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Applicability of DFTB+ Method for the Calculations of O–H Bond Dissociation Enthalpies of Phenols

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Abstract

In this work, O–H bond dissociation enthalpies (BDE) of non-substituted phenol and 26 *meta*- and *para*-substituted phenols were calculated using semiempirical DFTB+ method. In comparison with available experimental BDE values, calculated BDEs are overestimated by ca 40 kJ mol^{-1}. DFTB+ method predicts lower substituent induced changes in BDE in comparison with experimental values. On the other hand, the found changes in O–H BDEs are in accordance with computationally significantly more demanding DFT/B3LYP/6-311++G** method. Obtained results show that DFTB+ method may be successfully employed for the fast estimation of substituent induced changes in phenolic O–H bond dissociation enthalpies.

Keywords: BDE, Hydrogen Atom Transfer Mechanism, Substituent effect, Antioxidant

Introduction

Phenols are widely employed as synthetic organic materials. Synthetic and natural phenolic compounds also represent important group of antioxidants in living organisms and synthetic polymers. Phenoxy radicals are intermediates in many biological and industrial applications (Halliwell and Gutteridge 1989, Gugumus 1990). The first step of the reactive radicals termination by phenolic antioxidants is the hydrogen atom transfer from the antioxidant molecule to the reactive radical intermediate (Gugumus 1990). A high rate of hydrogen atom transfer is expected to be related to a low O–H bond dissociation enthalpy (BDE). Phenols are also of special interest in organic chemistry – their acid-base equilibriums have often been used as reference values in establishing linear free energy relationships (Hine 1975).

Bond dissociation enthalpies are important thermodynamic quantities that contribute to the understanding of many processes in chemistry and biochemistry. The knowledge of the BDEs has been accumulated substantially for the past twenty years due to the development of both experimental (Hine 1975, Denisov 1995, Bordwell et al. 1991 and 1994, Lind et al. 1990, Mulder et al. 1988, Wayner et al. 1995 and 1996, Zhu et al. 1997, Correia et al. 2004) and quantum chemical techniques (Pratt et al. 2004, Wright et al. 1997 and 2008, Johnson et al. 2003, DiLabio et al. 1999, Brinck et al. 1997, Justino et al. 2010, Chandra et al. 2002, Klein and Lukeš 2006, Cabral and Canuto 2005, Bakalbassis et al. 2003, Haeberlein et al. 1996). Recent advances in theoretical techniques enable to calculate the enthalpies of the processes where X–H bonds are broken, ideally with an accuracy approaching to 4 kJ mol^{-1} in the gas phase. Since in chemistry one often needs to compare a group of reactions differing only in the substitution, it is important to study also the effect of the substituents on bond dissociation enthalpies.

The goal of this work is to calculate O–H BDEs of phenol and 26 *meta*- and *para*-substituted phenols (Fig. 1) using semi-empirical DFTB+ method in order to assess the method reliability in the description of substituent induced changes in BDE. In addition to the comparison of the obtained values with available experimental BDEs and especially with calculated DFT/B3LYP/6-311++G** values (Klein and Lukeš 2006), the obtained DFTB+ values will be correlated with Hammett constants (Hansch et al. 1991). This enables the comparison of the substituent effects predicted by the two methods.

Fig. 1. Studied *meta* and *para*-substituted phenols, X = *t*-Bu, CF_3, CN, F, Me, MeCO, MeO, $MeSO_2$, NH_2, NMe_2, NO_2, OH, Ph.

Computational details

The geometries of studied parent phenols and corresponding phenoxy radicals were optimized using the Tight Binding Density-Functional based (DFTB+) approach (Aradi et al. 2007). This method is comparable in its computational efficiency with popular semi-empirical methods, e.g. AM1 or PM3, but it is based on Density Functional Theory. For the species with several conformers, all conformers were investigated. The conformer with the lowest total electronic energy was used in this work. Bond dissociation enthalpies were determined on the basis of the obtained total electronic energies of the molecule and the corresponding radical.

Results and Discussion

Bond dissociation enthalpy, BDE, is defined as

$$\mathrm{BDE} = H(\mathrm{R}^{\bullet}) + H(\mathrm{H}^{\bullet}) - H(\mathrm{R{-}H}) \tag{1}$$

where $H(\mathrm{R}^{\bullet})$ is the total enthalpy of the radical, $H(\mathrm{H}^{\bullet})$ is the total enthalpy of the abstracted hydrogen atom, and $H(\mathrm{R{-}H})$ is the total enthalpy of the molecule. In this work, BDEs are approximated using the total electronic energies of the above mentioned species as in the works (Brinck et al. 1997, Klein and Lukeš 2006, Haeberlein et al. 1996).

Obtained DFTB+ values, together with available experimental (Zhu et al. 1997, Denisov 1995, Bordwell et al. 1991, Lind et al. 1990) and DFT/B3LYP/6-311++G** (Klein and Lukeš 2006) values are compiled in Tables 1 and 2. Experimental data in the tables were determined using four methods. Bordwell and Cheng's electrochemical (EC) method uses the equilibrium acidity (pK_a) and oxidation potential (E_{ox}) values of the conjugated anion for the BDE calculation (Bordwell et al. 1991). Thermodynamic cycle (TDC) method (Zhu et al. 1997) gives BDEs analogous to EC method. The method employs pK_a and E_{ox} values, too. TDC provides slightly higher BDEs, however differences between individual EC and TDC values do not exceed 3 kJ mol^{-1}. In the two experiments, dimethylsulfoxide (DMSO) was used as a solvent. Lind et al. carried out pulse radiolysis (PR) experiments in water (Lind et al. 1990). PR method provides BDEs lower in comparison with EC and TDC methods. Differences between EC and PR BDEs, with the exception of *p*-NMe$_2$ group, are within the usual experimental errors range of 4–10 kJ mol^{-1}. Denisov estimated BDEs using parabolic model (column denoted as "PM") from the kinetic measurements (Denisov 1995). All values, except *p*-NH$_2$ substituted phenol, are lower than BDEs from EC or TDC experiments. The differences against EC values reach 3–18 kJ mol^{-1}. The largest difference (32 kJ mol^{-1}) was found in the case of *p*-NH$_2$ group. In (Klein and Lukeš 2006), it was found that B3LYP/6-311++G** BDEs are in very good accordance with the solution-phase experimental values, especially with EC and TDC ones. As it can be seen in Tables 1 and 2, DFTB+

method tends to overestimate individual O–H bond dissociation enthalpies. In comparison to B3LYP results, DFTB+ gives BDEs larger by 31–51 kJ mol^{-1}. Average differences between B3LYP and DFTB+ values reached 42 and 46 kJ mol^{-1} for *para*- and *meta*-substituted phenols, respectively. However, for all *meta*-substituted phenols, the differences between B3LYP and

Table 1. Experimental and theoretical O–H BDEs of *para*-substituted phenols in kJ mol^{-1}.

Substituent	EC[a]	TDC[b]	PM[c]	PR[d]	DFT[e]	DFTB+	σ_p[f]
—	376	379	367	369	375	419	—
p-NMe_2	336	338		310	332	378	–0.83
p-NH_2	323	326	355	316	337	388	–0.66
p-OH	341			335	352	395	–0.37
p-MeO	354	356	341	345	351	391	–0.27
p-*t*-Bu	371	374	357		367	411	–0.20
p-Me	371	374		360	366	411	–0.17
p-Ph	366				365	407	–0.01
p-F				365	368	408	0.06
p-MeCO	388	391	370	377	383	414	0.50
p-CF_3	398	401			388	431	0.54
p-CN	394	397		388	385	422	0.66
p-$MeSO_2$	397				391	433	0.72
p-NO_2	396	399		394	394	434	0.78

[a] From (Bordwell et al. 1991). [b] From (Zhu et al. 1997). [c] From (Denisov et al. 1995).
[d] From (Lind et al. 1990). [e] From (Klein and Lukeš 2006). [f] From (Hansch et al. 1991).

Table 2. Experimental and theoretical O–H BDEs of *meta*-substituted phenols in kJ mol^{-1}.

Substituent	EC[a]	TDC[b]	PM[c]	PR[d]	DFT[e]	DFTB+	σ_m[f]
—	376	379	367	369	375	419	—
m-NH_2	368	368	365		370	419	–0.16
m-NMe_2	367				372	417	–0.16
m-*t*-Bu					371	417	–0.10
m-Me	374				373	419	–0.07
m-Ph					376	420	0.06
m-OH					374	420	0.12
m-MeO	377				370	419	0.12
m-F					380	427	0.34
m-MeCO	384				377	423	0.38
m-CF_3	392				383	431	0.43
m-CN	393				386	429	0.56
m-$MeSO_2$	386				384	433	0.60
m-NO_2	394				387	435	0.71

[a] From (Bordwell et al. 1991). [b] From (Zhu et al. 1997). [c] From (Denisov et al. 1995).
[d] From (Lind et al. 1990). [e] From (Klein and Lukeš 2006). [f] From (Hansch et al. 1991).

DFTB+ values lie in the very narrow range of 45–49 kJ mol^{-1}. The average differences between DFTB+ and available experimental EC BDEs are of 40 and 43 kJ mol^{-1} for *para*- and *meta*-substituted phenols, respectively. Electron-donating substituents decrease O–H BDE, whereas electron-withdrawing groups increase BDE.

The Hammett equation has been one of the most widely used means for the study and interpretation of organic reactions and their mechanisms. Hammett constants σ_m (for a substituent in *meta* position) and σ_p (for a substituent in *para* position) are able to successfully predict the equilibrium and rate constants for a variety of types of reactions (Hansch et al. 1991, Krygowski et al. 2005). They represent one of the most often used descriptors of the substituent effects (Hansch et al. 1991, Krygowski et al. 2005). They are successfully used also as the descriptor of the substituent induced changes in BDE. Obtained BDE = $f(\sigma_p)$ and BDE = $f(\sigma_m)$ dependences show good linearity. Such dependences may be also employed for the estimation of BDE from the Hammett constant of a substituent. For DFTB+ O–H BDE values we have obtained

$$\text{BDE/kJ mol}^{-1} = 407 + 31\sigma_p \qquad (\textit{para}, \text{DFTB+}) \qquad (2)$$
$$\text{BDE/kJ mol}^{-1} = 419 + 20\sigma_m \qquad (\textit{meta}, \text{DFTB+}) \qquad (3)$$

with correlation coefficients of 0.941 (*para*) and 0.943 (*meta*). The linearity of these dependences can be considered as good (Figs. 2 and 3). Standard deviations of the line slopes reached 2 for *meta*- and 3 for *para*-substituted phenols. For B3LYP data it was found

$$\text{BDE/kJ mol}^{-1} = 365 + 37\sigma_p \qquad (\textit{para}, \text{B3LYP}) \qquad (4)$$
$$\text{BDE/kJ mol}^{-1} = 373 + 19\sigma_m \qquad (\textit{meta}, \text{B3LYP}) \qquad (5)$$

with correlation coefficients of 0.979 (*para*) and 0.934 (*meta*); standard deviation of found line slopes are of 2. Considering the values of the standard deviations of the line slopes in Eqs. 2,4 and 3,5, there is no substantial difference between the dependences obtained from B3LYP and DFTB+ results. The groups in *para* position affect the BDE more than the same groups located in *meta* position. From the intercepts of the obtained dependences, it is again apparent that DFTB+ method overestimates individual BDE values. Using experimental EC values (Bordwell et al. 1991) for the available substituents (14 *para* and 10 *meta*), it was found

$$\text{BDE/kJ mol}^{-1} = 367 + 44\sigma_p \qquad (\textit{para}, \text{EC}) \qquad (6)$$
$$\text{BDE/kJ mol}^{-1} = 375 + 29\sigma_m \qquad (\textit{meta}, \text{EC}) \qquad (7)$$

with correlation coefficients of 0.951 (*para*) and 0.954 (*meta*). Standard deviations of the line slopes reached 3 for *meta*- and 4 for *para*-substituted phenols. Equations 2–7 indicate that both computational approaches tend to underestimate the substituent effects. On the other hand, the two computational methods provide analogous results. Besides, DFTB+ method requires significantly shorter computational times. The method provides the results within several minutes using standard PC.

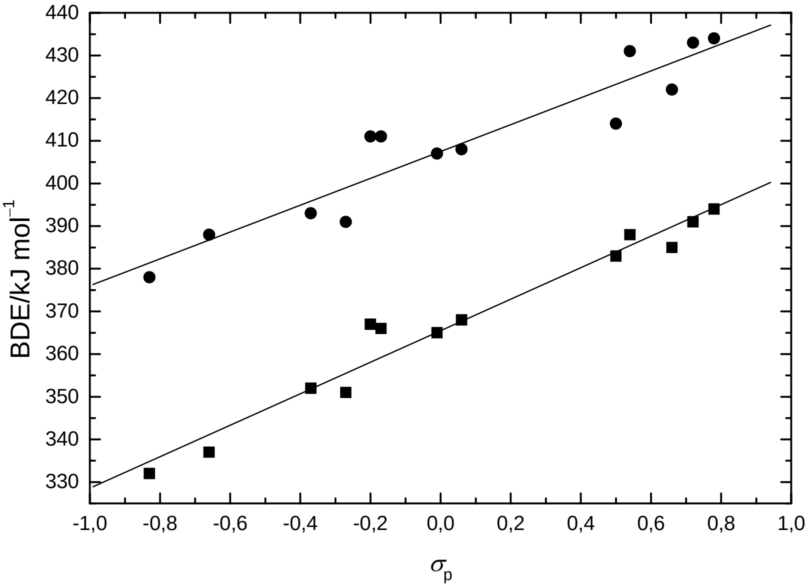

Fig. 2. Dependence of BDE *vs* σ_p. Squares stand for BFTB+ values, circles stand for DFT/B3LYP/6-311++G** values.

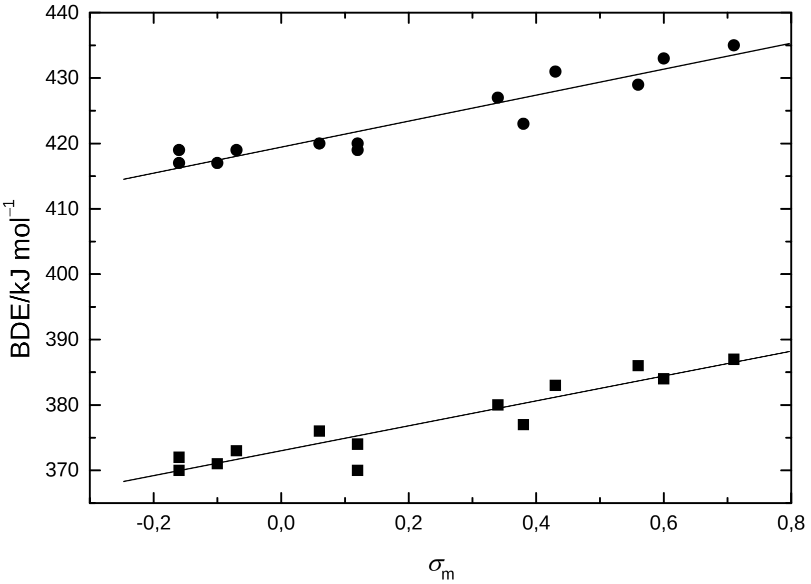

Fig. 3. Dependence of BDE *vs* σ_m. Squares stand for BFTB+ values, circles stand for DFT/B3LYP/6-311++G** values.

Conclusion

O–H bond dissociation enthalpies for phenol and 26 *meta*- and *para*-substituted phenols calculated using DFTB+ semi-empirical method confirmed that the method is able to describe substituent induced changes as reliably as DFT/B3LYP/6-311++G** method. The two methods provide almost identical line slopes for the linear BDE *vs* σ_m or σ_p dependences. In the case of studied phenols, DFTB+ BDEs are overestimated by ca 40 kJ mol^{-1}. Therefore, DFTB+ method is suitable for the fast predictions of substituent induced changes in phenolic O–H bond dissociation enthalpies. In the future, it would be worth to test the reliability of the method for O–H bond dissociation enthalpies for polyphenolic compounds.

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References

Aradi B, Hourahine B, Frauenheim Th (2007) J. Phys. Chem. A 111: 5678-5684

Bakalbassis EG, Lithoxoidou AT, Vafiadis AP (2003) J. Phys. Chem. A 107: 8594-8606

Bordwell FG, Cheng J-P (1991) J. Am. Chem. Soc. 113: 1736-1743

Bordwell FG, Zhang X-M, Satish AV, Cheng J-P (1994) J. Am. Chem. Soc. 116: 6605-6610

Brinck T, Haeberlein M, Jonsson M (1997) J. Am. Chem. Soc. 119: 4239-4244

Cabral BJC, Canuto S (2005) Chem. Phys. Lett. 406: 300-305

Chandra AK, Uchimaru T (2002) Int. J. Mol. Sci. 3: 407-422

Correia CF, Nunes PM, dos Santos RMB, Simões JAM (2004) Thermochimica Acta 420: 3-11

Denisov ET (1995) Polym. Degrad. Stab. 49: 71-75

DiLabio GA, Pratt DA, LoFaro AD, Wright JS (1999) J. Phys. Chem. A 103: 1653-1661

Gugumus F (1990) Oxidation inhibition in organic materials, Vol. 1. CRC Press, Boca Raton

Haeberlein M, Brinck T (1996) J. Phys. Chem. 100: 10116-10120

Halliwell B, Gutteridge JMC (1989) Free Radicals in Biology and Medicine. Oxford University Press, Oxford

Hansch C, Leo A, Taft RW (1991) Chem. Rev. 91: 165-195

Hine J (1975), Structural Effects on Equilibria in Organic Chemistry, Wiley-Interscience, New York

Johnson ER, Clarkin OJ, DiLabio GA (2003) J. Phys. Chem. A 107: 9953-9963

Justino GC, Vieira, AJSC (2010) J. Mol. Model. 16: 863-876

Klein E, Lukeš V (2006) J. Mol. Struct. (Theochem) 767: 43-50

Krygowski TM, Stępień BT (2005) Chem. Rev. 105: 3482-3512

Lind J, Shen X, Eriksen TE, Merenyi G (1990) J. Am. Chem. Soc. 112: 479-482

Mulder P, Saastad OW, Griller D (1988) J. Am. Chem. Soc. 110: 4090-4092

Pratt DA, DiLabio GA, Mulder P, Ingold KU (2004) Acc. Chem. Res. 37: 334-340

Wayner DDM, Lusztyk E, Ingold KU, Mulder P (1996) J. Org. Chem. 61: 6430-6433

Wayner DDM, Lusztyk E, Pagé D, Ingold KU, Mulder P, Laarhoven LJJ, Aldrich HS (1995) J. Am. Chem. Soc. 117: 8737-8744

Wright JS, Carpenter DJ, McKay DJ, Ingold KU (1997) J. Am. Chem. Soc. 119: 4245-4252

Wright JS, Shadnia H (2008) Chem. Res. Toxicol. 21: 1426-1431

Zhu Q, Zhang XM, Fry AJ (1997) Polym. Degrad. Stab. 57: 43-50