

DFT/B3LYP Study of the Enthalpies of Homolytic and Heterolytic O–H Bond Dissociation in Sterically Hindered Phenols

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Abstract

For 15 *para*-substituted sterically hindered phenols, i.e. phenols with large *tert*-butyl groups in the two *ortho* positions, the reaction enthalpies related to three mechanisms of phenolic antioxidants action: (i) hydrogen atom transfer (HAT), (ii) single-electron transfer – proton transfer (SET-PT), and (iii) sequential proton loss electron transfer (SPLET) in gas-phase, were calculated using DFT/B3LYP/6-311++G** method. Computed enthalpies were compared with available experimental values and with data obtained for *para*-substituted phenols. Obtained reaction enthalpies were also correlated with Hammett constants, σ_p . Electron-donating groups lower BDE, IP and ETE and induce an increase in PA and PDE. Electron-withdrawing groups cause a decrease in PA and PDE and a rise in BDE, IP and ETE. Dependences of studied reaction enthalpies on Hammett constants can be considered linear. In the case of HAT and SPLET mechanisms, we have found linear dependences between corresponding enthalpies (BDE, PA, ETE) and length of phenolic C–O bond. Linear dependence between this bond length and Hammett constant, σ_p , has been obtained, too.

Keywords: sterically hindered phenol, antioxidant, substituent effect, reaction mechanism

Introduction

Oxidation causes an irreversible deterioration of biological systems and synthetic polymers. Generally, it corresponds to a free radical chain reaction (Gugumus 1990). The most important reactive radical intermediates formed during oxidation reactions are hydroxyl (HO•), alkoxy (RO•) and peroxy (ROO•) radicals (Gugumus 1990, Halliwell 1989, Zhu 1997).

Antioxidants are chemical compounds able to quench reactive radical intermediates formed during the oxidation. It is well-known fact that phenolic compounds act as chain-breaking (primary) antioxidants. Sterically hindered phenols (Fig. 1) represent a large group of synthetic antioxidants widely used in synthetic polymers stabilization (Gugumus 1990).

Besides the two generally accepted mechanisms of phenols (denoted as ArOH) antioxidant action (Wright 2001, Vafiadis 2005, Musialik 2005), namely hydrogen atom transfer (HAT)



and single-electron transfer followed by proton transfer (SET-PT),



another mechanism has been discovered and confirmed on the basis of kinetics experiments – sequential proton loss electron transfer (SPLET) (Foti 2004, Litwinienko 2003, 2004 and 2007, Musialik 2005 and 2009, Staško 2007)



From the antioxidant action point of view, the net result of all three mechanisms is the same, i.e. the formation of phenoxy radical ArO^\bullet . Kinetic measurements showed that the balance among these mechanisms depends on both the environment and the reactants (Litwinienko 2007, Musialik 2009). Reaction enthalpies related to individual steps of the above described mechanisms are usually denoted as follows:

BDE – O–H bond dissociation enthalpy related to eq. 1,

IP – ionization potential, enthalpy of electron transfer from the antioxidant, eq. 2a,

PDE – proton dissociation enthalpy, eq. 2b,

PA – proton affinity of phenoxide anion, eq. 3a,

ETE – electron transfer enthalpy, eq. 3b.

In our previous work, we found that DFT/B3LYP method with 6-311++G** basis set provides results in very good accordance with available experimental or theoretical BDEs, IPs, PDEs and PAs of various mono-substituted phenols, tocopherols and chromans in the gas-phase (Klein 2006 and 2007). This computational approach described the effect of the

substituents correctly, too. We have also found that DFT/B3LYP tends to slightly underestimate absolute values of studied reaction enthalpies. However, this is generally known fact (Costa Cabral 2005).

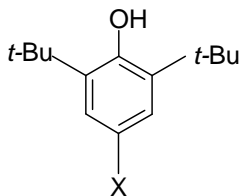


Fig. 1. Studied sterically hindered phenols, X = H, Br, *t*-Bu, CF₃, CN, Cl, F, Me, MeCO, MeO, MeSO₂, NH₂, NMe₂, NO₂, OH, Ph.

The main aim of this work is to calculate O–H BDEs, IPs, PDEs, PAs and ETEs of 15 *para*-substituted sterically hindered phenols (Fig. 1) in gas-phase and to assess the effect of various electron-donating or electron-withdrawing groups in *para*-position on these enthalpies. Obtained results will be compared with available experimental data. One of the main goals is the comparison of obtained results with data published for non-hindered mono-substituted phenols, with identical group of substituents in *para* position, in order to describe the effect of the two *tert*-butyl groups on studied enthalpies. Substituent effects represent an important concept of structural effects influencing the chemical, physicochemical, and biochemical properties of chemical species (Hansch 1991, Krygowski 2005). Although in the literature it is possible to find several experimental O–H BDEs for *para*-substituted sterically hindered phenols (Luo 2003), enthalpies related to the SET-PT and SPLET mechanisms of the antioxidant action were not systematically studied, yet. In this work, we have investigated these substituents (in alphabetical order): Br, *t*-Bu, CF₃, CN, Cl, F, Me, MeCO, MeO, MeSO₂, NH₂, NMe₂, NO₂, OH, phenyl (further denoted as Ph). In the case of molecule with O–H group in *para* position, we have calculated all quantities just for hindered O–H group.

Computational details

All calculations were performed using Gaussian 03 program package (Frisch 2003). The geometry of each molecule, radical, anion or radical cation in the gas-phase was optimized using DFT method with UB3LYP functional (Becke 1993) without any constraints (energy cut-off of 10⁻⁵ kJ mol⁻¹, final RMS energy gradient under 0.01 kJ mol⁻¹ Å⁻¹). The calculations were performed in 6-311++G** basis set (Binkley 1980). For the species having more conformers, all conformers were investigated. The conformer with the lowest electronic

energy was used in this work. Computed gas-phase hydrogen atom, H^\bullet , enthalpy was $-0.499897 E_h$. The calculated gas-phase enthalpy of proton, $H(H^+)$, is $6.197 \text{ kJ mol}^{-1}$, for gas-phase enthalpy of electron, $H(e^-) = 3.145 \text{ kJ mol}^{-1}$ (Bartmess 1994) was used. All enthalpies were calculated for 298 K.

Accuracy of the energy evaluation in the case of systems involving open-shell species is sensitive to spin contamination. Spin contaminations of radicals were found in the 0.76–0.78 range. After the annihilation of the first spin contaminant, they dropped to correct value 0.75. Therefore, spin contamination should not bias computed enthalpies.

Results and discussion

In the case of DFT method, which does not provide enthalpies directly, the total enthalpies of the species X, $H(X)$, at temperature T are usually estimated from the expression (Wright 2001, Bakalbassis 2003, Klein 2006, Chandra 2002)

$$H(X) = E_0 + ZPE + \Delta H_{\text{trans}} + \Delta H_{\text{rot}} + \Delta H_{\text{vib}} + RT \quad (4)$$

where E_0 is the calculated total electronic energy, ZPE stands for zero-point energy, ΔH_{trans} , ΔH_{rot} , and ΔH_{vib} are the translational, rotational and vibrational contributions to the enthalpy. Finally, RT represents PV-work term and it is added to convert the energy to enthalpy. ΔH_{trans} ($3/2 RT$), ΔH_{rot} ($3/2 RT$ or RT for a linear molecule), and ΔH_{vib} contributions to the enthalpy are calculated from standard formulas (Atkins 1998).

From the calculated total enthalpies we have determined following quantities:

$$\text{BDE} = H(\text{ArO}^\bullet) + H(H^\bullet) - H(\text{ArOH}) \quad (5)$$

$$\text{IP} = H(\text{ArOH}^{+\bullet}) + H(e^-) - H(\text{ArOH}) \quad (6)$$

$$\text{PDE} = H(\text{ArO}^\bullet) + H(H^+) - H(\text{ArOH}^{+\bullet}) \quad (7)$$

$$\text{PA} = H(\text{ArO}^-) + H(H^+) - H(\text{ArOH}) \quad (8)$$

$$\text{ETE} = H(\text{ArO}^\bullet) + H(e^-) - H(\text{ArO}^-) \quad (9)$$

O–H Bond Dissociation Enthalpies

Calculated BDEs of *para*-substituted sterically hindered phenols and available experimental values taken from (Luo 2003) are summarized in the Table 1. Experimental values were obtained using various techniques, such as EPR (Lucarini 1994), electrochemical

measurements (Bordwell 1991, Zhu 1997) or they were determined from kinetic data (Denisov 2000). All experimental BDEs were obtained in solution-phase. Table 1 also contains gas-phase BDE values of *para*-substituted phenols from (Klein 2006) and Hammett constants σ_p taken from (Hansch 1991). Only $\sigma_p(\text{NMe}_2) = -0.63$ was used from (Pytela 1994), because in the previous paper (Klein 2006) it was found that $\sigma_p(\text{NMe}_2) = -0.83$ (Hansch 1991) clearly did not correspond to the overall trend in $\text{BDE} = f(\sigma_p)$ dependence. Besides, $\sigma_p(\text{NMe}_2) = -0.63$ is close to $\sigma_p(\text{NMe}_2)$ published in (Šterba 1985), where -0.57 and -0.61 values were determined.

Table 1. Gas-phase B3LYP/6-311++G** BDEs of sterically hindered and non-hindered *para*-substituted phenols in kJ mol^{-1} , and Hammett constants σ_p .

Substituent	Sterically Hindered		Non-hindered ^b	σ_p^c
	Calculated	Experimental ^a		
—	314	343.5–346.4	347	
<i>p</i> -NH ₂	279	334.6	308	-0.66 ^d
<i>p</i> -NMe ₂	276		306	-0.63
<i>p</i> -OH	293		325	-0.37
<i>p</i> -MeO	292	324.7–333.5	323	-0.27
<i>p</i> - <i>t</i> -Bu	307	334.0–345.6	339	-0.20
<i>p</i> -Me	306	334.3–338.9	337	-0.17
<i>p</i> -Ph	305	337.7, 339.7	337	-0.01
<i>p</i> -F	307		340	0.06
<i>p</i> -Cl	310	344.5, 344.8	342	0.23
<i>p</i> -Br	311		343	0.23
<i>p</i> -MeCO	322	347.8	354	0.50
<i>p</i> -CF ₃	325		358	0.54
<i>p</i> -CN	322	352.4	355	0.66
<i>p</i> -MeSO ₂	329		361	0.72
<i>p</i> -NO ₂	330	355.2–362.8	364	0.78

^a From Ref. (Luo 2003).

^b From Ref. (Klein 2006).

^c From Ref. (Hansch 1991).

^d From Ref. (Pytela 1994).

Values in Table 1 indicate that computed gas-phase O–H BDEs for hindered phenols are lower than the experimental ones; differences reached ca 30 kJ mol^{-1} . As we have already mentioned, it is known that DFT/B3LYP method tends to underestimate BDEs (Costa Cabral 2005). However, one should keep in mind that gas-phase BDEs are usually close, but not identical to solution-phase ones. Usually, gas-phase values are by $4\text{--}10 \text{ kJ mol}^{-1}$ lower (Wright 2001). Standard deviations of experimentally determined BDEs are usually in

1–8 kJ mol⁻¹ range (Bordwell 1991, Lucarini 1994, Zhu 1997, Luo 2003). In the case of *para*-substituted phenols, we found (Klein 2006) that used computational approach describes substituent induced changes in BDEs satisfactorily. Theoretical and experimental values in Table 1 indicate that this conclusion also holds for sterically hindered phenols.

In comparison to non-hindered *para*-substituted phenols, BDEs of sterically hindered phenols are lower by ca 30 kJ mol⁻¹. Differences are in narrow, 29–34 kJ mol⁻¹, range. The decrease in BDEs is caused by the presence of two electron-donating *tert*-butyl groups in *ortho*-positions to the phenolic O–H bond. Electron-donating groups induce decrease in BDEs, while the presence of electron-withdrawing ones in molecule results in growth of BDE. BDEs obtained for studied molecules are in 54 kJ mol⁻¹ range.

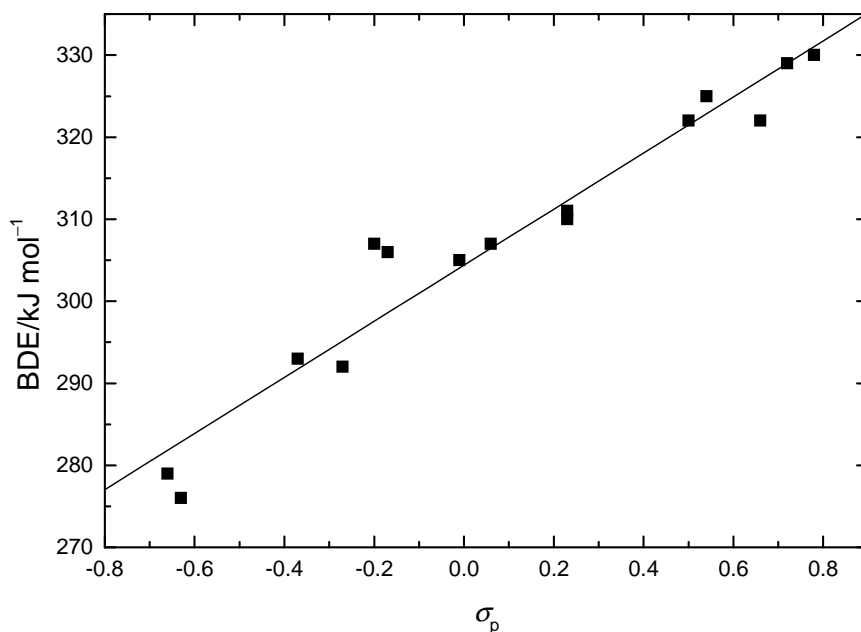


Fig. 2. Dependence of BDE vs. σ_p .

We found following dependence of BDEs on Hammett σ_p constants (Klein 2006) for non-hindered phenols

$$\text{BDE/kJ mol}^{-1} = 337 + 38\sigma_p \quad (\text{non-hindered}) \quad (10)$$

with correlation coefficient value of 0.978. In this work, for sterically hindered phenols we have obtained (Fig. 2)

$$\text{BDE/kJ mol}^{-1} = 305 + 34\sigma_p \quad (\text{hindered}) \quad (11)$$

The correlation coefficient reached value of 0.968. With respect to the standard deviations of the two linear dependences, there is no significant difference between the two lines slopes.

Ionization potentials

IPs computed for sterically hindered phenols are compiled in Table 2. This table also summarizes values for *para*-substituted phenols from the previous study (Klein 2006), which confirmed that applied DFT/B3LYP method gives reliable gas-phase IP values of *para*- and *meta*- substituted non-hindered phenols. Obtained results also showed that the method describes effect of substituents on IP correctly.

Table 2. Gas-phase B3LYP/6-311++G** IPs and PDEs of sterically hindered and non-hindered *para*-substituted phenols in kJ mol^{-1} .

Substituent	IP		PDE	
	Hindered	Non-hindered ^a	Hindered	Non-hindered ^a
—	737	806	899	861
<i>p</i> -NH ₂	638	685	963	943
<i>p</i> -NMe ₂	609	645	988	982
<i>p</i> -OH	690	748	926	898
<i>p</i> -MeO	673	726	941	918
<i>p</i> - <i>t</i> -Bu	703	759	926	901
<i>p</i> -Me	710	770	918	888
<i>p</i> -Ph	685	726	942	932
<i>p</i> -F	737	808	891	853
<i>p</i> -Cl	735	798	897	865
<i>p</i> -Br	732	792	900	782
<i>p</i> -MeCO	757	817	886	857
<i>p</i> -CF ₃	781	855	866	824
<i>p</i> -CN	782	851	862	824
<i>p</i> -MeSO ₂	784	852	867	830
<i>p</i> -NO ₂	804	879	848	806

^a From Ref. (Klein 2006).

Only for two sterically hindered phenols IP values were published. For the 2,6-di-*tert*-butyl phenol, i.e. the molecule without substitution in *para* position, IP = 743 kJ mol^{-1} (Maier 1973) and IP = 786 kJ mol^{-1} (Cetinkaya 1983) are available. For sterically hindered phenol with third *tert*-butyl group located in *para* position, experimentally determined IP reached the value of 724 kJ mol^{-1} (Cetinkaya 1983). These values are in fair agreement with values for these two compounds in Table 2. Since no other experimental or theoretical results are available yet, calculated ionization potentials (Table 2) can serve as predicted values.

Values in Table 2 show that electron-donating groups cause a decrease in IP, while electron-withdrawing ones cause an increase in IP. Obtained IPs are in wide, 195 kJ mol⁻¹, range. Presence of two *tert*-butyl groups results in the lower IP values of hindered phenols. Differences between hindered and non-hindered phenols are in 36–75 kJ mol⁻¹ range. For strong electron-donating groups (NH₂, NMe₂), differences are lowest. On the contrary, largest differences can be found for strong electron-withdrawing CN, MeSO₂ and NO₂ substituents.

In (Klein 2006) we obtained from the linear regression following IP = $f(\sigma_p)$ dependence for *para*-substituted phenols

$$\text{IP/kJ mol}^{-1} = 770 + 128\sigma_p \quad (\text{non-hindered}) \quad (12)$$

with correlation coefficient of 0.957. For hindered phenols, we have found

$$\text{IP/kJ mol}^{-1} = 712 + 113\sigma_p \quad (\text{hindered}) \quad (13)$$

Here, correlation coefficient is 0.956. The line slope indicates that the effect of substituents in *para* position is slightly attenuated by *tert*-butyl groups in hindered phenols.

Proton dissociation enthalpy

PDE represents the reaction enthalpy of the second step in SET-PT mechanism (Eq. 2b). Calculated PDE values with those obtained for non-hindered *para*-substituted phenols (Klein 2006) are summarized in Table 2. For this reaction enthalpy, no experimental values are available in the literature. For mono-substituted phenols, used method provided description of substituent effect in terms of ΔPDE values, where $\Delta\text{PDE} = \text{PDE}(\text{X-ArOH}) - \text{PDE}(\text{ArOH})$, in good accordance with other theoretical studies (Klein 2006).

Electron-donating substituents cause an increase in PDE, electron-withdrawing substituents induce a decrease in PDE. PDEs of hindered phenols in Table 2 lie in 140 kJ mol⁻¹ range. Differences between non-hindered and hindered phenols PDE values are in the range from -6 to -42 kJ mol⁻¹, i.e. *tert*-butyl groups in *ortho* positions cause a growth of PDE. Lower differences are observed between analogous molecules with strong electron-donating substituents, while larger differences can be found for molecules with strong electron-withdrawing groups in *para* position. For *para*-substituted phenols, using linear regression, we obtained (Klein 2006)

$$\text{PDE/kJ mol}^{-1} = 887 - 93\sigma_p \quad (\text{non-hindered}) \quad (14)$$

For sterically hindered phenols we have found

$$\text{PDE/kJ mol}^{-1} = 914 - 79\sigma_p \quad (\text{hindered}) \quad (15)$$

In both cases, individual points are more scattered along the regression line, absolute values of correlation coefficients reached 0.933 (non-hindered) and 0.940. Again, small decrease in the substituent effect expressed in terms of the line slope values is observed.

Proton affinities

Contrary to mono-substituted phenols, experimental gas-phase proton affinities of hindered phenoxide anions are not available. Therefore, the reliability of calculated values cannot be verified directly. However, in (Klein 2006) we have shown that calculated proton affinities of various *para*- and *meta*-substituted phenols were in very good agreement with two large series of experimental PAs (Fujio 1981, McMahon 1977) and differences between calculated and experimental values were within errors of experimentally determined values for the vast majority of studied molecules. In Table 3, PAs of hindered phenols and their non-hindered analogues are compiled. Confrontation of the two data-sets indicates that PAs of hindered phenols are lower than those obtained for non-hindered phenols. Differences are in 21–40 kJ mol⁻¹ range. Larger differences between two groups of phenols were found in the case of electron-donating substituents. Differences tend to drop with the increase in electron-withdrawing effect of substituent.

Table 3. Gas-phase B3LYP/6-311++G** PAs and ETEs of sterically hindered and non-hindered *para*-substituted phenols in kJ mol⁻¹.

Substituent	PA		ETE	
	Hindered	Non-hindered ^a	Hindered	Non-hindered ^a
—	1411	1449	224	218
<i>p</i> -NH ₂	1427	1466	174	162
<i>p</i> -NMe ₂	1413	1453	184	174
<i>p</i> -OH	1419	1455	197	191
<i>p</i> -MeO	1420	1456	194	188
<i>p</i> - <i>t</i> -Bu	1411	1449	218	210
<i>p</i> -Me	1416	1454	212	204
<i>p</i> -Ph	1388	1419	240	238
<i>p</i> -F	1401	1436	228	224
<i>p</i> -Cl	1389	1422	243	241
<i>p</i> -Br	1385	1417	248	247
<i>p</i> -MeCO	1360	1387	283	287
<i>p</i> -CF ₃	1363	1390	284	288
<i>p</i> -CN	1347	1372	297	304
<i>p</i> -MeSO ₂	1347	1371	303	311
<i>p</i> -NO ₂	1325	1346	327	339

^a From Ref. (Klein 2006).

Lower proton affinities of hindered phenols with two electron-donating *tert*-butyl groups are a little bit surprising. In general, electron-donating groups induce an increase in PA. With exception of NH_2 group, for studied hindered phenols, electron-donating groups in *para* position cause rise in PA within 10 kJ mol^{-1} . On the other hand, PAs in (Klein 2006) showed that presence of *tert*-butyl group in *para* and *meta* position in non-hindered phenols did not affect PA. Their values were identical with PA of the non-substituted phenol. This indicates that *tert*-butyl groups in *ortho* positions exert opposite effect in comparison to *meta* and *para* positions and they lower PA. Electron-donating substituents in *para* position induce a small increase in PAs of hindered phenols (maximum 16 kJ mol^{-1}), while electron-withdrawing groups are able to lower PA significantly. For sterically hindered phenol with strong electron-withdrawing NO_2 group in *para* position, PA is lower by 86 kJ mol^{-1} . Obtained PAs lie in 102 kJ mol^{-1} range.

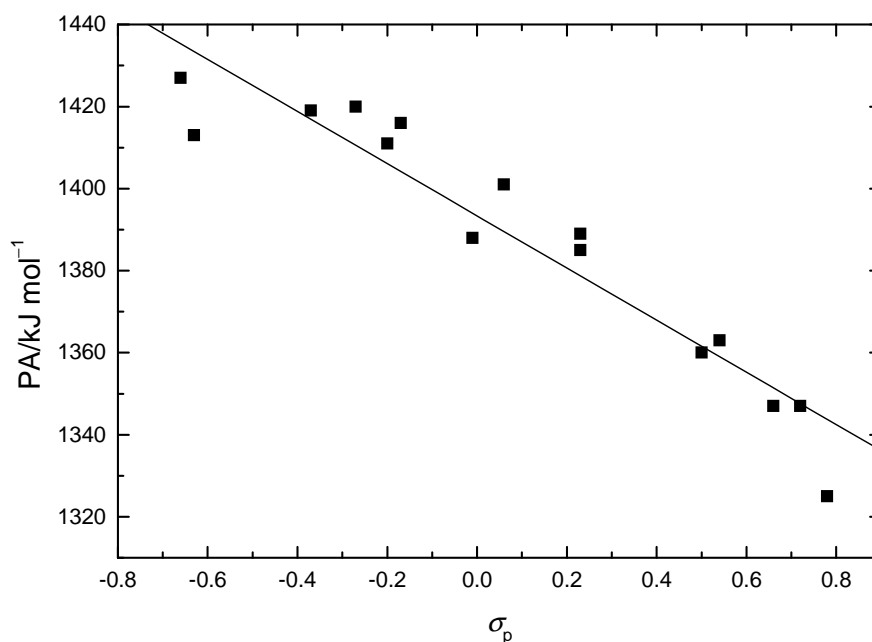


Fig. 3. Dependence of PA vs. σ_p .

In (Klein 2006) following dependence of PAs on Hammett constants σ_p was found for non-hindered phenols

$$\text{PA}/\text{kJ mol}^{-1} = 1429 - 82\sigma_p \quad (\text{non-hindered}) \quad (16)$$

In this work, we have obtained dependence for hindered phenols (Fig. 3) as follows

$$\text{PA}/\text{kJ mol}^{-1} = 1396 - 69\sigma_p \quad (\text{hindered}) \quad (17)$$

The correlation coefficients reached almost identical values of 0.965 (non-hindered) and 0.967 (hindered). In the two dependences, NMe₂ group was omitted from regression, since the corresponding PA value clearly did not follow the general trend. Eqs. 16 and 17 clearly demonstrate that in the case of PAs, presence of *tert*-butyl groups in *ortho* positions slightly attenuates the effect of substituents in *para* position.

Electron transfer enthalpies

Electron transfer from the phenoxide anion is the second step in SPLET mechanism, Eq. 3b. Values obtained for sterically hindered phenols are shown in Table 3. In this case no experimental values are available. There is also no theoretical study of substituent effect on non-hindered phenols ETEs available, except the paper (Klein 2006), where the reliability of obtained ETEs was supported indirectly on the basis of good agreement between experimental and calculated values of proton affinities and phenolic O–H bond dissociation enthalpies.

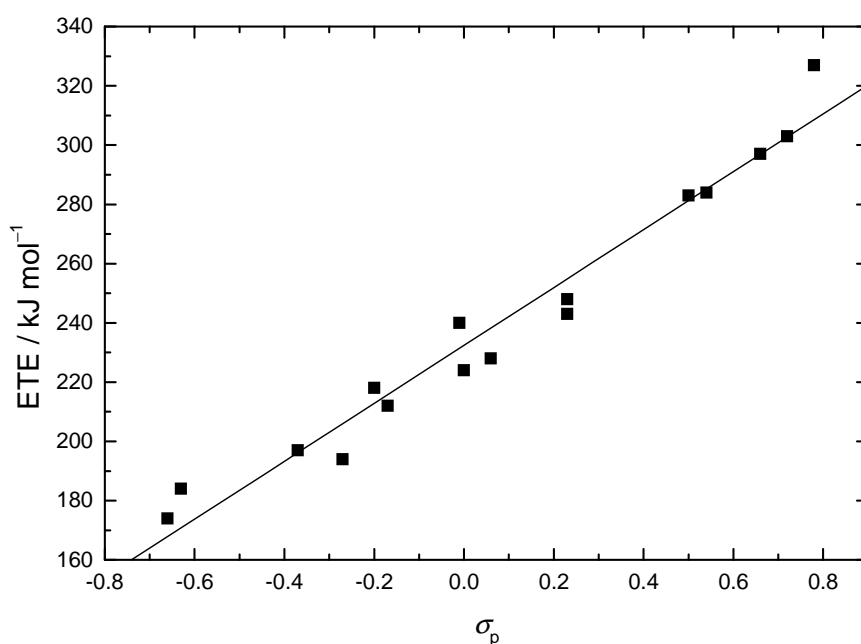


Fig. 4. Dependence of ETE vs. σ_p .

These ETE values are shown in the third column of Table 3. Comparison of ETEs obtained for non-hindered and hindered phenols indicates that ETEs of the majority of

hindered phenols are larger. On the other hand, ETEs of sterically hindered phenols with strong electron-withdrawing groups *p*-MeCO, *p*-CN, *p*-MeSO₂ and *p*-NO₂ groups are lower than ETEs of their non-hindered analogues. However, differences between ETEs for anions with the same substituent in *para* position are relatively small. They do not exceed 12 kJ mol⁻¹. The generally observed trend is also preserved: electron-donating groups cause a decrease in ETE and electron-withdrawing groups induce a rise in ETE. ETEs of studied hindered phenols are in 153 kJ mol⁻¹ range.

Dependence of ETEs on Hammett constants for non-hindered phenols (Klein 2006) showed very good linearity with correlation coefficient 0.970

$$\text{ETE/kJ mol}^{-1} = 232 + 105\sigma_p \quad (\text{non-hindered}) \quad (18)$$

In this work, we have found (Fig. 4)

$$\text{ETE/kJ mol}^{-1} = 233 + 97\sigma_p \quad (\text{hindered}) \quad (19)$$

with even higher value of correlation coefficient, $R = 0.982$.

Thermodynamically preferred mechanism

The criterion of the thermodynamically preferred mechanism is free energy, $\Delta_r G = \Delta_r H - T\Delta_r S$. However, in the case of studied processes, the absolute values of the entropic term $-T\Delta_r S$ reach only few units or tens of kJ mol⁻¹ and all free energies are only slightly shifted in comparison to corresponding enthalpies (Dewar 1990, Rimarčík 2010). Therefore, the values of BDE, PA and IP can show thermodynamically preferred mechanism. Due to the large differences, exceeding several hundreds of kJ mol⁻¹, HAT mechanism is thermodynamically preferred in gas-phase, where BDEs are significantly lower than ionization potentials. Proton transfer described by proton affinity is by ca one order higher than BDE.

On the other hand, especially in polar solvents (such as water, DMSO or ethanol), where proton solvation enthalpy is lower than -1000 kJ mol⁻¹ (Atkins 1998, Fifen 2011, Rimarčík 2010), domination of SPLET mechanism can be anticipated due to proton affinities significantly lower than O–H bond dissociation enthalpies. Contrary to proton affinities, bond dissociation enthalpies in gas-phase and solution-phase reach similar values and differences are usually within 10 kJ mol⁻¹ (Fifen 2011, Klein 2006 and 2007, Najafi 2011, Rimarčík 2010, Wright 2001). In the case of ionization potentials (the first step of SET-PT mechanism), solvents induce their decrease. However, ionization potential values in solution-phase remain higher than bond dissociation enthalpies (Fifen 2011, Klein 2006 and 2007, Rimarčík 2010

and 2011). Moreover, in (Musialik 2009), for various flavonoids – polyphenolic compounds, it was experimentally confirmed that SPLET dominates in polar solvents. Therefore, in future work, attention to solvent effect on the enthalpies related to reactions of charged species (IP, PDE, PA, ETE) will be in the interest of current research.

Correlation of BDE, PA and ETE with phenolic C–O bond length

In (Klein 2006), we have found that the increase in the Hammett constant of a substituent causes a shortening of the C–O bond. Absolute value of the correlation coefficient of linear $R(\text{C–O}) = f(\sigma_p)$ dependence reached 0.978. Therefore, in this work, we decided to investigate this type of dependence for sterically hindered phenols, too. In Table 4, we have compiled calculated lengths of phenolic C–O bond lengths of sterically hindered and non-hindered phenols from (Klein 2006). In comparison to non-hindered phenols, C–O bonds in hindered phenols are longer, average difference reached value of 0.0069 Å. Differences in C–O bond lengths are in 0.0058–0.0075 Å range. Despite the presence of large substituents in the two *ortho* positions, the linear trend between phenolic C–O bond length and Hammett constants is maintained

$$R(\text{C–O})/\text{Å} = 1.3767 - 0.0134\sigma_p \quad (\text{hindered}) \quad (20)$$

with absolute value of correlation coefficient of 0.981.

Table 4. Gas-phase B3LYP/6-311++G** phenolic C–O bond lengths in Å.

Substituent	Hindered	Non-hindered ^a
—	1.3771	1.3704
<i>p</i> -NH ₂	1.3841	1.3767
<i>p</i> -NMe ₂	1.3844	1.3771
<i>p</i> -OH	1.3819	1.3744
<i>p</i> -MeO	1.3824	1.3749
<i>p</i> - <i>t</i> -Bu	1.3785	1.3715
<i>p</i> -Me	1.3789	1.3719
<i>p</i> -Ph	1.3761	1.3693
<i>p</i> -F	1.3779	1.3707
<i>p</i> -Cl	1.3753	1.3684
<i>p</i> -Br	1.3747	1.3675
<i>p</i> -MeCO	1.3688	1.3628
<i>p</i> -CF ₃	1.3699	1.3632
<i>p</i> -CN	1.3676	1.3612
<i>p</i> -MeSO ₂	1.3678	1.3616
<i>p</i> -NO ₂	1.3643	1.3585

^a From Ref. (Klein 2006).

In previous papers (Klein 2006 and 2007) it was found that BDEs, PAs, and ETEs of *meta*- and *para*-substituted phenols also depend on C–O bond length linearly. Therefore, we have tried to plot the same dependences for sterically hindered phenols. For BDE, obtained dependence is as follows

$$\text{BDE/kJ mol}^{-1} = 3700 - 2500 R(\text{C-O})/\text{\AA} \quad (\text{hindered}) \quad (21)$$

with absolute value of correlation coefficient $|R| = 0.955$. For enthalpies related to SPLET mechanism, we have found

$$\text{PA/kJ mol}^{-1} = -5200 + 4800 R(\text{C-O})/\text{\AA} \quad (\text{hindered}) \quad (22)$$

$$\text{ETE/kJ mol}^{-1} = 10200 - 7300 R(\text{C-O})/\text{\AA} \quad (\text{hindered}) \quad (23)$$

Absolute values of correlation coefficients reached values of 0.977 (PA) and 0.996 (ETE). In Fig. 5, ETE = $f(R(\text{C-O}))$ dependence is depicted.

Unfortunately, in the case of IPs and PDEs worse correlations between these two enthalpies and phenolic C–O bond length have been found, absolute values of correlation coefficients have not exceed 0.92.

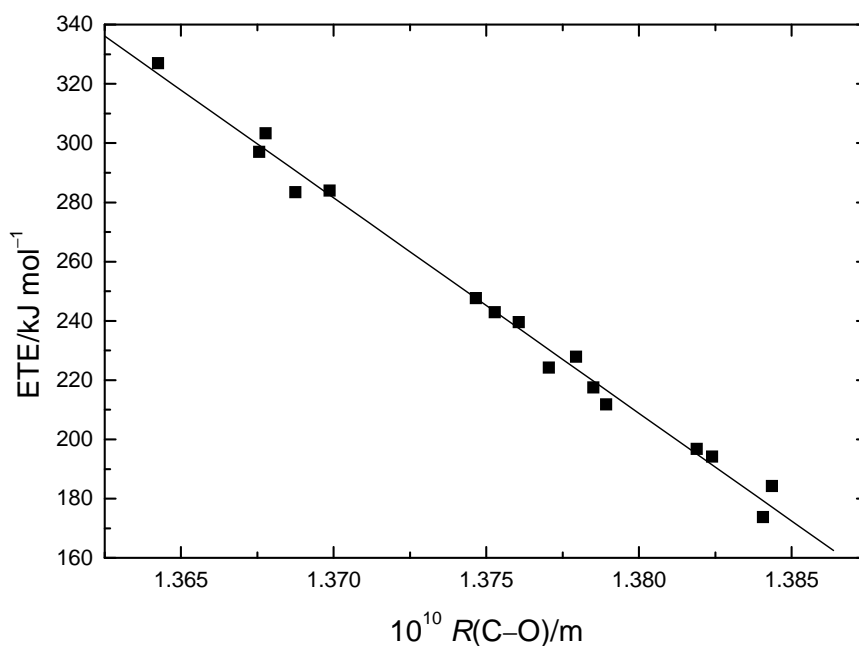


Fig. 5. Dependence of ETE vs. phenolic C–O bond length.

Conclusion

In this article, the phenolic O–H bond dissociation enthalpies, ionization potentials, proton dissociation enthalpies, proton affinities and electron transfer enthalpies for *para*-substituted sterically hindered phenols related to HAT, SET-PT and SPLET mechanisms of phenols antioxidant action were studied. DFT/B3LYP method with 6-311++G** basis set was used on the basis of previous experiences that confirmed that chosen approach offers reliable results with reasonable computational costs. Investigated substituents induce largest changes in IP (195 kJ mol^{-1}), then in ETEs (153 kJ mol^{-1}) and PDEs (140 kJ mol^{-1}). PAs lie in range of 102 kJ mol^{-1} and BDEs lie in relatively narrow range of 54 kJ mol^{-1} . Only in the case of BDEs, differences between for non-hindered and hindered phenols are approximately identical, i.e. two *tert*-butyl groups induce similar changes in BDE for molecules with all studied substituents in *para* position, regardless their electron-donating or electron-withdrawing character. For reaction enthalpies involving charged species (radical cations and anions), shifts in corresponding enthalpies (IP, PDE, PA, ETE) caused by two *tert*-butyl groups depend on the character of the third substituent in *para* position. Therefore, overall effect of the three substituents in sterically hindered phenols cannot be considered additive.

The linearity of all Hammett type dependences is satisfactory and obtained equations may be used for estimation of studied reaction enthalpies for *para*-substituted sterically hindered phenols from substituents Hammett constants or vice versa. Besides, O–H BDEs, PAs and ETEs are linearly dependent on phenolic C–O bond length. Therefore, the length of this bond may be successfully employed for prediction of reaction enthalpies related to HAT and SPLET mechanisms.

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