

## Carbon–hydrogen bond dissociation enthalpies in ethers: a theoretical study

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### Abstract

Density functional theory calculations based on different representations of the exchange-correlation functional (BLYP, B3LYP, B3PW91, mPW1PW91, B1LYP, BHandHLYP, BHandH, and B3P86) were carried out to predict C–H bond dissociation enthalpies in selected ethers (dimethyl ether, tetrahydrofuran (thf), and 1,4-dioxane), and some related molecules. Comparison with available experimental information shows that bond dissociation enthalpies are accurately predicted by several functionals when isodesmic and isogyric reactions are considered. However, for bond homolysis reactions only the hybrid functional B3P86 has an acceptable performance, slightly underestimating bond dissociation enthalpies. DFT calculations were further compared with the multilevel CBS-Q method. The analysis of structural properties of the radical species suggests that hyperconjugation and ring strain are the main features to consider for understanding their thermodynamic stabilization. These effects are also useful to explain some trends of bond dissociation enthalpies that are observed for the compounds involved in the present study. The C–H bond dissociation enthalpies of thf (leading to  $\beta$ -furyl) and 1,4-dioxane, for which no experimental information is available, are 410 and 381 kJ mol<sup>-1</sup>, respectively, at the CBS-Q level.  
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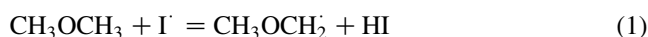
**Keywords:** Bond dissociation enthalpies; Ethers; Carbon–hydrogen bond dissociation enthalpies

### 1. Introduction

Gas-phase bond dissociation enthalpies,  $DH^0$  (R–H), are available for a large number of organic compounds [1–4]. This experimental database has played a crucial role in our understanding of the nature of chemical bonds and has fostered the development of methods to predict new values [5–7]. Not surprisingly, however, there are still many important gaps in our knowledge. One of them is related to the energetics of C–H bonds in groups which have at least one neighboring heteroatom. For instance, the number of available enthalpies of formation of carbon-centered radicals derived from ethers, esters, peroxides, and carbonyl compounds, is quite small [4]. In the case of ethers only

values for three compounds have been reported: dimethyl ether (R=CH<sub>3</sub>OCH<sub>2</sub>), diethyl ether (R=C<sub>2</sub>H<sub>5</sub>OCHCH<sub>3</sub>), and tetrahydrofuran, (thf; R= $\alpha$ -furyl).

The experimental value for the C–H bond dissociation enthalpy in dimethyl ether, 389 ± 4 kJ mol<sup>-1</sup> [1], was derived from the activation energy of the gas-phase reaction (1) by assuming a negligible (ca. 4 kJ mol<sup>-1</sup>) activation barrier for the reverse reaction [8].



The above value for  $DH^0$  (CH<sub>3</sub>OCH<sub>2</sub>-H) was later reassessed as 402.2 kJ mol<sup>-1</sup> [4] (no uncertainty is given). This upwards adjustment is in line with literature discussions regarding the reliability of enthalpy of formation data of free radicals obtained from gas-phase iodination studies [9].

The value recommended for  $DH^0$  (C<sub>2</sub>H<sub>5</sub>OCHCH<sub>3</sub>-H), 383.7 ± 1.7 kJ mol<sup>-1</sup> [4], is 18.5 kJ mol<sup>-1</sup> lower than the one accepted for  $DH^0$  (CH<sub>3</sub>OCH<sub>2</sub>-H). This difference illustrates the effect of the ethoxy group on  $DH^0$  (C–H) by comparison with the difference between the primary and

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secondary C–H bond dissociation enthalpies in propane,  $12 \text{ kJ mol}^{-1}$  [10].

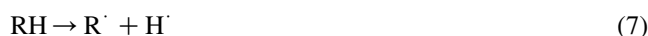
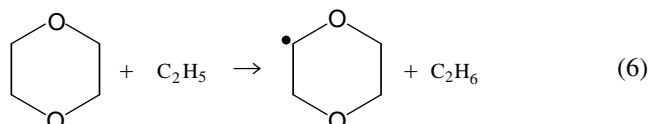
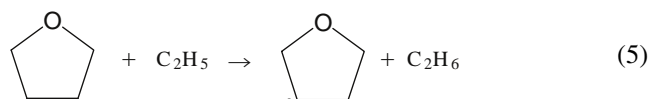
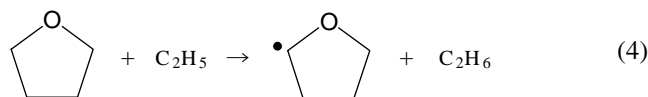
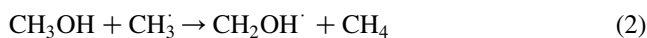
Gas-phase iodination kinetic studies were also the source of one of the experimental values for the  $\alpha$  C–H bond dissociation enthalpy in thf,  $385 \pm 4 \text{ kJ mol}^{-1}$  [1], obtained from the activation enthalpy of a reaction similar to (1) and under the same assumption. In this case, however, no upwards adjustment was made in a later reassessment [4]. Two other experimental values of  $DH^0$  ( $\alpha$ -furyl-H) have been reported:  $389.9 \text{ kJ mol}^{-1}$  [11] and  $385.3 \pm 6.7 \text{ kJ mol}^{-1}$  [12]. The former is an estimate based on Cier equation and the latter was derived from photoacoustic calorimetry experiments and kinetic data.

As theoretical methods provide a good alternative to obtain reliable bond dissociation enthalpies, we decided to use them to study the thermochemistry of C–H bonds in several molecules containing the ether group, including some of the above. We were particularly interested in the  $\alpha$  and  $\beta$  C–H bond dissociation enthalpies in thf and also in the C–H bond dissociation enthalpy in dioxane. Surprisingly, no experimental  $DH^0$  (C–H) is available for dioxane, despite its importance as a solvent (time-resolved photoacoustic calorimetry experiments in our laboratory were not successful [13]). The value for dioxane would also allow an interesting comparison with the data for tetrahydrofuran.

## 2. Computational details

Density functional theory (DFT) [14] is a widely used tool to calculate bond dissociation enthalpies (as well as many other properties), since it includes correlation effects and takes approximately the same computing time as a Hartree-Fock calculation [15]. In the present work, DFT calculations, as well as the complete basis set method CBS-Q [16], were used to determine C–H bond dissociation enthalpies in methanol, dimethyl ether, thf (considering the formation of both  $\alpha$ - and  $\beta$ -furyl radicals), and 1,4-dioxane. The calculations were carried out with the Gaussian 98 package of programs [17]. For the DFT calculations we used a variety of functionals, namely BLYP [18–20], B3LYP [19–21], B3PW91 [21,22], mPW1PW91 [22,23], B1LYP [19,23,24], BHandHLYP [25], BHandH [25], and B3P86 [21,26], all with the 6–311+G(d,p) basis set [27], in order to assess their performances.

The bond dissociation enthalpies were computed from isodesmic and isogyric reactions (reactions (2)–(6)) and from the respective bond homolysis reactions (reaction (7)).



The computed enthalpies of reactions (2)–(6) were related to the bond dissociation enthalpies through Eqs. (8) and (9) and the values of interest were derived by using the experimental values for  $DH^0$  (CH<sub>3</sub>–H) and  $DH^0$  (C<sub>2</sub>H<sub>5</sub>–H),  $439.3 \pm 0.2$  and  $423.0 \pm 1.7 \text{ kJ mol}^{-1}$ , respectively [3].

$$DH^0(\text{HOCH}_2 - \text{H}) = \Delta_r H(2) + DH^0(\text{CH}_3 - \text{H}) \quad (8)$$

$$DH^0(\text{R} - \text{H}) = \Delta_r H + DH^0(\text{C}_2\text{H}_5 - \text{H}) \quad (9)$$

The C–H bond dissociation enthalpies of methanol, methane, and ethane [3], were also computed for testing each theory level.

The geometries of reactants and products of all the reactions were optimized at each of the various theory levels, followed by a frequency calculation at that same level. Vibrational frequency analysis was used to confirm that stationary points were minimum energy structures and to calculate zero point energy (ZPE) and thermal corrections to 298 K. The computed total energies and reaction enthalpies refer to this temperature.

## 3. Results and discussion

### 3.1. Bond dissociation enthalpies

All the results obtained for the bond dissociation enthalpies and the available experimental data are summarized in Table 1. They are also displayed in Figs. 1 and 2.

The analysis of the data in Table 1 and Fig. 1 reveals that, when isodesmic and isogyric reactions were used, all the hybrid functionals provide bond dissociation enthalpies ranging from fair to very good agreement with the experimental values. The hybrid functional B1LYP is the one that performs better, with a root-mean-square error (RMSE) of  $1.3 \text{ kJ mol}^{-1}$ , which is equal to that of the CBS-Q method. Note, however, that the comparison lacks some significance because only one rather accurate experimental value is available.

Table 1

C–H bond dissociation enthalpies computed at several theory levels, using the 6–311+G(d,p) basis set

Bond	$DH^0$ (C–H) (kJ mol <sup>-1</sup> )									
	BLYP	B3LYP	B3PW91	mPW1PW91	B1LYP	BHandHLYP	BHandH	B3P86	CBS-Q	Experimental
Isodesmic and isogyric reactions										
HOCH <sub>2</sub> –H	395.0	398.5	398.5	399.6	400.3	404.8	396.8	397.7	404.3	402.1 ± 0.8 <sup>a</sup>
CH <sub>3</sub> OCH <sub>2</sub> –H	398.7	401.3	402.1	402.9	402.4	405.7	402.2	401.8	402.3	402.2 <sup>b</sup>
α-furanyl-H	383.9	387.3	387.3	388.5	388.8	393.0	388.4	387.1	389.7	390.0 ± 8.0 <sup>c</sup>
β-furanyl-H	404.3	405.9	405.7	406.2	406.6	408.4	407.1	405.6	410.0	
1,4-dioxyl-H	370.2	374.1	374.7	375.8	375.5	379.8	376.2	374.4	381.3	
RMSE <sup>d</sup>	5.8	2.6	2.6	1.7	1.3	3.1	3.2	3.0	1.3	
Bond homolysis reactions										
HOCH <sub>2</sub> –H	383.5	390.5	386.4	383.4	385.7	387.8	405.4	400.8	404.5	402.1 ± 0.8 <sup>a</sup>
CH <sub>3</sub> OCH <sub>2</sub> –H	382.3	390.3	386.9	384.4	385.7	388.8	407.9	401.4	404.8	402.2 <sup>b</sup>
α-furanyl-H	367.6	376.3	372.2	369.9	372.2	376.1	394.1	386.7	392.2	390.0 ± 8.0 <sup>c</sup>
β-furanyl-H	387.9	394.8	390.5	387.6	390.0	391.5	412.8	405.1	412.5	
1,4-dioxyl-H	353.8	363.1	359.5	357.3	358.9	362.9	381.9	374.0	383.8	
CH <sub>3</sub> –H	427.8	431.2	427.1	423.1	424.7	422.4	447.9	442.3	439.6	439.3 ± 0.2 <sup>a</sup>
C <sub>2</sub> H <sub>5</sub> –H	406.6	412.0	407.8	404.5	406.4	406.1	428.7	422.6	425.5	423.0 ± 1.7 <sup>a</sup>
RMSE <sup>d</sup>	18.1	11.4	15.3	18.3	16.4	15.2	5.8	2.1	2.2	

<sup>a</sup> Ref. [3].<sup>b</sup> Ref. [4].<sup>c</sup> Ref. [10].<sup>d</sup> Root-mean-square error.

With regard to the results of the bond dissociation enthalpies calculated from bond homolysis reactions (Table 1 and Fig. 2), it is noted that B3P86 predicts the experimental data fairly well, with a RMSE of 2.1 kJ mol<sup>-1</sup>, similar to the one obtained with CBS-Q. The same cannot be said for the remaining functionals, which perform rather poorly. Although bond dissociation enthalpies are correctly predicted by the B3P86 functional, it should be observed that this method leads to enthalpies of formation in poor agreement with experiment [28]. Moreover, some specific procedures for radical species, as for example the restricted open shell

method, may improve the performance of some functionals (ROB3LYP) for predicting the energetics of bond homolysis [29].

Comparison with experiment indicates that, with the exception of BHandHLYP for isodesmic and isogyric reactions and BHandH for bond homolysis reactions, DFT calculations underestimate bond dissociation enthalpies, while, in general, CBS-Q slightly overestimates them.

Our CBS-Q calculations lead to  $DH^0$  (β-furanyl-H) = 410.0 kJ mol<sup>-1</sup> and  $DH^0$  (1,4-dioxyl-H) = 381.3 kJ mol<sup>-1</sup>. These values are in very good agreement with DFT

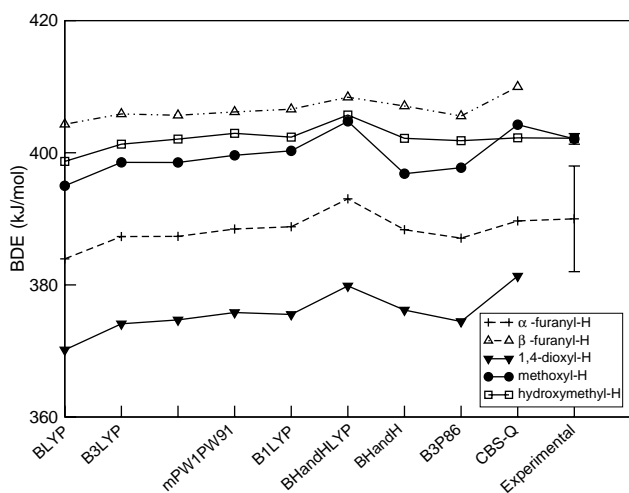


Fig. 1. Dependence of the C–H bond dissociation enthalpies from isodesmic and isogyric reactions on the theory level. Experimental values, with respective errors, are represented when available.

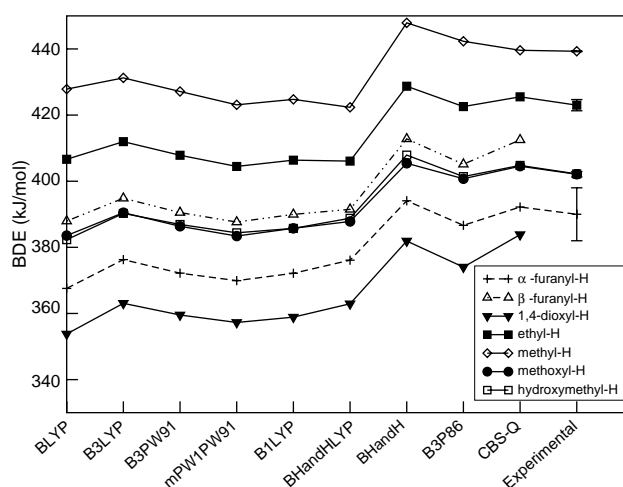


Fig. 2. Dependence of the C–H bond dissociation enthalpies from bond homolysis reactions on the theory level. Experimental values, with respective errors, are represented when available.

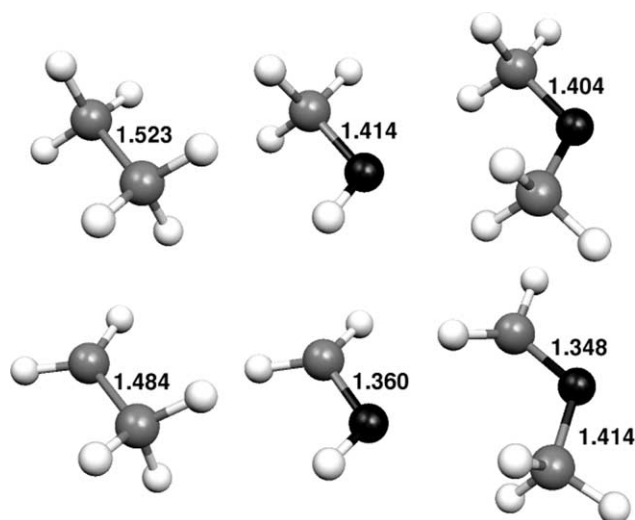


Fig. 3. B3P86/6-311+G(d,p) optimized structures of ethane, methanol, and dimethyl ether (above) and their respective carbon radicals (below). Bond distances in Å.

calculations, particularly when the isodesmic and isogyric reaction route is adopted, which is a strong indication on the reliability of the present predictions for these compounds.

### 3.2. Structure and bond dissociation enthalpy

A bond dissociation enthalpy reflects the thermodynamic stability of two species: the parent molecule and the corresponding radical fragment. A low bond dissociation enthalpy can be caused either by stabilization of the radical, by a destabilization of the parent or by both of these effects. Therefore, it is of great interest to discuss, at a molecular level, what factors may contribute to the thermodynamic stabilization of radical species. In the case of ethane, it is observed (Table 1) that  $DH^0$  (C–H) is some  $16 \text{ kJ mol}^{-1}$  lower than the value for methane. This well known feature has been attributed to a stabilization of the ethyl radical by hyperconjugation [30], as a result of the overlap between the half-occupied orbital at the carbon atom, where the bond dissociation occurred, and

the neighbour C–H bond  $\sigma$  orbital. Since this effect leads to an increase of the electronic density between the two carbon atoms, it causes a shortening of the C–C bond, as shown in Fig. 3.

A decrease of the C–O bond length is observed when a radical species is formed by a C–H bond cleavage in the  $\alpha$  position (see Figs. 3–5). This is again a consequence of hyperconjugation [30], which in this case involves the overlap between the oxygen non-bonding orbital and the half-occupied orbital of the carbon atom.

From experimental information for the C–H bond dissociation enthalpies of methanol and methane, hyperconjugation stabilizes the methoxy radical by about  $37 \text{ kJ mol}^{-1}$ . A similar difference ( $35 \text{ kJ mol}^{-1}$ ) is predicted by CBS-Q. In addition, as can be viewed in Table 1, C–H bond dissociation enthalpies in methanol and dimethyl ether are quite similar. Therefore, the substitution of a methyl group by hydrogen does not have any significant influence on hyperconjugation, which is obviously a consequence of the fact that the oxygen electrons involved are non-bonding.

The homolytic cleavage of the C–H bond in the vicinity of the oxygen atom in thf, leading to the formation of  $\alpha$ -furyl, has the second lowest enthalpy in Table 1. This is probably due to the fact that hyperconjugation leads to a shortening of both C–C and C–O bonds involving the carbon with a partially occupied orbital. The formation of  $\beta$ -furyl, by cleavage of a C–H bond in  $\beta$  position, has a higher bond dissociation enthalpy since the partially unoccupied orbital is too far away from the oxygen to be involved in the electronic delocalization over the radical center. Nevertheless, the carbon is in the vicinity of two  $-\text{CH}_2-$  groups, so the radical is doubly hyperconjugated. This is corroborated by the fact that, according to the data obtained by CBS-Q, this C–H bond dissociation enthalpy is  $27 \text{ kJ mol}^{-1}$  lower than in methane and  $13 \text{ kJ mol}^{-1}$  lower than in ethane, which is consistent with the prediction that hyperconjugation stabilizes a radical by ca.  $16 \text{ kJ mol}^{-1}$ . A shortening of the C–C bonds near the radical is also observed (Fig. 5).

The C–H bond dissociation in 1,4-dioxane and thf (when  $\alpha$ -furyl is formed) occur in similar chemical

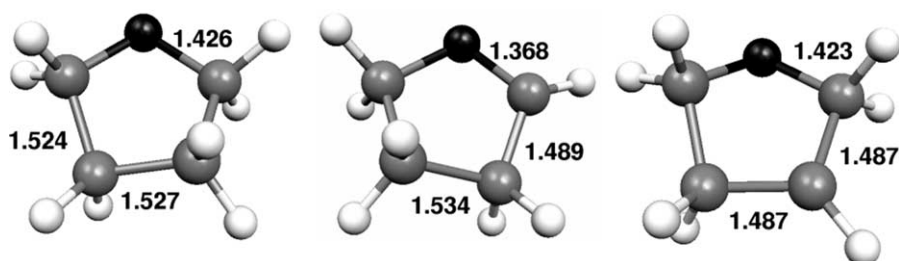


Fig. 4. B3P86/6-311+G(d,p) optimized structures of thf (left),  $\alpha$ -furyl radical (middle) and  $\beta$ -furyl radical (right). Bond distances in Å.

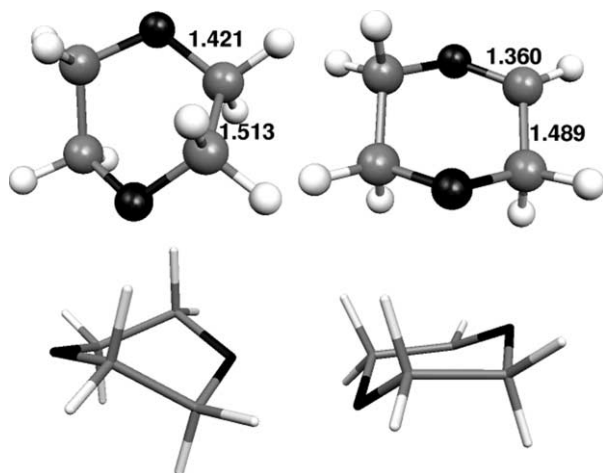


Fig. 5. B3P86/6-311+G(d,p) optimized structures of 1,4-dioxane (left) and respective radical. The parent compound adopts a twist conformation while the radical is in a chair conformation. Bond distances in Å.

environments so it could be expected that their bond dissociation enthalpies were close. However, in Table 1 it is seen that the C–H bond dissociation enthalpy of 1,4-dioxane is some  $29 \text{ kJ mol}^{-1}$  lower. This difference can be attributed to a release of ring strain upon radical formation: as shown in Fig. 5, the puckered twist conformation of dioxane relaxes into a chair conformation when dioxy radical is formed [30].

Fig. 6 summarizes some important points of the previous discussion. Ethyl and  $\beta$ -furanyl radicals, which are stabilized by hyperconjugation involving the electrons of a C–H bond  $\sigma$  orbital are nearly planar, whereas hydroxymethyl, methoxymethyl,  $\alpha$ -furanyl, and dioxyl radicals, which are stabilized by hyperconjugation

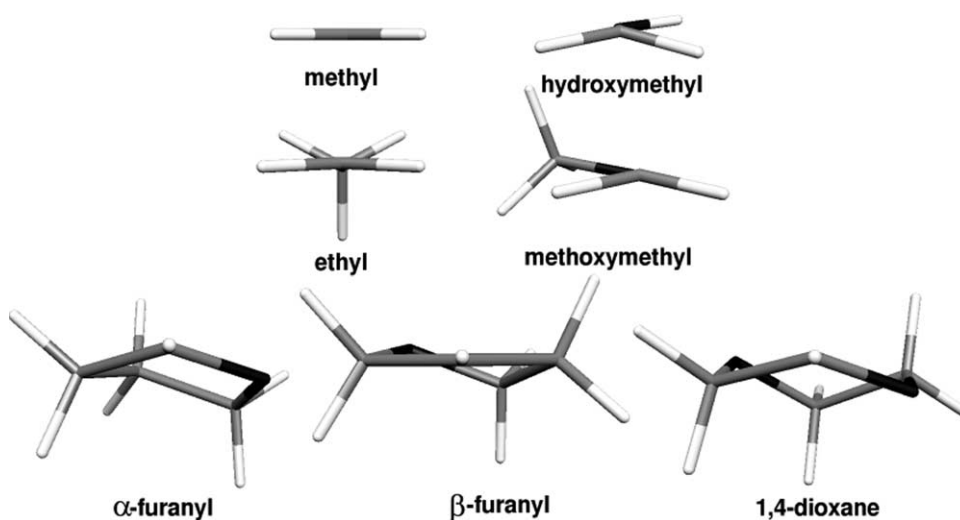


Fig. 6. B3P86/6-311+G(d,p) optimized structures of methyl, hydroxymethyl, ethyl, methoxymethyl,  $\alpha$ -furanyl,  $\beta$ -furanyl and 1,4-dioxyl radicals. Ethyl and  $\beta$ -furanyl radicals are planar while the remaining are pyramidal.

involving the non-bonding electrons of the oxygen atom, are pyramidal.

#### 4. Conclusions

C–H bond dissociation enthalpies in methanol, dimethyl ether, tetrahydrofuran, and 1,4-dioxane were estimated by DFT and multilevel CBS-Q calculations. DFT calculations were based on different representations of the exchange-correlation including BLYP, B3LYP, B3PW91, mPW1PW91, B1LYP, BHandHLYP, BHandH, and B3P86. Our results illustrate that, when isodesmic and isogyric reactions are used, all the hybrid functionals provide good estimates of the bond dissociation enthalpies, especially B1LYP or mPW1PW91. On the other hand, when bond homolysis reactions are used, only the B3P86 functional predicts bond dissociation enthalpies accurately. In agreement with previous investigations on the energetics of homolytic bond dissociation [31,32], the present results also indicate that, in general, bond dissociation enthalpies can be significantly underestimated by DFT calculations, particularly when bond homolysis reactions are used. Moreover, although not unexpected, it is worthwhile to note that by using a more sophisticated approach, such as CBS-Q, quite similar bond dissociation enthalpy values are predicted, independently of the adopted procedure.

Another relevant conclusion concerns the role played by hyperconjugation effects on the thermodynamic stabilization of the radical species. It was found that these effects, associated with the electronic density reorganization upon radical formation, may be responsible for the trends of bond dissociation enthalpies that were observed in the present study.



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