

Theoretical study of the energetics of carboxylic O—H bond cleavage in the *para*- and *meta*-substituted benzoic acid derivatives

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Abstract: Gas phase bond dissociation enthalpies (BDE) of *para*- and *meta*-substituted benzoic acids and proton affinities (PA) of their carboxylate anions were investigated using the B3LYP/6-311++G** method for 15 substituents with various electron-donating and electron-withdrawing effects. The employed computational method provided BDE and PA values in fair agreement with experimental data. The substituent effect on BDEs and PAs was analyzed in terms of Hammett constants. Found dependences exhibit satisfactory linearity and enable quick estimation of BDEs and PAs from the Hammett constants.

Keywords: bond dissociation enthalpy, proton affinity, hydrogen atom transfer (HAT), deprotonation, benzoic acid, phenol

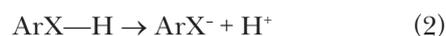
Introduction

Benzoic acid (ArCOOH) and phenol (ArOH) are weak acids and their acidity depends on the environment. In solutions, the solvent and counter ions play important roles and benzoic acid is more acidic than phenol. In the gas phase, benzoic acid is still more acidic, however, the difference between the two compounds is relatively small (Galaverna, 2015). The acidity is also affected by substituents attached to their aromatic rings. The knowledge of the most favorable deprotonation site in a molecule is the subject of great relevance in physical and organic chemistry. In antioxidant action research, experimental studies have shown that free radical scavenging of phenolic compounds significantly depends on pH, i.e. deprotonation of a compound affects its overall antioxidant effect (Lemańska et al., 2001; Halliwell and Gutteridge, 1989). Many naturally occurring antioxidants are polyphenolic substances possessing a different number of OH groups and showing various acidities (Álvarez-Diduk et al., 2013). Moreover, some antioxidants have also a carboxylic COOH group attached either directly to the aromatic ring (gallic acid, vanillic acid or syringic acid), or present in another fragment of the molecule (e.g. derivatives of cinnamic acid with a —CH=CH—COOH group).

In the study on the antioxidant effect and radical scavenging action thermodynamics, hydrogen atom transfer (HAT) from the parent molecule, ArXH:



and sequential proton-loss electron-transfer (SPLET) mechanisms seem to be the most important reaction pathways (Lemańska et al., 2001; Musialik et al., 2009; Vagánek et al., 2014) in ionization supporting solvents. In the two-step SPLET mechanism, the first step:



represents the deprotonation of the parent molecule. From the thermodynamic point of view, HAT is governed by the X—H bond dissociation enthalpy, BDE. In SPLET, proton affinity (PA) of the formed anion represents the reaction enthalpy of the process shown in eq. 2.

Bond dissociation enthalpies, as well as proton affinities, depend on the substituent and its position at the aromatic ring *via* inductive and spin delocalization effects (Bordwell et al., 1994; Klein and Lukeš, 2006a, 2006b).

The main aim of this work was to calculate the gas phase O—H BDE and PA values of the carboxylic group and to assess the substituent effect on the two reaction enthalpies for a set of 15 *para*- and *meta*-substituted benzoic acids, Fig. 1. Reliability of the obtained values was assessed by means of their comparison with available experimental data. Also, the results were compared with those obtained for *para*- and *meta*-substituted phenols (Klein and Lukeš, 2006a, 2006b) calculated for the same group

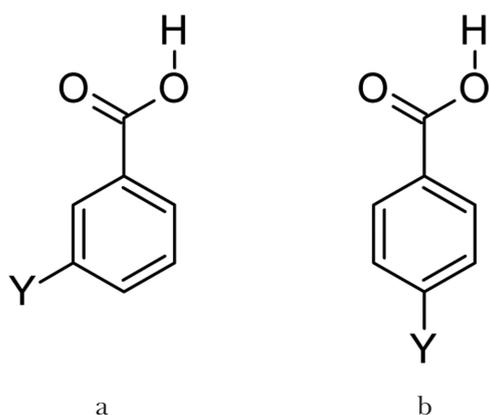


Fig. 1. Structure of meta- (a) and para-substituted (b) benzoic acids.

of substituents using identical computational approach.

Computational details

All calculations were performed using the Gaussian 09 program package (Frisch et al., 2009). Geometries of the studied molecules, radicals, and anions in the gas phase were optimized using the DFT method and the B3LYP functional (Becke, 1988; Lee et al., 1988; Frisch et al., 2009) without

any constraints (energy cut-off of 10^{-5} kJ mol $^{-1}$, final RMS energy gradient below 0.01 kJ mol $^{-1}$ Å $^{-1}$). For species having more conformers, all conformers were investigated. The conformer with the lowest electronic energy was used in this work. Calculations were performed in the 6-311++G** basis set (Krishnan et al., 1980; McLean and Chandler, 1980; Curtiss et al., 1995). The optimized structures were confirmed to be real minima by the frequency analysis (no imaginary frequency). All enthalpies were calculated for 298.15 K. From the total enthalpies, H , bond dissociation enthalpies and proton affinities were calculated as follows:

$$\text{BDE} = H(\text{ArCOO}^\bullet) + H(\text{H}^\bullet) - H(\text{ArCOOH}) \quad (3)$$

$$\text{PA} = H(\text{ArCOO}^-) + H(\text{H}^+) - H(\text{ArCOOH}) \quad (4)$$

Hydrogen atom and proton total enthalpies in the gas phase reached the following values: $H(\text{H}^\bullet) = -1312.75$ kJ mol $^{-1}$, $H(\text{H}^+) = 6.197$ kJ mol $^{-1}$.

Results and discussion

Bond dissociation enthalpies

Tables 1 and 2 compile calculated BDE of *para*- and *meta*-substituted benzoic acids together with available experimental data. For non-substituted benzoic

Tab. 1. Gas phase B3LYP/6-311++G** bond dissociation enthalpies, BDE, experimental values for *para*-substituted benzoic acids and Hammett constants, σ_p .

Substituent (Y)	BDE/kJ mol $^{-1}$		$\Delta\text{BDE}^a/\text{kJ mol}^{-1}$	σ_p^b
	Calculated	Experimental		
-	434	439 ^c , 444 ^d , 464 ^c , 469 ^c	0	0
<i>p</i> -NMe ₂	426		-8	-0.83
<i>p</i> -NH ₂	430		-4	-0.66
<i>p</i> -OH	433		-1	-0.37
<i>p</i> -OMe	432	447 ^d	-2	-0.27
<i>p</i> - <i>t</i> Bu	432	448 ^d	-2	-0.20
<i>p</i> -Me	433	451 ^d	-1	-0.17
<i>p</i> -Ph	433		-1	-0.01
<i>p</i> -F	435		1	0.06
<i>p</i> -Br	436	449 ^d	2	0.23
<i>p</i> -Cl	435	442 ^d	1	0.23
<i>p</i> -COMe	436		2	0.50
<i>p</i> -CF ₃	438		4	0.54
<i>p</i> -CN	439		5	0.66
<i>p</i> -SO ₂ Me	438		4	0.72
<i>p</i> -NO ₂	439	448 ^d	5	0.78

^a $\Delta\text{BDE} = \text{BDE}(\text{Y}-\text{ArCOOH}) - \text{BDE}(\text{ArCOOH})$.

^bData taken from Hansch et al., 1991.

^cData taken from Luo, 2005.

^dData taken from Denisov and Tumanov, 2005.

Tab. 2. Gas phase B3LYP/6-311++G** bond dissociation enthalpies, BDE, experimental values for *meta*-substituted benzoic acids and Hammett constants, σ_m .

Substituent (Y)	BDE/kJ mol ⁻¹		Δ BDE ^a /kJ mol ⁻¹	σ_m ^b
	Calculated	Experimental		
-	434	439 ^c , 444 ^d , 464 ^c , 469 ^c	0	0
<i>m</i> -NH ₂	433		-1	-0.16
<i>m</i> -NMe ₂	431		-3	-0.16
<i>m</i> - <i>t</i> Bu	433		-1	-0.10
<i>m</i> -Me	433	449 ^d	-1	-0.07
<i>m</i> -Ph	433		-1	0.06
<i>m</i> -OH	433		-1	0.12
<i>m</i> -OMe	433	448 ^d	-1	0.12
<i>m</i> -F	436		2	0.34
<i>m</i> -Cl	436	449 ^d	2	0.37
<i>m</i> -COMe	436		2	0.38
<i>m</i> -Br	436	450 ^d	2	0.39
<i>m</i> -CF ₃	438		4	0.43
<i>m</i> -CN	439		5	0.56
<i>m</i> -SO ₂ Me	438		4	0.60
<i>m</i> -NO ₂	439		5	0.71

^a Δ BDE = BDE(Y—ArCOOH) - BDE(ArCOOH).^bData taken from Hansch et al., 1991.^cData taken from Luo, 2005.^dData taken from Denisov and Tumanov, 2005.

acid, published experimental BDEs are in relatively wide range of 30 kJ mol⁻¹. The lowest experimental value is higher than the calculated one by 5 kJ mol⁻¹. Experimental BDEs for substituted benzoic acids are, unfortunately, rather scarce. All experimental values published by Denisov and Tumanov using the correlation method (Denisov and Tumanov, 2005) are higher than the calculated ones. For *para*-substituted benzoic acids, differences between the calculated and the six experimental BDEs are in the range from 7 to 18 kJ mol⁻¹. Only four experimental values for *meta*-substituted benzoic acids are available, which are higher by 13–16 kJ mol⁻¹ than calculated BDEs. It may indicate that the determined BDE values were underestimated. However, it should be noted that available experimental values were obtained from the solution phase experiments. Gas phase values are usually close, but not necessarily identical, to the solution phase BDEs (Bakalbassis et al., 2003; Klein and Lukeš, 2006a; Rimarčík et al., 2011; Vagánek et al., 2014). Therefore, usual confrontation of calculated gas phase BDEs with solution phase experimental data may not be fully correct.

Substituent (Y) induced changes in BDE, defined in terms of Δ BDE values, where Δ BDE = BDE(Y—ArCOOH) - BDE(ArCOOH) of the investigated

groups are also summarized in Tables 1 and 2. For *para*-substituted benzoic acid derivatives, electron-donating groups (*t*Bu, OMe, NH₂, NMe₂) tend to reduce BDEs by 2–8 kJ mol⁻¹. On the other hand, strong electron-withdrawing groups, such as CN, CF₃, NO₂ and SO₂Me, increase the BDE values by 4–5 kJ mol⁻¹. The studied substituents in the *para* position induce changes up to 13 kJ mol⁻¹, which are significantly less pronounced than those obtained for *para*-substituted phenols, where substituent induced changes in BDE were up to 58 kJ mol⁻¹ (Klein and Lukeš, 2006b). Analogously, for *meta*-substituted phenols, the changes in BDEs up to 17 kJ mol⁻¹ were observed, while for benzoic acid derivatives, the effect of substituents was considerably weaker, up to 8 kJ mol⁻¹. Again, the presence of strong electron-donating groups resulted in lower BDEs, while strong electron-withdrawing groups caused an increase in the BDE values. For the majority of substituents in the *meta* position, BDE values were in a very narrow range, up to 4 kJ mol⁻¹. Thus, it can be concluded that substituents in the *meta* position alter BDEs only in a very small extent. Moreover, with the exception of the two strongest electron-donating (NH₂ and NMe₂) groups, BDE values for *para*- and *meta*-substituted benzoic acid derivatives are practically identical; differences do

not exceed 1 kJ mol⁻¹, which clearly demonstrates that the majority of the studied substituents exert practically the same effect on BDE in the two positions.

Comparing BDEs found for benzoic acid derivatives with values obtained for *para*- and *meta*-substituted phenols (Klein and Lukeš, 2006b), homolytic cleavage of the phenolic O—H bond shows lower energy requirement. In phenols, gas phase BDEs in the range from 306 to 364 kJ mol⁻¹ were observed and all values are lower than O—H BDEs of the carboxylic group in substituted benzoic acids. Differences are in tens of kJ mol⁻¹. In case of strong electron-donating groups, they even exceed 100 kJ mol⁻¹. It should be noted that in case of *p*-OH and *m*-OH substituted benzoic acids, dissociation of the phenolic OH group is thermodynamically preferred. For its homolytic cleavage, BDE values of 357 kJ mol⁻¹ (*para*) and 353 kJ mol⁻¹ (*meta*) were obtained. Analogously, for *p*-NH₂ and *m*-NH₂ substituted benzoic acids, computed N—H BDEs are lower than carboxylic group O—H BDE, reaching the values of 381 kJ mol⁻¹ (*para*) and 351 kJ mol⁻¹ (*meta*). Hence, the COOH group represents the electron-withdrawing substituent with the Hammett constants $\sigma_p = 0.45$ and $\sigma_m = 0.37$ (Hansch et al., 1991).

The Hammett equation (and its extended forms) represents one of the most widely used means for the study and interpretation of organic reactions and their mechanisms. Hammett constants, σ_p (for substituent in the *para* position) and σ_m (for substituent in the *meta* position), are able to successfully predict the equilibrium and rate constants for a

variety of reactions (Hansch et al., 1991; Krygowski and Stępień, 2005). Fig. 2 presents the correlation between calculated gas phase BDEs and Hammett constants, σ_p , for 15 studied *para*-substituted benzoic acid derivatives. The equation obtained from the linear regression is as follows:

$$\text{BDE}/\text{kJ mol}^{-1} = 433.75 + 7.0 \times \sigma_p \quad (5)$$

The correlation coefficient, R , reached the value of 0.978. In Fig. 3, an analogous dependence is depicted for *meta*-substituted derivatives and the following equation was obtained:

$$\text{BDE}/\text{kJ mol}^{-1} = 432.92 + 8.7 \times \sigma_m \quad (6)$$

with correlation coefficient $R = 0.961$. Both dependences showed good linearity and they can be used for fast estimation of BDEs from the Hammett constant of a substituent or *vice versa*. For *meta*-substituted benzoic acids, the line slope value is larger though the two values can be considered similar with respect to their standard deviations. An opposite trend was observed for phenols (Klein and Lukeš 2006b). Moreover, both dependences were significantly steeper with the line slopes values of 36.7 (*para*) and 18.7 (*meta*).

Proton affinities

Calculated gas phase proton affinities are summarized in Tables 3 and 4 together with experimental data available for eight substituents (McMahon and Kebarle, 1977) obtained using a pulsed beam high-pressure mass spectrometer (HPMS); with only one exception (*m*-NO₂), the experimental values are lower than the calculated ones. Found compu-

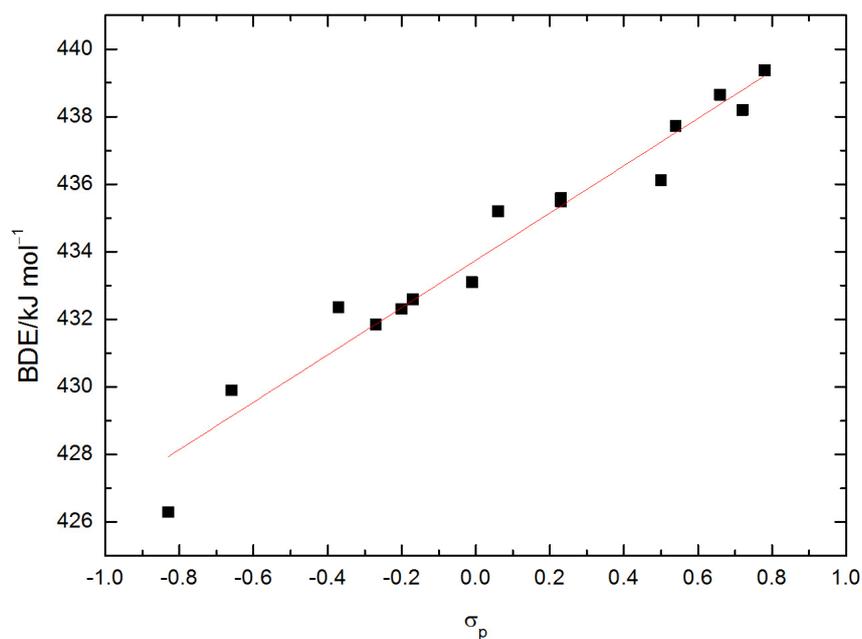


Fig. 2. Dependence of the gas phase O—H BDE on Hammett constants, σ_p .

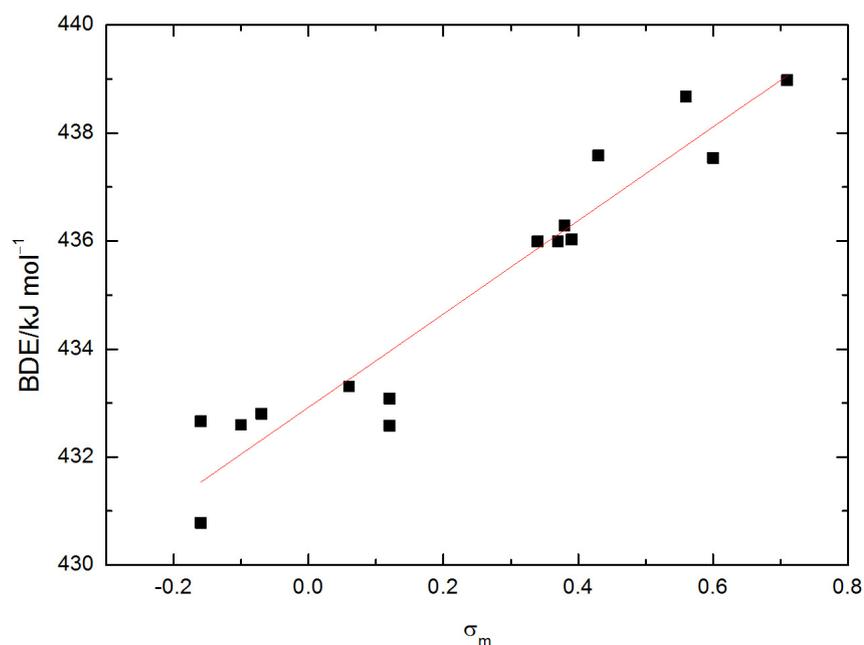


Fig. 3. Correlation of the gas phase O—H BDE with Hammett constants, σ_m .

Tab. 3. Gas phase B3LYP/6-311++G** proton affinities, PA, experimental values for *para*-substituted benzoic acids and Hammett constants, σ_p .

Substituent (Y)	PA/kJ mol ⁻¹		ΔPA^a /kJ mol ⁻¹	σ_p^b
	Calculated	Experimental ^c		
-	1417	1411	0	0
<i>p</i> -NMe ₂	1438	1421	21	-0.83
<i>p</i> -NH ₂	1438		21	-0.63
<i>p</i> -OH	1422	1394	5	-0.37
<i>p</i> -OMe	1426	1414	9	-0.27
<i>p</i> - <i>t</i> Bu	1421		4	-0.20
<i>p</i> -Me	1425	1416	8	-0.17
<i>p</i> -Ph	1410		-7	-0.01
<i>p</i> -F	1404	1399	-13	0.06
<i>p</i> -Br	1396		-21	0.23
<i>p</i> -Cl	1398	1393	-19	0.23
<i>p</i> -COMe	1391		-26	0.50
<i>p</i> -CF ₃	1381		-36	0.54
<i>p</i> -CN	1371	1366	-46	0.66
<i>p</i> -SO ₂ Me	1372		-45	0.72
<i>p</i> -NO ₂	1363	1362	-54	0.78

^a $\Delta PA = PA(Y-ArCOOH) - PA(ArCOOH)$.

^bData taken from Hansch et al., 1991.

^cData taken from McMahon and Kebarle, 1977.

tational results are in very good agreement with experimental data. The average deviation reached 10 kJ mol⁻¹ for *para*-substituted benzoic acids and 5 kJ mol⁻¹ for *meta*-substituted ones. The largest discrepancy between the calculated and experimental HPMS values was found for *para*-hydroxybenzoic

acid (28 kJ mol⁻¹). Exceptionally low HPMS PA did not follow the general rule that the presence of an electron-donating substituent results in an increase in PA. Very recently, Galaverna et al. (2015) have computed gas phase PA values of *ortho*-, *meta*-, and *para*-substituted hydroxybenzoic acids at the

G3MP2 level using MP2/6-31++G** optimized geometries and vibrational frequencies. The found values are in accordance with our obtained PAs, differences are lower than 3 kJ mol⁻¹.

Tables 3 and 4 present also Δ PA values, where Δ PA = PA(Y—ArCOOH) - PA(ArCOOH), which show that electron-donating substituents cause

an increase in the PA values, whereas electron-withdrawing substituents are able to lower PA by a larger extent. PAs found were in the range up to 75 kJ mol⁻¹. For phenols, the calculated PA values were in a wider range, up to 121 kJ mol⁻¹. Figs. 4 and 5 show PA = $f(\sigma_p)$ and PA = $f(\sigma_m)$ dependences, respectively.

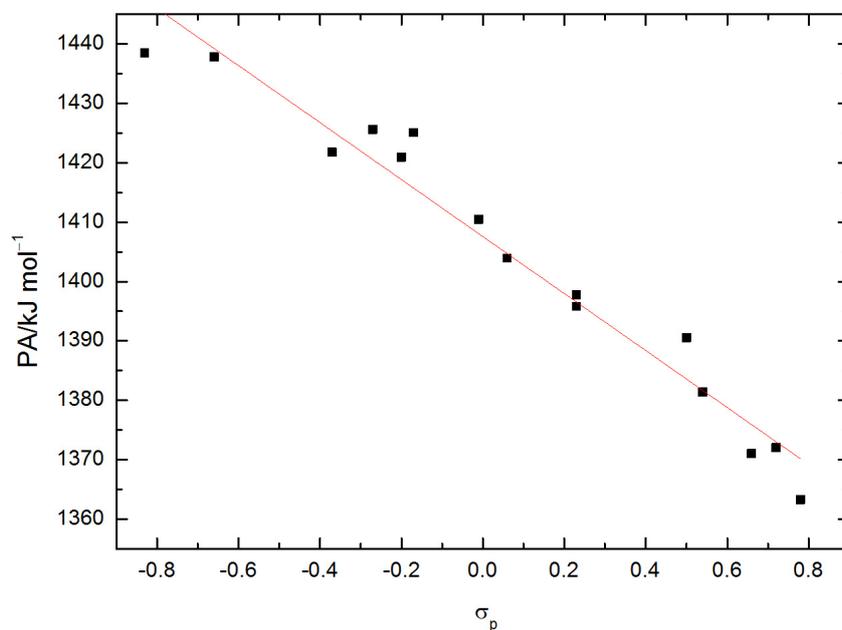


Fig. 4. Correlation of the gas phase PA with Hammett constants, σ_p .

Tab. 4. Gas phase B3LYP/6-311++G** proton affinities, PA, experimental values for *meta*-substituted benzoic acids and Hammett constants, σ_m .

Substituent (Y)	PA/kJ mol ⁻¹		Δ PA ^a /kJ mol ⁻¹	σ_m ^b
	Calculated	Experimental ^c		
-	1417	1411	0	0
<i>m</i> -NH ₂	1420	1418	3	-0.16
<i>m</i> -NMe ₂	1427		10	-0.16
<i>m</i> - <i>t</i> Bu	1418		1	-0.10
<i>m</i> -Me	1420	1414	3	-0.07
<i>m</i> -Ph	1409		-8	0.06
<i>m</i> -OH	1416	1406	-1	0.12
<i>m</i> -OMe	1420	1409	3	0.12
<i>m</i> -F	1399	1395	-18	0.34
<i>m</i> -Cl	1394	1392	-23	0.37
<i>m</i> -COMe	1390		-27	0.38
<i>m</i> -Br	1392		-25	0.39
<i>m</i> -CF ₃	1384		-33	0.43
<i>m</i> -CN	1373	1369	-44	0.56
<i>m</i> -SO ₂ Me	1373		-44	0.60
<i>m</i> -NO ₂	1369	1371	-48	0.71

^a Δ PA = PA(Y—ArCOOH) - PA(ArCOOH).

^bData taken from Hansch et al., 1991.

^cData taken from McMahon and Kebarle, 1977.

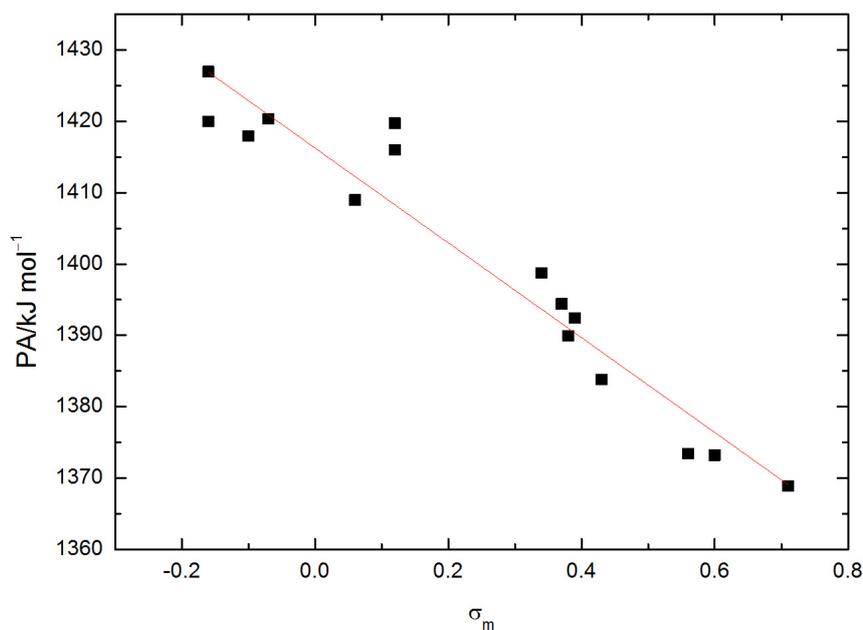


Fig. 5. Correlation of the gas phase PA with Hammett constants, σ_m .

Linear regression provided these equations:

$$\text{PA}/\text{kJ mol}^{-1} = 1407.6 - 48.0\sigma_p \quad (7)$$

$$\text{PA}/\text{kJ mol}^{-1} = 1416.3 - 66.5\sigma_m \quad (8)$$

with the correlation coefficient values of -0.979 (*para*) and -0.967 (*meta*).

A comparison with phenols indicated that gas phase PA values of substituted benzoic acids are, with three exceptions, lower for the investigated substituents. For phenols (Klein and Lukeš, 2006a), calculated PAs were in the range from 1346 kJ mol^{-1} (*p*-NO₂) to 1466 kJ mol^{-1} (*p*-NH₂). Only for the COMe, SO₂Me, and NO₂ groups in the *para* position, PAs of the corresponding phenols are lower than values obtained for benzoic acids.

For OH and NH₂ groups, proton affinities corresponding to their deprotonation were also calculated. The following values were found: PA(*p*-OH) = 1387 kJ mol^{-1} , PA(*m*-OH) = 1419 kJ mol^{-1} , PA(*p*-NH₂) = 1467 kJ mol^{-1} , PA(*m*-NH₂) = 1481 kJ mol^{-1} . Only in case of an OH group placed in the *para* position to the COOH group, its deprotonation is thermodynamically preferred in terms of the gas phase PA values. This result is in agreement with the work of Galaverna et al. (2015). Moreover, the calculated value is very close to the value assigned by McMahon and Kebarle (1977) to carboxylic COOH group deprotonation (1394 kJ mol^{-1}), which did not follow the overall trend. In comparison to non-substituted phenol PA (Klein and Lukeš, 2006a), the COOH group located in the *para* position to the OH group resulted in a 62 kJ mol^{-1} decrease in its PA. If the two groups are mutually in the *meta* position, a

30 kJ mol^{-1} drop in the phenolic OH group PA was found.

Conclusion

In this work, the gas phase O—H bond dissociation enthalpies of carboxylic COOH group for *para*- and *meta*-substituted benzoic acid derivatives and proton affinities of the corresponding carboxylate anions were investigated using B3LYP/6-311++G** method. Employed computational approach gives gas phase reaction enthalpies of homolytic carboxylic OH group cleavage and COOH group deprotonation in good agreement with available experimental data. The electron-donating groups decrease the BDE and increase the PA values. On the other hand, the presence of electron-withdrawing groups resulted in higher BDE and lower PA values. Linearity of the corresponding Hammett type dependences can be considered satisfactory. As it was expected, gas phase O—H BDEs are considerably lower in phenols. The majority of the calculated gas phase PA values is lower for COOH deprotonation. However, computed proton affinities indicate that the presence of strong electron-withdrawing groups causes higher acidity of the phenolic OH group in comparison to the COOH one. In terms of the obtained PA values, OH group deprotonation was found to be thermodynamically preferred in *p*-OH substituted benzoic acid. Because the SPLET mechanism is relevant mainly in the solution phase, a study of non-polar and polar solvents effect on the investigated proton affinities is inevitable. From the phenolic acids antioxidant action point of view,

the carboxylic COOH group attached to the aromatic ring considerably lowers PA of the phenolic OH group (especially in the *para* position) and may enhance its antioxidant potency in the SPLET mechanism.

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