for some of the molecules at the B3LYP/6-311+G(2df,2p) level using the B3LYP/6-31G(d,p) (or B3LYP/6-31+G(d,p) for the anions) geometries.

We have also performed energy calculations using a modified form (G2MS)[16] of the G2 theory.[7] In the regular G2 method the energy is calculated at the QCISD(T)6-311G(d,p) level using (U)MP2(full)/6-31G(d) geometries. A basis set correction to this

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10.1021/jp991191z CCC: $18.00

TABLE 1: Absolute and Relative C−H Bond Dissociation Enthalpies ($RH \rightarrow R^\bullet + H^\bullet$)[a]

	B3LYP/6-31G(d,p)		B3LYP/6-311+G(2df,2p)		G2MS		G2[c]		exp	
$R^\bullet$	BDE	ΔBDE[b]	BDE	ΔBDE[b]	BDE	ΔBDE[b]	BDE	ΔBDE[b]	BDE	ΔBDE[b]
$^\bullet CH_3$	105.2	0.0	102.8	0.0	105.7	0.0	105.8	0.0	104.9 ± 0.1[d]	0.0
$CF_3CH_2^\bullet$	105.1	−0.1							106.7 ± 1.1[e]	1.8
$CH_3CH_2^\bullet$	100.8	−4.4	98.4	−4.3	102.5	−3.2			101.1 ± 0.4[d]	−3.8
$O_2NCH_2^\bullet$	99.3	−5.9					102.9	−2.9		
$(CH_3)_2CH^\bullet$	96.9	−8.3							98.6 ± 0.4[d]	−6.3
$HOCH_2^\bullet$	95.0	−10.2	93.5	−9.3	97.8	−7.9	97.7	−8.1	96.1 ± 0.2[d]	−8.8
$CH_3COCH_2^\bullet$	94.4	−10.8							98.3 ± 1.8[e]	−6.6
$(CH_3)_3C^\bullet$	93.8	−11.4							96.5 ± 0.4[d]	−8.4
$NCCH_2^\bullet$	93.6	−11.6	92.4	−10.3	98.2	−7.5	97.9	−7.9	94.8 ± 2.1[d]	−10.1
$HCOCH_2^\bullet$	93.2	−12.0	91.9	−10.9	97.1	−8.6	97.0	−8.8	94.3 ± 2.2[d]	−10.6
$NH_2CH_2^\bullet$	92.0	−13.2	89.6	−13.2	94.7	−11.0	94.6	−11.2	93.3 ± 2[e]	−11.6
$HCOCH^\bullet CH_3$	86.9	−18.3	85.4	−17.3	92.2	−13.5				
$CH_2CHCH_2^\bullet$	85.7	−19.5	83.9	−18.9	89.7	−16.0			88.2 ± 2.1[f]	−16.7
$NH_2CH_2^\bullet COOH$	77.1	−28.1	74.4	28.4	82.9	−22.8	(82.5)[g]		≤78.6[h]	26.3
									(79.1)[i]	(25.8)
$HCOCH^\bullet NH_2$	71.1	−34.1	68.6	−34.2	77.1	−28.6			(73.6)[j]	(31.3)
$HCOC^\bullet(CH_3)NH_2$	67.2	−38.0								

[a] All values (in kcal/mol) correspond to 298 K and 1 atm. [b] $\Delta BDE = BDE(R{-}H) - BDE(CH_3{-}H)$. [c] Data from ref 27. [d] Data from ref 53. [e] Data from ref 54. [f] Data from ref 55. [g] G2(MP2) calculation from ref 42. [h] Data from ref 41. [i] Calculated from G2(MP2) and experimental enthalpies of formation using isodesmic reactions.[42] [j] Calculated from G2(MP2) and experimental enthalpies of formation using isodesmic reactions.[5]

energy is derived from MP4 and MP2 calculations with large basis sets. The energy after this correction corresponds effectively to the QCISD(T)/6-311+G(3df,2p) level. To eliminate further basis set deficiencies, an empirical high-level correction (HLC), which depend on the number of electron pairs, is added. The G2MS method utilizes B3LYP/6-31G(d) instead of MP2-(full)/6-31G(d) geometries. This leads to savings in computer time. In addition, the B3LYP method has been shown to give more accurate geometries of radicals than UMP2, mainly because B3LYP is less prone to be affected by spin contamination.[17] The high-level calculation in G2MS is done at the CCSD-(T)/6-31G(d) level and the basis set extrapolation at the MP2/6-311+G(2df,2p) level. Both these modifications lead to considerable savings in computer time over regular G2 theory. The CCSD(T) method is also considered slightly more reliable than QCISD(T).[17,18] The final energy expression in G2MS has the following form:

$$\Delta E(\mathrm{G2MS}) = \Delta E[\mathrm{MP2/6\text{-}311{+}G(2df,2p)}] - \Delta E[\mathrm{MP2/6\text{-}31G(d)}] + \Delta E[\mathrm{CCSD(T)/6\text{-}31G(d)}] + \mathrm{HLC}$$

The HLC is defined by $\mathrm{HLC} = An_\alpha + Bn_\beta$, where n_α and n_β are the number of α and β electrons, respectively. The B coefficient has the same value as in G2, 0.19 mH, while A is slightly bigger, 6.06 compared to 4.81 mH. Zero-point and vibrational temperature corrections are in G2MS calculated using unscaled B3LYP/6-31G(d) frequencies, while G2 employs scaled HF//6-31G(d) frequencies. In this work, we have followed the G2MS protocol, with the exception that we have used the B3LYP/6-31G(d,p) (B3LYP/6-31+G(d,p) for anions) level of theory rather than B3LYP/6-31G(d) for computing geometries and frequencies.

In addition to the G2MS and B3LYP calculations, we have also performed G2 and CBS-Q[8] calculations on a limited number of molecules for comparative purposes. The CBS-Q method involves geometry optimization at the (U)MP2/6-31G† level and a high-level calculation at the QCISD/6-31+G† level. The energy is extrapolated to the infinite basis limit based on the results of MP2 and MP4 calculations with different basis sets. No HLC correction is needed within the CBS approach.

The accuracy of the G2MS scheme has been shown to be similar to G2. For the 32 atomization energies of compounds containing first row atoms in the G2 test set, G2MS gives an average absolute deviation and an absolute maximum deviation of 1.1 and 4.5 kcal/mol, respectively.[16] The corresponding values for G2 are 1.0 and 2.7 kcal/mol.[16] The CBS-Q method is slightly more accurate than G2 with a maximum deviation of 2.2 kcal/mol.[8] The B3LYP/6-31G(d,p) level gives an average absolute deviation and an absolute maximum deviation of 3.4 and 8.3 kcal/mol, respectively.[19] This improves to 2.1 and 8.1 kcal/mol when the larger 6-311+G(2df,2pd) basis set is used.[19]

For the substituted methyl radicals investigated in this study, we computed spin densities at the B3LYP/6-31G(d,p) level. The spin density, $\rho^{\mathrm{S}}(\mathbf{r})$, is defined as

$$\rho^{\mathrm{S}}(\mathbf{r}) = \rho^{\alpha}(\mathbf{r}) - \rho^{\beta}(\mathbf{r}) \qquad (1)$$

where $\rho^{\alpha}(\mathbf{r})$ and $\rho^{\beta}(\mathbf{r})$ are the densities of the electrons with α spin and β spin, respectively. $\rho^{\mathrm{S}}(\mathbf{r})$ were computed on molecular surfaces defined in accordance to Bader et al.[20] by a constant contour of the total electron density of 0.002 au. By calculating the spin density at the molecular surface rather than at the positions of the nuclei, the spin density will emphasize the spin delocalization of the valence electrons, which is expected to be the most important for chemical reactivity. For example, the spin density at the nuclei does not reflect the spin delocalization of the π-orbitals, since they generally have nodes at the nuclei. We have previously shown for a set of substituted phenoxyl radicals that the surface maximum ($\rho^{\mathrm{S}}_{\mathrm{max}}$) of $\rho^{\mathrm{S}}(\mathbf{r})$ in the vicinity of the oxygen atom reflects the stabilization of the phenoxyl radical due to spin delocalization.[21] In this work, we have computed the $\rho^{\mathrm{S}}_{\mathrm{max}}$ associated with the central carbon in alkyl radicals to estimate the importance of spin delocalization on alkyl radical stability.

The Gaussian 94[22] suite of programs has been used for the ab initio and DFT calculations reported in this study. A locally developed code (hs95) was used for the spin density calculations.

Results and Discussion

C−H Bond Dissociation Enthalpies. An important property pertaining to the stability of alkyl radicals is the C−H bond dissociation enthalpy (BDE) of the parent alkane. Absolute and relative C−H BDEs calculated at different levels of theory for a set of substituted methanes are listed in Table 1 together with some experimental values. The B3LYP/6-31G(d,p), G2MS, and the G2 values of the BDE of CH_4 are all in good agreement with experiment. Surprisingly, the use of a larger basis set with the B3LYP method gives a significantly worse result than the small basis calculation; the B3LYP/6-311+G(2df,2p) level underestimates the BDE by 2.4 kcal/mol.

Turning to the relative BDEs (ΔBDE), we note that, except for CF_3CH_3, the B3LYP/6-31G(d,p) level consistently overestimates the substituent effects. However, for most systems the difference between theory and experiment is within 2.0 kcal/mol. The only exception is the dissociation of CH_2CHCH_3 to $CH_2CHCH_2^•$, where the B3LYP/6-31G(d,p) level overestimates the substituent effect by 2.6 kcal/mol. The B3LYP/6-311+G-(2df,2p) ΔBDEs show a very similar trend as the B3LYP/6-31G(d,p) values. Also at this level, the substituent effects are consistently overestimated. However, the deviations from the experimental values are generally smaller. For example, the error in the CH_2CHCH_3 value is reduced to 2.2 kcal/mol, which is close to the uncertainty in the experiment (2.1 kcal/mol). In contrast to the B3LYP calculations, the G2 and G2MS methods consistently underestimate the substituent effects on the BDE. The largest deviations are found for $NCCH_3$, with errors of 2.2 and 2.6 kcal/mol at the G2 and G2MS levels, respectively. It should be noted that the uncertainty in the experimental value is rather large, 2.1 kcal/mol. Overall, there is a very good agreement between the G2 and G2MS BDEs, both in relative and absolute values. This is encouraging and suggests that G2MS is a good alternative to the much more computationally expensive G2 procedure.

The calculation of ΔBDES for monosubstituted methanes has been the focus of several theoretical studies.[15,23−27] Most of these studies have been conducted at the HF level or HF with correction for electron correlation by Möller−Plesset perturbation theory (MP2 or MP4).[15,23−25] A comparison with the results of these studies indicates that for many substituents the ΔBDE is fairly well predicted already at the HF level. The most problematic cases are the ΔBDEs for the methanes with resonance electron-withdrawing substituents (e.g. CHO, CN, and $CHCH_2$), where there are large differences between the results from UHF and ROHF calculations. The UHF wave functions for the corresponding radicals are strongly spin contaminated (the $\langle S^2 \rangle$ values lie in the range 0.93−0.97 at the UHF/6-31G* level in contrast to the other monosubstituted methyl radicals which have $\langle S^2 \rangle$ values lower than 0.78 at the same level). This indicates that the "true" wave functions are largely multiconfigurational in nature and cannot be correctly described using either the UHF method or the ROHF method. It is also well-known that Möller−Plesset perturbation theory at lower orders cannot correct for nondynamical correlation.[28,29] On the other hand, the coupled cluster and quadratic configuration methods that are utilized in the G2MS and G2 procedures have been shown to describe multiconfigurational effects rather accurately and to reduce spin contamination.[28,29] Also the UB3LYP method has been shown to give good results for many radical systems that are multiconfigurational in nature and for which the UHF method give wave functions with high degrees of spin contamination.[21,30−32] Consistent with these results we find low degrees of spin contamination for all methyl radicals at the B3LYP level; $\langle S^2 \rangle$ is in all cases lower than 0.78.

Compounds containing both electron-donating and electron-withdrawing substituents, e.g. $HCOCH_2NH_2$ and NH_2CH_2COOH, show very large substituent effects. Both the B3LYP and the G2MS results indicate that these effects are nonadditive; i.e., the total substituent effect for a given substituent combination is larger than the sum of the effects of the substituents taken separately. This effect, which is referred to as the capto-dative effect, is commonly believed to be the result of an increased radical stabilization when a resonance electron-donating substituent is combined with a resonance electron-withdrawing substituents.[33−35] Experimental and theoretical studies have shown that the combination of a carbonyl substituent (e.g. HCO, RCO, or PhCO) and a strong donor (e.g. NH_2, $N(CH_3)_2$, or OH) leads to particularly stable alkyl radicals. Bordwell and coworkers argued that the stabilizing effect of the substituents is mainly additive in nature.[36,37] However, more recent experimental work indicates that the capto-dative effect in α-amino-α-carbonylmethyl radicals is as large as 10−12 kcal/mol.[38] Theoretical estimates of the capto-dative stabilization differ considerably depending upon the theoretical level. Leroy et al.[25] found a capto-dative stabilization of 7 kcal/mol in $HCOCH^•NH_2$ using unrestricted Hartree−Fock theory, while Davidson et al.[39] calculated the capto-dative stabilization in $HCOC^•(CH)_3NH_2$ to 12 kcal/mol[40] using multireference second-order Möller−Plesset perturbation theory (MRMP2 OPT2). In our calculations the nonadditive effect on the BDE of $HCOCH_2NH_2$ varies between 8.9 and 10.1 kcal/mol. The B3LYP/6-31G(d,p) and G2MS results are almost identical, 8.9 and 9.0 kcal/mol, respectively, while the B3LYP/6-311+G(2df,2p) result indicates the nonadditive effect to be slightly larger (10.1 kcal/mol). Our calculations show a nonadditive substituent effect also on the BDE of $HCOCH_2CH_3$. The CH_3 substituent is not generally considered as a π-donor, but it is likely to interact with the π-system through hyperconjugation, and this can explain the nonadditive stabilization. However, the nonadditive effect on the BDE of $HCOCH_2CH_3$ varies between 1.7 and 2.1 depending upon the computational level, and thus it is considerably smaller than for $HCOCH_2NH_2$.

There are rather large differences between the B3LYP and the G2MS ΔBDEs for the molecules with capto-dative stabilization. As for the monosubstituted methanes, the B3LYP/6-31G-(d,p) level gives larger substituent effects than G2MS. It is hard to judge the performance of the methods, since there are few experimental data for capto-dative stabilized radicals. However, the BDE of glycine (NH_2CH_2COOH) has experimentally been estimated to be ≤78.6 kcal/mol.[41] This is very close to the value of Yu et al.,[42] 79.1 kcal/mol, derived from isodesmic reactions using G2(MP2) energies and experimental heats of formation. The direct G2(MP2) BDE[42] is very similar to the G2MS result; the values are 82.5 and 82.9 kcal/mol, respectively. Thus, these calculations underestimate the substituent effect. In the case of G2MS, the underestimation is 3.0 kcal/mol compared to the isodesmic G2(MP2) result. The B3LYP/6-31G(d,p) and B3LYP/6-311+G(2df,2p) levels of theory overestimate the substituent effect by 2.3 and 2.6 kcal/mol, respectively. Thus, judging from the glycine results, the different methods behave in the same way for the disubstituted methanes as for the monosubstituted; i.e., the B3LYP levels overestimate and the G2MS procedure underestimates the substituent effects. Overall, the B3LYP/6-311+G(2df,2p) level gives slightly better ΔBDEs than B3LYP/6-31G(d,p). However, as already noted, the absolute BDEs are more accurate at the B3LYP/6-31G(d,p) level.

It is widely accepted that the substituent effects on the stabilization of methyl radicals are strongly linked to the spin delocalization of the unpaired electron.[35,43,44] Within this concept, the stabilizing effects of both resonance donors and acceptors as well as capto-dative stabilization can be rationalized using resonance terminology (see Figure 1). In Figure 2, we have plotted carbon spin density maxima on the molecular surface of the methyl radicals versus the BDEs for the

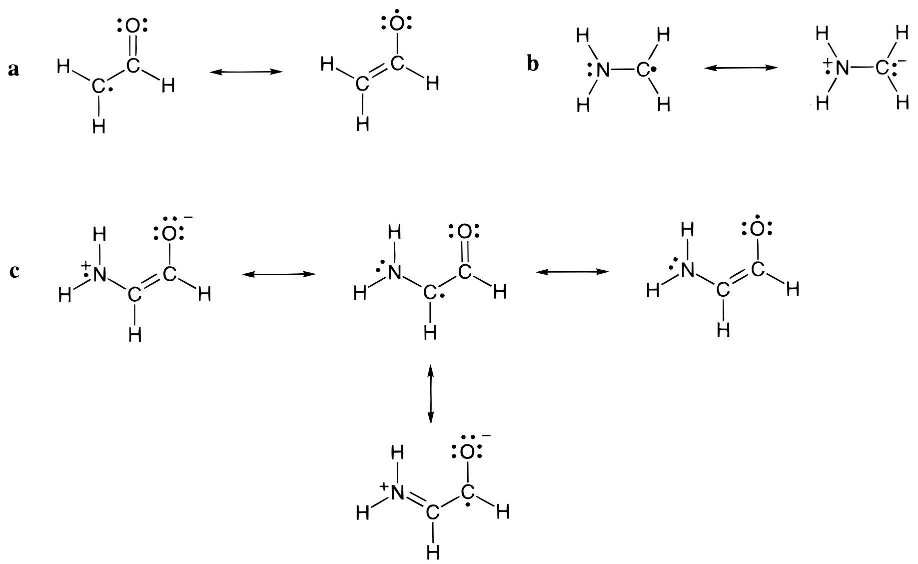

Figure 1. Important resonance structures for alkyl radicals: (a) radical stabilized by electron-withdrawing substituent; (b) radical stabilized by electron-donating substituent; (c) capto-dative stabilized radical.

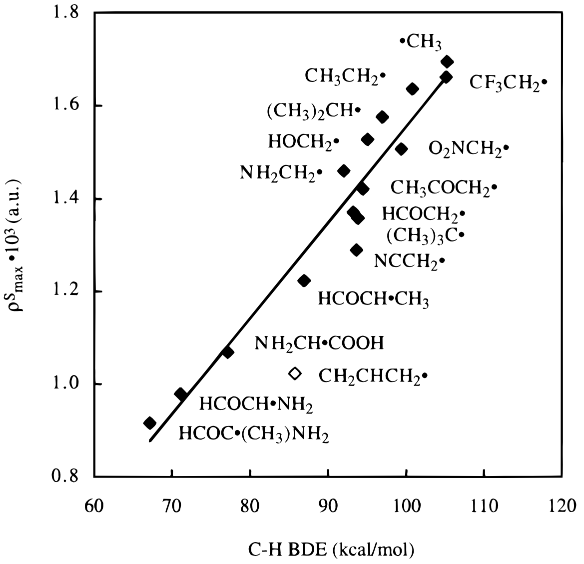

Figure 2. Plot of carbon ρ^S_{max} for methyl radicals versus C−H BDE for methanes. The solid line represents the linear correlation between ρ^S_{max} and BDE, when $CH_2CHCH_2^•$ (open diamond) is excluded. The correlation coefficient is 0.967.

substituted methanes. It is clear that there is a correlation between the spin delocalization and the radical stabilization, but the relationship is not perfect. In particular, $CH_2CHCH_2^•$ is a clear outlier. Not surprisingly, $CH_2CHCH_2^•$ possesses a large degree of spin delocalization. However, this spin delocalization is not accompanied by a corresponding decrease in the BDE of the parent molecule. We also note that the molecules with only electron-donating substituents are on a separate side of the correlation line from those with electron-withdrawing substituents. The electron-donating substituents are not as effective at delocalizing the unpaired electron, but are still capable of reducing the BDE significantly. It is also interesting to note that the introduction of a CH_3 group leads to a significant increase in the spin delocalization and that the CH_3-substituted molecules deviate no more from the general relationship than those containing NH_2 and OH. This is rather surprising considering that spin delocalization generally is considered to be mediated through π-orbitals. The most likely explanation is that the methyl groups interact with the π-system through hyperconjugation.

Alkyl Radical Ionization Energies. Another property of importance for the stability of alkyl radicals is the ionization energy (IE). In Table 2 are listed computed and experimental IEs for the same set of substituted methyl radicals as in Table 1. The table shows that all three levels of theory provide rather accurate absolute and relative IEs (i.e., ΔIEs). Looking first at the results for CH_3, we note that the B3LYP/6-31G(d,p) level is within 0.04 eV of the experimental value. As for the BDE of CH_4, B3LYP/6-311+G(2df,2p) performs significantly worse and overestimates the IE of CH_3 by 0.12 eV. The fact that this level underestimates the BDE and overestimates the IE by approximately the same amount indicates that the error mainly is the result of an overestimation of the stability of the $CH_3^•$ radical. The two B3LYP levels produce relative IEs of nearly equal quality. Relative large errors are found for the $CH_2CHCH_2^•$ radical. The error at the B3LYP/6-31G(d,p) level is 0.23 eV while B3LYP/6-311+G(2df,2p) performs slightly better with an error of 0.17 eV. The G2MS calculated IE of $CH_3^•$ is overestimated by 0.10 eV compared to experiment. This level of theory performs even better for the ΔIEs; all values are within 0.07 eV of experiment. In contrast to B3LYP, G2MS performs well also for the $CH_2CHCH_2^•$ radical.

It is shown in Table 2 that, except for CN, all substituents traditionally considered as electron withdrawing lower the IE when compared to the unsubstituted methyl radical. Since most of these substituents have a radical stabilizing effect (see the ΔBDEs in Table 1), this implies that they also have a stabilizing effect on the cation. As shown below, the ionization process for several radicals with electron-withdrawing groups is accompanied by considerable changes in the nuclear configuration, and these changes are likely to be largely responsible for the stabilization.

$F_2C^+—CH_2F$

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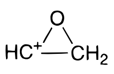

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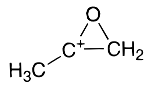

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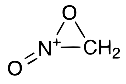

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Particularly interesting is the formation of three-membered rings (**2**−**4**) from the $HCOCH_2^+$, $CH_3COCH_2^+$, and $O_2NCH_2^+$

TABLE 2: Absolute and Relative Ionization Energies ($R^\bullet \rightarrow R^+ + e^-$)[a]

	B3LYP/6-31G(d,p)		B3LYP/6-311+G(2df,2p)		G2MS		exp	
$R^\bullet$	IE	ΔIE[b]	IE	ΔIE[b]	IE	ΔIE[b]	IE	ΔIE[b]
$NCCH_2^\bullet$	10.14	0.33	10.33	0.37	10.17	0.43	10.28 ± 0.01[c]	0.44
$^\bullet CH_3$	9.80	0.00	9.96	0.00	9.74	0.00	9.843 ± 0.002[d]	0.00
$O_2NCH_2^\bullet$	9.24	−0.56						
$HCOCH_2^\bullet$	9.14	−0.67	9.35	−0.62	9.01	−0.74		
$HCOCH^\bullet CH_3$	8.91	−0.89	9.10	−0.86	8.93	−0.81		
$CF_3CH_2^\bullet$	8.81	−1.00						
$CH_3COCH_2^\bullet$	8.23	−1.58						
$CH_3CH_2^\bullet$	8.09	−1.71	8.23	−1.74	8.05	−1.70	8.12 ± 0.01[d]	−1.72
$CH_2CHCH_2^\bullet$	7.91	−1.89	8.14	−1.83	8.04	−1.71	8.18 ± 0.07[e]	−1.66
$HOCH_2^\bullet$	7.43	−2.38	7.70	−2.27	7.43	−2.32	7.55 ± 0.01[d]	−2.29
$HCOCH^\bullet NH_2$	7.27	−2.54	7.59	−2.37	7.16	−2.58		
$(CH_3)_2CH^\bullet$	7.23	−2.57					7.37 ± 0.02[f]	−2.47
$NH_2CH^\bullet COOH$	6.91	−2.89						
$HCOC^\bullet(CH_3)NH_2$	6.87	−2.94						
$(CH_3)_3C^\bullet$	6.62	−3.19					6.70 ± 0.03[g]	−3.14
$NH_2CH_2^\bullet$	6.14	−3.66	6.41	−3.55	6.13	−3.62	6.29 ± 0.03[h]	−3.55

[a] All values (in eV) are calculated for 0 K. [b] ΔIE = IE(R) − IE(CH_3). [c] Data from ref 56. [d] Data from ref 53. [e] Data from ref 57. [f] Data from ref 58. [g] Data from ref 59. [h] Data from ref 60.

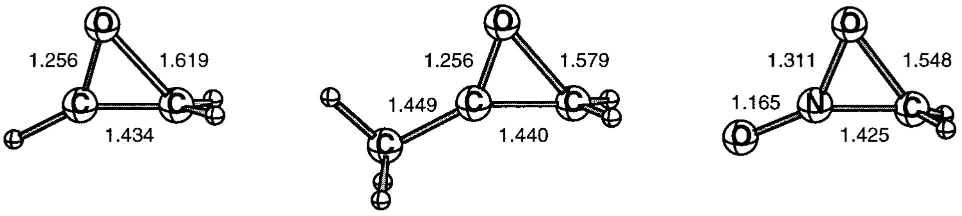

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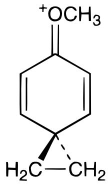
Figure 3. B3LYP/6-31G(d,p) optimized geometries of the carbocations that rearrange spontaneously to three-membered rings. Selected bond lengths are given in angstroms.

ions (see Figure 3). It may seem strange that a strained ring system is lower in energy than an open chain. However, it is well-known that primary carbocations in general are rather unstable and often rearrange spontaneously.[35,45] Rearrangements to three-membered rings have also been observed previously.[35,45] For example, the reaction of SbF5 with *p*-$CH_3OC_6H_4CH_2CH_2$-Cl in liquid SO_2 leads to such a bridged carbocation (**5**).[45]



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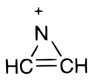
Also for $NCCH_2^+$ a cyclic structure (**6**) is lower in energy than the open chain structure (**7**).[46]



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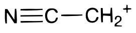

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However, both structures are minima on the potential energy surface.[46] This is in contrast to the $HCOCH_2^+$, $CH_3COCH_2^+$, and $O_2NCH_2^+$ ions for which our calculations indicate that only ring structures (**2**−**4**) are stable. It should be emphasized that the computed and experimental ionization energies for $NCCH_2$ reported in Table 2 correspond to the open chain $NCCH_2^+$ (**7**) as the ionization product.

Not surprisingly, the monosubstituted radicals with electron-donating substituents, e.g. CH_3, OH, and NH_2, have considerably lower IEs than those with electron-withdrawing substituents. Considering the radicals with multiple substituents, we notice that the addition of an electron-withdrawing substituent, e.g. CHO or COOH, to a radical containing NH_2 leads to an increase in the IE. However, this effect can mainly be attributed to the capto-dative stabilization of the radical; for example, the difference in BDE between NH_2CH_3 and $HCOCH_2NH_2$, which can be used as an estimate of the difference in the radical stabilization, is nearly equal to the difference in IE between $NH_2CH_2^\bullet$ and $HCOCHNH_2^\bullet$.

C−O Bond Dissociation Enthalpies in Peroxyl Radicals. A key reaction in many oxidative processes is the formation of a peroxyl radical by the addition of molecular oxygen to an alkyl radical.

$$R^\bullet + O_2 \rightarrow RO_2^\bullet \qquad (2)$$

In this work, we will discuss the energetics of this reaction in terms of the C−O BDE of the peroxyl radical, which corresponds to the negative Δ*H* of the reaction. There exists only a limited number of experimental determinations of C−O BDEs. In addition, Benson has criticized the mechanistic assumptions that have been the basis for the derivation of many of these values.[47] However, some of the values have recently been recalculated by Knyazev and Slagle after consideration of Benson's criticism.[48] In Table 3 we have listed calculated C−O BDEs and ΔBDEs, together with the latest experimental data. Focusing first at the BDE of CH_3OO, we note that the B3LYP/6-31G(d,p) level underestimate the BDE by 2.1 kcal/mol. Again, we find that B3LYP/6-31+G(2df,2p) performs slightly worse in the absolute calculation, and underestimates the BDE by 3.6

TABLE 3: Absolute and Relative C−O Bond Dissociation Enthalpies ($ROO^\bullet \rightarrow R^\bullet + O_2$)[a]

	B3LYP/6-31G(d,p)		B3LYP/6-311+G(2df,2p)		G2MS		high-level theory		exp	
$R^\bullet$	BDE	ΔBDE[b]	BDE	ΔBDE	BDE	ΔBDE	BDE	ΔBDE	BDE	ΔBDE
$HOCH_2^\bullet$	33.8	3.2	31.1	2.0	39.1	4.5	36.6^c	4.0	16.3 ± 0.3^e	−16.44
$(CH_3)_2CH^\bullet$	32.0	1.4							37.1 ± 2.3^f	4.4
$CH_3CH_2^\bullet$	31.6	1.0	30.1	1.1	37.4	2.8			35.5 ± 2.0^f	2.8
$NH_2CH_2^\bullet$	31.6	1.0	28.7	−0.4	36.9	2.3				
$(CH_3)_3C^\bullet$	31.3	0.7							36.5 ± 1.8^f	3.8
									30.2 ± 1.1^e	−2.5
$^\bullet CH_3$	30.6	0.0	29.1	0.0	34.6	0.0	35.4^d	0.0	32.7 ± 0.9^f	0.0
							32.6^c		32.2 ± 1.5^e	
$CF_3CH_2^\bullet$	27.2	−3.5								
$O_2NCH_2^\bullet$	24.1	−6.6								
$CH_3COCH_2^\bullet$	21.7	−8.9								
$CHOCH_2^\bullet$	19.4	−11.2	18.0	−11.1	26.6	−8.0				
$HCOCH^\bullet CH_3$	17.0	−13.6	15.1	−14.0	26.5	−8.1				
$CH_2CHCH_2^\bullet$	14.9	−15.7	13.4	−15.7	23.4	−11.2			18.2 ± 0.5^e	−14.5
$NCCH_2^\bullet$	14.1	−16.5	13.1	−16.0	22.4	−12.2				
$NH_2CH^\bullet COOH$	11.8	−18.8								
$HCOC^\bullet(CH_3)NH_2$	5.9	−24.7								
$HCOCH^\bullet NH_2$	5.6	−25.0	2.3	−26.8	14.1	−20.5				

[a] All values (in kcal/mol) are calculated for 298 K and 1 atm. [b] ΔBDE = BDE(ROO) − BDE(CH_3OO). [c] CBS-Q calculation. [d] G2 calculation. [e] Data from ref 47. [f] Data from ref 48.

kcal/mol. The G2MS theory, on the other hand, overestimates the BDE by 1.9 kcal/mol. For comparison, we also calculated the BDE using the G2 and CBS-Q methods. The G2 theory predicts a BDE that is 2.7 kcal/mol larger than the experimental value, while the CBS-Q result is in almost perfect agreement with experiment.

When it comes to the ΔBDEs, it is harder to judge the performance of the different methods due to the shortage of reliable experimental data. However, we note that the G2MS value for $CH_3CH_2OO^\bullet$ is in better agreement with experiment than the B3LYP values. For $CH_2CHCHOO^\bullet$, the opposite is true. This is rather surprising, considering that G2MS performed better than B3LYP for the two other reactions involving the $CH_2CHCH_2^\bullet$ radical, i.e., the C−H BDE for CH_2CHCH_3 and the IE for $CH_2CHCH_2^\bullet$. It is possible that the experimental BDE[47] is underestimated by around 3 kcal/mol. A considerably larger disagreement between experiment and theory exists for the $HOCH_2OO^\bullet$ radical. Benson has estimated the BDE to 18.2 kcal/mol using experimental data and to 18.6 kcal/mol using his group additivity scheme.[47] Our computed BDEs lie in the range of 33.8−39.1 kcal/mol. When the computed ΔBDE is added to the experimental BDE of $CH_3OO^\bullet$, the agreement between the different levels is better; the values are 35.9, 34.8, and 37.2 kcal/mol at the B3LYP/6-31G(d,p), B3LYP/6-311+G-(2df,2p), and G2MS levels, respectively. We also computed the BDE using the CBS-Q method and got a value of 36.6 kcal/mol before and 36.7 kcal/mol after correction with the experimental $CH_3OO^\bullet$ BDE. It seems unlikely that the theoretical approaches we have utilized could overestimate the BDE by close to 20 kcal/mol, in particular, since they perform so well for the C−H BDE of $HOCH_3$ and the IE of $HOCH_2^\bullet$. Thus, the conclusion must be that the experimental value is seriously in error. We suggest 36.5 ± 2 kcal/mol as a more reliable estimate of the C−O BDE of $HOCH_2OO^\bullet$.

It could have been anticipated that the substituent effects on the C−O BDE, in the same way as for the C−H BDE, should be dominated by the stabilization of the alkyl radical. This would imply the C−O and C−H ΔBDEs to be nearly identical. As seen in Figure 4, there is indeed a correlation between the C−O and C−H ΔBDEs, but there is by no means a perfect one to one relationship. In particular, compounds with electron-donating substituents deviate strongly from the unity relationship line. It is clear that the C−O ΔBDE reflects the stabilization of both the peroxyl and alkyl radical. To get an estimate of the peroxyl radical stabilization solely, we suggest to take the difference between the C−O ΔBDE and the C−H ΔBDE. This value, which we will refer to as ΔPRSE (relative peroxyl radical stabilization enthalpy), corresponds to the enthalpy of the reaction:

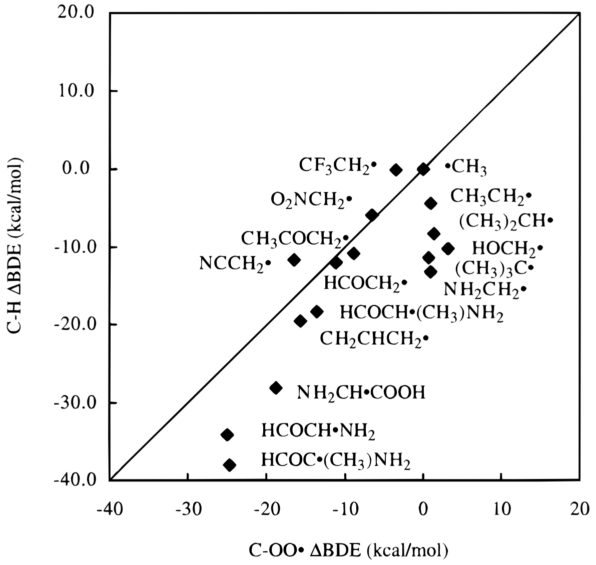


Figure 4. Plot of C−O ΔBDE for peroxyl radicals versus C−H BDE for the corresponding alkanes. The solid line corresponds to a 1:1 relationship between C−H ΔBDE and C−O ΔBDE.

$$ROO^\bullet + CH_4 \rightarrow RH + CH_3OO^\bullet \qquad (3)$$

In Table 4, we have listed ΔPRSE values calculated at the three levels of theory. First of all, we note that the agreement between the B3LYP and the G2MS results is much better than for the C−O ΔBDEs. In addition, the few experimental values available are in relatively good agreement with the computed data. The only exception is the agreement for $HOCH_2OO^\bullet$ which is, as expected, very bad due to the erroneous experimental C−O BDE. For the $(CH_3)_3COO^\bullet$ BDE there exist two relatively recent experimental values which differ by as much as 6.3 kcal/mol. It is hard to judge which of these values is the more correct

TABLE 4: Relative Peroxyl Radical Stabilization Enthalpies ($ROO^\bullet + CH_4 \rightarrow RH + CH_3OO^\bullet$)[a]

$ROO^\bullet$	B3LYP/ 6-31G(d,p) ΔPRSE	B3LYP/ 6-311+G(2df,2p) ΔPRSE	G2MS ΔPRSE	exp[b] ΔPRSE
$NCCH_2OO^\bullet$	−4.9	−5.7	−4.7	
$CF_3CH_2OO^\bullet$	−3.4			
$O_2NCH_2OO^\bullet$	−0.7			
$CH_3OO^\bullet$	0.0	0.0	0.0	0.0
$HCOCH_2OO^\bullet$	0.8	0.2	0.6	
$CH_3COCH_2OO^\bullet$	1.9			
$CH_2CHCH_2OO^\bullet$	3.8	3.2	4.8	2.2
$HCOCH(OO^\bullet)CH_3$	4.7	3.3	5.4	
$CH_3CH_2OO^\bullet$	5.4	5.4	6.0	6.6
$HCOCH(OO^\bullet)NH_2$	9.1	7.4	8.1	
$NH_2CH_2(OO^\bullet)COOH$	9.3			
$(CH_3)_2CHOO^\bullet$	9.7			10.7
$(CH_3)_3COO^\bullet$	12.1			12.2 5.9
$HCOC(OO^\bullet)(CH_3)NH_2$	13.3			
$HOCH_2OO^\bullet$	13.4	11.3	12.4	(−7.6)
$NH_2CH_2OO^\bullet$	14.2	12.8	13.3	

[a] All values (in kcal/mol) correspond to 298 K and 1 atm. [b] The experimental values have been calculated from the experimental BDEs in Tables 1 and 2. For the CH_3OO BDE, the first value listed in Table 2 has been used. Both values for the $(CH_3)_3COO$ BDE that are listed in Table 2 have been used, and the resulting ΔPRSE values are listed in the corresponding order.

solely based on a comparison with the B3LYP/6-31G(d,p) computed BDE (see Table 3). However, if the ΔPRSE values computed from these experimental BDEs are compared with the computed ΔPRSE value, the conclusion is obvious; The ΔPRSE value calculated from the more recent $(CH_3)_3COO^\bullet$ BDE (36.5 kcal/mol) of Knyazev and Slagle[48] is in almost perfect agreement with the computed ΔPRSE, while Benson's[47] value (30.2 kcal/mol) differs from the computed ΔPRSE by 6.2 kcal/mol. In addition, Knyazev and Slagle's value fits in with the general trend regarding the effect of methyl substitution on ΔPRSE, i.e., $CH_3OO^\bullet < CH_3CH_2OO^\bullet < (CH_3)_2CHOO^\bullet < (CH_3)_3COO$, whereas Bensons BDE results in the strange ordering $CH_3OO^\bullet < (CH_3)_3COO^\bullet < CH_3CH_2OO^\bullet < (CH_3)_2CHOO$. In conclusion, it seems clear that the calculation of relative peroxyl radical stabilization is much less sensitive to the level of theory than relative alkyl radical stabilization.

Interestingly, we find that, in general, electron-donating substituents have a stabilizing effect and electron-withdrawing substituents have a destabilizing effect on the peroxyl radical. This may not be so surprising considering the electronegative nature of the oxygen atom. It should be noted that the electron-donating substituents show comparatively larger substituent effects. The relative ordering, $CH_2CH < CH_3 < OH \approx NH_2$, essentially follows the common σ_p scale of substituent constants. The large stabilizing effects of the last two substituents is partly a consequence of favorable internal hydrogen bonding in the $ROO^\bullet$ radical. For the electron-withdrawing substituents the ordering according to the ΔPRSE values is $CN < CF_3 < NO_2 < CHO$. However, the weakly stabilizing effect of the CHO substituent can be attributed to a internal hydrogen bond between the CHO and $OO^\bullet$ groups. Internal hydrogen bonding also makes it difficult to interpret the substituent effects in the peroxyl radicals with multiple substituents. However, the results from additional calculations on non-hydrogen-bonded conformations on some of the molecules in Table 4 indicate that the substituent effects are nearly additive if the effects of internal hydrogen bonding are removed.

O−H Bond Dissociation Enthalpies in Hydroperoxides. Another property which is of key importance for understanding the reactive behavior of peroxyl radicals is the O−H BDE of the corresponding hydroperoxides. Unfortunately, the availability of reliable experimental hydroperoxide O−H BDEs is very limited. The O−H BDE of H_2O_2 has been estimated to 88.2 ± 0.6 kcal/mol, and this is probably the most reliable value available.[47] In Table 5 we have listed computed BDEs for H_2O_2 and some alkyl hydroperoxides. We first note that the B3LYP/6-31+G(d,p) level underestimates the BDE of H_2O_2 by as much as 7.5 kcal/mol. The B3LYP/6-311+(2df,2p) level performs slightly better but the error remains as high as 5.5 kcal/mol. In contrast, the G2MS level is in good agreement with experiment, overestimating the BDE by no more than 0.7 kcal/mol. The G2 and CBS-Q values are both very close to experiment, 87.8 and 88.0 kcal/mol, respectively. To our knowledge, there exists no highly accurate experimental determination of the O−H BDE of CH_3OOH. Benson has, based on the O−H BDE of H_2O_2, estimated that all alkyl hydroperoxides have O−H BDEs of 88.6 ± 0.6 kcal/mol.[47] However, all our calculations indicate that the BDE of CH_3OOH is lower than that of H_2O_2. The difference is 1.0, 1.9, 1.7, 1.6, and 2.4 kcal/mol at the B3LYP/6-31+G-(d,p), B3LYP/6-311+(2df,2p), G2MS, G2, and CBS-Q levels of theory, respectively. On the basis of these results, we estimate the O−H BDE of CH_3OOH to 86.2 ± 1.5 kcal/mol. This is in good agreement with a recent estimate of the BDE (87 ± 1 kcal/mol), which is based on experimental enthalpies of formation.[49]

Our computational data on the O−H BDEs of the substituted hydroperoxides shows the substituent effects to be smaller than for the previously discussed reactions. The agreement between the different levels of theory is quite satisfactory. In no case does the ΔBDE differ by more than 2.2 kcal/mol between the different levels. For the monosubstituted hydroperoxides, the general trend is that electron-donating substituents decrease the BDE, while electron-accepting substituents have the opposite effect. The comparatively larger effects of the accepting substituents are mostly an effect of internal hydrogen bond stabilization of the hydroperoxide. In essentially all hydroperoxides with electron-accepting substituents, it is possible to form an internal hydrogen bond between the OOH group and the substituent. Except for $HCOCH_2OO^\bullet$, which has a weak hydrogen bond between the $OO^\bullet$ group and CHO, internal hydrogen bonds are not formed in the peroxyl radicals that have only electron-accepting substituents. The electron-donating substituents, OH and NH_2, form hydrogen bonds with both the $OO^\bullet$ and OOH groups and thus they stabilize both the hydroperoxide and the peroxyl radical. However, calculations on nonhydrogen bond conformations indicate that for both substituents the hydrogen bond stabilization of the hydroperoxide is bigger. For the CH_3 group, we do not have the problem of separating hydrogen bond effects from other substituent effects, and it is clear from Table 5 that the substituent slightly weakens the O−H bond. This observation is also supported by the recent experimental determination of the $(CH_3)_3COOH$ BDE (85 ± 2 kcal/mol),[49] which not only shows that the BDE of this molecule is lower than that of HOOH, but also that it most probably is lower than the BDE of CH_3OOH.

Electron Affinities of Peroxyl Radicals. The electron affinity (EA) is also of importance for understanding the reactivity of peroxyl radicals. In Table 6 we have listed computed EAs for the peroxyl radicals investigated in this study. Very few reliable experimental data on EAs of peroxyl radicals exist. One exception is the $HOO^\bullet$ radical whose EA has been determined to 1.08 eV in two independent experiments.[50,51] The B3LYP/6-31+G(d,p) and B3LYP/6-311+G(2df,2p) levels are both found to slightly underestimate the EA, by 0.05 and 0.09 eV,

TABLE 5: Absolute and Relative O−H Bond Dissociation Enthalpies ($ROOH \rightarrow ROO^\bullet + H^\bullet$)[a]

	B3LYP/6-31G(d,p)		B3LYP/6-311+G(2df,2p)		G2MS		high-level theory		exp	
$ROO^\bullet$	BDE	ΔBDE	BDE	ΔBDE	BDE	ΔBDE	BDE	ΔBDE	BDE	ΔBDE
$HOO^\bullet$	80.7	1.0	82.7	1.9	88.8	1.0	87.8[c]	1.6	88.2 ± 0.2[e]	1
							88.0[d]	2.4		
$O_2NCH_2OO^\bullet$	88.8	9.1								
$NCCH_2OO^\bullet$	83.9	4.2	84.6	3.8	91.3	4.1				
$CF_3CH_2OO^\bullet$	83.9	4.2								
$CHOCH(OO^\bullet)NH_2$	83.2	3.5	83.8	3.0	92.4	5.2				
$CH_3COCH_2OO^\bullet$	83.0	3.3								
$HCOCH_2OO$	82.9	3.2	83.1	2.3	90.1	2.9				
$HCOC(OO^\bullet)(CH_3)NH_2$	82.2	2.5								
$CHOCH(OO^\bullet)CH_3$	81.9	2.2	82.8	2.0	89.3	2.1				
$NH_2CH(OO^\bullet)COOH$	81.8	2.1								
$HOCH_2OO^\bullet$	81.1	1.4	82.8	2.0	89.2	2.0				
$CH_3OO^\bullet$	79.7	0.0	80.8	0.0	87.2	0.0	86.2[c]	0.0	87 ± 1[f]	0
							85.6[c]	0.0	(88.6 ± 0.6)[g]	
$CH_3CH_2OO^\bullet$	79.3	−0.4	80.4	−0.4	86.9	−0.3			85 ± 2[f]	−2
$CH_2CHCH_2OO^\bullet$	79.0	−0.7	80.6	−0.2	86.2	−1.0				
$(CH_3)_2CHOO^\bullet$	78.6	−1.1								
$NH_2CH_2OO^\bullet$	78.0	−1.7	79.3	−1.5	86.2	−1.0				
$(CH_3)_3COO^\bullet$	78.0	−1.7							85 ± 2[f]	−2

[a] All values (in kcal/mol) are calculated for 298 K and 1 atm. [b] ΔBDE = BDE(ROOH) − BDE(CH_3OOH). [c] G2 calculation. [d] CBS-Q calculation. [e] Data from ref 47. [f] Data from ref 49. [g] Estimated value from ref 47.

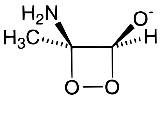
TABLE 6: Absolute and Relative Electron Affinities ($ROO^\bullet + e^- \rightarrow ROO^-$)[a]

	B3LYP/6-31+G(d,p)		B3LYP/6-311+G(2df,2p)		G2MS		high-level theory		exp
$ROO^\bullet$	EA	ΔEA[b]	EA	ΔEA	EA	ΔEA	EA	ΔEA	EA
$HOO^\bullet$	1.03	−0.06	0.99	−0.09	1.08	−0.11	1.11[c]	−0.11	1.08 ± 0.02[e]
							1.10[d]	−0.08	
$(CH_3)_3COO^\bullet$	1.08	−0.01							1.20 ± 0.01[f]
$CH_3OO^\bullet$	1.09	0.00	1.08	0.00	1.19	0.00	1.22[c]	0.00	
							1.18[d]	0.00	
$CH_3CH_2OO^\bullet$	1.09	0.00	1.08	0.00	1.21	0.02			
$(CH_3)_2CHOO^\bullet$	1.10	0.01							
$NH_2CH_2OO^\bullet$	1.14	0.05	1.13	0.05	1.30	0.11			
$CH_2CHCH_2OO^\bullet$	1.30	0.21	1.28	0.20	1.36	0.18			
$NH_2CH(OO^\bullet)COOH$	1.71	0.62							
$CH_3COCH_2OO^\bullet$	1.77	0.68							
$HOCH_2OO^\bullet$	1.77	0.68	1.72	0.64	1.87	0.68			
$HCOCH(OO^\bullet)CH_3$	1.80	0.71	1.78	0.70	1.92	0.74			
$HCOCH_2OO^\bullet$	1.84	0.75	1.82	0.74	1.90	0.72			
$CF_3CH_2OO^\bullet$	1.86	0.77							
$HCOC(OO^\bullet)(CH_3)NH_2$	1.92[g]	0.83							
	(1.70)	(0.61)							
$HCOCH(OO^\bullet)NH_2$	1.93	0.84	1.92	0.84	2.16	0.97			
$NCCH_2OO^\bullet$	2.00	0.91	1.99	0.92	2.09	0.90			
$O_2NCH_2OO^\bullet$	2.19	1.11							

[a] All values (in eV) are calculated for 0 K. [b] ΔEA = EA($ROO^\bullet$) − EA($CH_3OO^\bullet$). [c] G2 calculation. [d] CBS-Q caculation. [e] Data from ref 51. [f] Data from ref 49. [g] This is the energy for forming a four-membered ring structure, a 1,2-dioxetane, upon addition of an electron. The value in parentheses corresponds to the formation of a regular open-chain anion. See the Results and Discussion section for more details.

respectively. The G2MS result is in perfect agreement with experiment. Also the CBS-Q and G2 methods give results that are very close to the experimental value. All investigated levels predict the EA of $CH_3OO^\bullet$ to be slightly higher than the EA of $HOO^\bullet$. The difference ranges from 0.06 eV at the B3LYP/6-31+G(d,p) level to 0.11 eV at the G2MS and G2 levels. On the basis of these results, we estimate the EA of $CH_3OO^\bullet$ to 1.18 ± 0.05 eV. The EA of $(CH_3)_3COO^\bullet$ has very recently been determined to 1.20 ± 0.01 eV.[49] The B3LYP/6-31+G(d,p) level underestimates the EA by as much as 0.12 eV, but correctly predicts it to be higher than the EA of $HOO^\bullet$.

Turning to the substituent effects on the EA, we note that there is a very good agreement in the predictions from the different levels of theory. The largest discrepancy is found for $HCOCH(OO)NH_2$ where the G2MS result is 0.13 eV higher than the B3LYP results. In general, it is found that electron-donating substituents have rather small effects on the EA. The only exception is OH, which increases the EA by 0.68 eV. However, this can be attributed mainly to a very favorable internal hydrogen bond in $HOCH_2OO^-$. The effects of electron-accepting substituents are much bigger, and in all cases they increase the EA.



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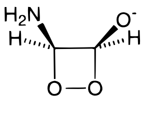

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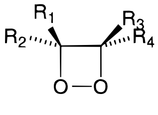
Interestingly, we find that $HCOC(OO^-)CH_3NH_2$ easily rearranges to a four membered ring structure (**8**), a 1,2-dioxetane, through an intramolecular nucleophilic attack of the O_2^- group on the carbonyl carbon. This structure is 5.1 kcal/mol lower in energy than the lowest nonring conformation. The barrier for

TABLE 7: Absolute and Relative Enthalpies of Deprotonation (ROOH → ROO$^-$ + H$^+$)[a]

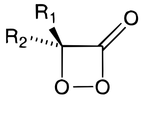
	B3LYP/6-31G+(d,p)		B3LYP/6-311+G(2df,2p)		G2MS	
ROOH	DPE	ΔDPE	DPE	ΔDPE	DPE	ΔDPE
CH_3OOH	368.5	0.0	371.0	−0.0	373.5	0.0
CH_3CH_2OOH	368.0	−0.5	370.5	−0.5	372.5	−1.0
$(CH_3)_2CHOOH$	367.3	−1.2				
$(CH_3)_3COOH$	367.1	−1.4				
NH_2CH_2OOH	365.7	−2.8	368.3	−2.7	370.9	−2.6
CH_2CHCH_2OOH	362.4	−6.1	366.0	−5.0	367.9	−5.6
$NH_2CH(OOH)COOH$	356.2	−12.3				
	(327.4)[c]	(−41.1)				
CH_3COCH_2OOH	355.9	−12.6				
CF_3CH_2OOH	354.9	−13.6				
$HCOCH(OOH)CH_3$	354.3	−14.2	356.7	−14.3	358.6	−14.9
$HCOCH_2OOH$	354.3	−14.2	356.1	−14.9	358.8	−14.7
$HOCH_2OOH$	354.1	−14.4	358.0	−13.0	359.6	−13.9
$HCOCH(OOH)NH_2$	352.4	−16.1	354.4	−16.6	356.2	−17.3
O_2NCH_2OOH	352.4	−16.1				
$NCCH_2OOH$	351.7	−16.8	354.8	−16.2	356.9	−16.6
$HCOC(OOH)(CH_3)NH_2$	351.4[d]	−17.1				
	(356.6)	(−11.9)				

[a] All values (in kcal/mol) are calculated for 298 K and 1 atm. The Δ*H* for this reaction has been computed by combining Δ*H* values for the reactions ROO$^\bullet$ + e$^-$ → ROO$^-$, ROOH → ROO$^\bullet$ + H$^\bullet$, and H$^\bullet$ → H$^+$ + e$^-$. The geometries and frequencies for the molecular species in the first and second reaction have been computed at the B3LYP/6-31+G(d,p) and B3LYP/6-31G(d,p) levels, respectively. [b] ΔDPE = DPE(XOOH) − DPE(CH_3OOH). [c] This value refers to the removal of the proton on the COOH group. [d] This is the enthalpy for forming a four-membered ring structure, a 1,2-dioxetane, upon deprotonation. The value in parentheses corresponds to the formation of a regular open-chain anion. See the Results and Discussion section for more details.

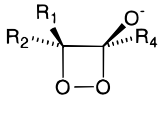
forming the ring structure seems to be very low, since several geometry optimization attempts, starting from different low-energy nonring structures, resulted in the ring structure. In order to verify that the ring structure is not a artifact of the B3LYP method, we also performed the optimizations at the MP2/6-31+G(d,p) level. This resulted in a structure very similar to that obtained at the B3LYP/6-31+G(d,p) level. A similar ring structure (**9**) was also found to be stable for $HCOCH(OO^-)NH_2$. However, this structure is 0.9 kcal/mol higher in energy than the lowest nonring conformation. It should be noted that this type of ring structures is well-known in peroxide chemistry, and that hundreds of 1,2-dioxetane (**10**) and 1,2-dioxetanone (**11**) derivatives have been isolated and characterized.[52] In addition, anionic dioxetanes of the same type (**12**) as those we have found to be formed by rearrangement of $HCOC(OO^-)CH_3NH_2$ and $HCOCH(OO^-)NH_2$ have been postulated as intermediates in base-catalyzed auto-oxidation of aromatic ketones and some pyruvic acids.[52]



10



11



12

Not surprisingly, the conversion of $NH_2CH(OO^-)COOH$ to $NH_2CH(OOH)COO^-$ is a highly exothermic process; the enthalpy change is −28.4 kcal/mol. However, this process is far from barrierless, since it requires the internal hydrogen bond (OH···OC) in the COOH group to be broken before the proton transfer can occur.

Deprotonation Enthalpies of Peroxides. Finally, in Table 7 we have listed the computed deprotonation enthalpies (DPE) for the hydroperoxides investigated in this study. The chemical species taking part in the deprotonation process have already been discussed in relation to the O−H BDEs of the hydroperoxides and the EAs of the peroxyl radicals. Thus, there is no reason for us to analyze the results of Table 6 in detail. However, a few general remarks can be made. First of all, we note that there are considerable differences in the absolute DPEs calculated at different levels. These differences are a result of the inability of the B3LYP method in describing O−H bond strengths (see Table 4). Since we found the G2MS level to predict both the O−H BDE of HOOH and EA of HOO$^\bullet$ in good agreement with experiment, we expect the G2MS result to be the most reliable. The agreement in relative DPEs (ΔDPE) is very good between the different levels. In no case is the difference between two levels larger than 1.1 kcal/mol. The general trend in the ΔDPEs is that all substituents lower the DPE. However, the effects of electron-withdrawing substituents are clearly much larger than the effects of electron-donating substituents. From comparing Table 5 and Table 6, it is clear that the substituent effect on the DPE is dominated by the stabilization of the peroxide anion.

Summary and Conclusions

Performance of Computational Methods. Our results show that the B3LYP method is not generally reliable for predicting absolute bond dissociation enthalpies (BDEs). In particular, we have found the B3LYP/6-31G(d,p) method to consistently underestimate O−H BDEs of hydroperoxides by around 8 kcal/mol. The use of the considerably larger 6-311+G(2df,2p) basis set improves the results slightly. However, this basis set performs worse than 6-31G(d,p) for C−H BDEs in substituted methanes and for C−O BDEs in peroxyl radicals. The B3LYP method has been found to be generally reliable for predicting substituent effects on BDEs, i.e., ΔBDEs. Only in a few cases have we found deviations from experiment that are larger than 2 kcal/mol. Again, there are no clear indications that the 6-311+G(2df,2p) basis set works significantly better than 6-31G(d,p). The B3LYP method has also been found to work well for prediction of ionization energies (IEs) and electron affinities (EAs). Absolute IEs and EAs are generally accurate to within 0.2 eV and relative values (ΔIEs and ΔEAs) to within 0.1 eV. The results are not improved by the use of the 6-311+G(2df,2p) basis set.

The G2MS method has been found to work consistently well for predicting the thermochemistry of alkyl and peroxyl radicals.

Absolute bond dissociation enthalpies are generally accurate to within 3 kcal/mol, and the prediction of substituent effects on BDEs, i.e., ΔBDEs, is even more accurate. The G2MS methods has also been found reliable for prediction of IEs and EAs with an accuracy equal to that for BDE prediction. The only cases where we have found the G2MS to have problems involves the thermochemistry of capto-dative stabilized alkyl radicals. Our results show that G2MS consistently underestimates the stability of these radicals, which leads to overestimated C−H BDEs of alkanes and C−O BDEs of peroxyl radicals. The B3LYP method has the opposite problem and overestimates the stability of capto-dative stabilized alkyl radicals. However, this problem is less severe. The general conclusion is that the B3LYP/6-31G(d,p) (6-31+G(d,p) for anions) level is an excellent choice when it comes to both accuracy and computer efficiency for prediction of substituent effects on the thermochemistry of alkyl and peroxyl radicals. However, for prediction of absolute enthalpies and energies, it is necessary to calibrate the calculations against reliable experimental data or high-level ab initio calculations, such as G2MS.

Observations Regarding the Thermochemical Data. Our calculations show that there are very large substituent effects on the C−H BDEs in substituted methanes. In particular, methanes that contain both a resonance-accepting substituent and a resonance-donating substituent have very low BDEs. This is due to the capto-dative stabilization of the alkyl radical formed in the bond dissociation. The capto-dative stabilization is distinctly nonadditive; i.e., the effect of the two substituents together is larger than the sum of the effects of the substituents taken separately. Surprisingly, we found a nonadditive capto-dative stabilization also in molecules in which a CH_3 substituent is combined with a resonance electron acceptor. Spin density calculations show that there is a clear correlation between the degree of spin delocalization in the alkyl radicals and their relative stabilization. However, the linear relationship between the radical spin density and the BDE is not perfect, which indicates that also other effects than spin delocalization are important for determining the BDE.

There are very large substituent effects on the IEs of the alkyl radicals. Radicals with electron-donating substituents have IEs that are up to 3.6 eV lower than the IE of CH_3. With the exception of $NCCH_2^•$, all the investigated alkyl radicals with electron-accepting substituents also have lower IEs than CH_3. However, it should be noted that for the monosubstituted radicals the ionization process is generally accompanied by a substantial reorganization of the nuclear configuration. In particular, several of the primary cations formed by ionization rearrange without barriers to three-membered rings.

The substituent effects on the C−O BDE in peroxyl radicals are of similar magnitude to the substituent effects on the C−H BDE in substituted methanes. Analogous to the methanes, the peroxyl radicals that form capto-dative stabilized alkyl radicals upon bond breakage have the lowest BDEs. However, our calculations show that the substituent effects on the C−O BDE are not only determined by the relative stabilization of the alkyl radical but that the stabilization of the peroxyl radical also is of importance. Electron-donating substituents stabilize the peroxyl radical rather strongly. For example, our calculations show that the stabilizing effect of the NH_2 group is around 13 kcal/mol. Electron-withdrawing substituents generally have an opposite but smaller effect on peroxyl radical stability than donating substituents.

The O−H BDE in hydroperoxides varies to lesser extent with the substituents than the C−O BDE of peroxyl radicals. The largest substituent effects are found for electron-withdrawing substituents, which strengthen the O−H bond. Donating substituents have the opposite effect. The ability of the substituents to form intramolecular hydrogen bonds with the $OO^•$ and OOH groups is also of vital importance for the O−H bond strength.

Electron-donating substituents have rather small effects on the EA of peroxyl radicals. The ability of the substituent to form an internal hydrogen bond with the OO^- group is of greater importance for the EA than its donating ability. On the other hand, electron-withdrawing substituents stabilize the peroxide anion strongly, which give rise to EAs that are significantly lowered.

Acknowledgment. We thank the Swedish Natural Science Research Council (NFR), and the Faculty of Chemistry and Chemical Engineering at the Royal Institute of Technology for financial support. This work was supported with computing resources by the Swedish Council for Planning and Coordination of Research (FRN) and Paralelldatorcentrum (PDC), Royal Institute of Technology.

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