

On the enthalpies of homolytic Se—H bond cleavage in *para*-substituted benzeneselenols

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Abstract: In this work, the substituent effect on the Se—H bond dissociation enthalpy (BDE) for benzeneselenol and ten *para*-substituted benzeneselenols was investigated. The set of various electron-donating and electron-withdrawing substituents was used. The gas-phase bond dissociation enthalpies were calculated using B3LYP/6-311++G** method. Obtained trends were compared with those found for *para*-substituted phenols and thiophenols for the same set of substituents. While the $BDE = f(\sigma_p)$ dependences for phenols and thiophenols exhibit very good linearity, for benzeneselenols, the linearity is rather insufficient. It was found for oxygen, sulphur and selenium that the larger the atom is, the weaker the substituent induced changes in corresponding BDE values are. It has been also observed that the larger the atom, the smaller corresponding BDEs.

Keywords: DFT, bond dissociation enthalpy, benzeneselenol

Introduction

Compounds containing C—Se bond represent an important group of key intermediates in various reactions in organic syntheses (Srinivas et al. 2009). Benzeneselenol and its derivatives have found the application also in the synthesis of electrically conductive polymers (Tsuchida et al. 1993; Metaka et al. 1995). The non-substituted benzeneselenol is widely used as a fast radical trapping agent (Choi et al. 1998) and polarity-reversal catalyst (Crich et al. 1996).

In general, on exposure to air, selenols readily undergo hydrogen abstraction by molecular oxygen to generate selenium radicals even at room temperature or below (Chu and Lewicki 1977). In the case of the benzeneselenol and its derivatives (ArSeH), a selenophenoxy radical (ArSe•) formation can be described by equation 1. Structure of benzeneselenol and its *para*-substituted derivatives studied is depicted in Figure 1.



Reaction enthalpy of this process is the bond dissociation enthalpy. It is given by equation 2, where the $H(\text{ArSe}^\bullet)$ stands for the total enthalpy of the selenophenoxy radical, the $H(\text{H}^\bullet)$ for the total enthalpy of the abstracted hydrogen atom and the $H(\text{ArSeH})$ is the total enthalpy of neutral molecule

$$\text{BDE} = H(\text{ArSe}^\bullet) + H(\text{H}^\bullet) - H(\text{ArSeH}) \quad (2)$$

There are no available experimental or theoretical BDE values of substituted benzeneselenols in the literature. Only the Se—H bond dissociation enthalpy for the benzeneselenol has been determined by D.

T. Leeck et al. in range of 318–335 kJ mol⁻¹ (Leeck et al. 1996). Here, the quantum chemistry appears as a suitable tool for estimation of unavailable quantities and trends between them without an experiment.

The main aim of this work is to investigate the substituent effect on BDEs in the set of ten *para*-substituted benzeneselenols using the same theoretical approach that provided reliable results for phenols and thiophenols studied in previous works (Klein and Lukeš 2006; Klein and Lukeš 2006; Rimarčík et al. 2011). Because the oxygen, sulphur and selenium belong to the same group in the periodic table of elements, we would like to perform also the comparison of the trends obtained for *para*-substituted phenols, thiophenols and benzeneselenols.

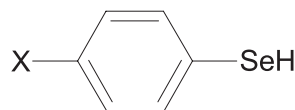


Fig. 1. Structure of benzeneselenol (X = H) and studied *para*-substituted benzeneselenols (X = NMe₂, NH₂, O-*i*-Pr, OMe, OH, SH, *t*-Bu, F, Br, Cl), where O-*i*-Pr is the isopropoxy group ((CH₃)₂—CH₂—O—).

Computational details

All calculations were performed using Gaussian 03 program package (Frisch et al. 2003). The geometry of each compound and radical structure was optimized in the gas-phase using DFT method with B3LYP functional without any constraints (energy

cut-off of 10^{-5} kJ mol⁻¹, final RMS energy gradient under 0.01 kJ mol⁻¹ Å⁻¹) (Becke 1993). For the species having more conformers, all conformers were investigated. Calculations were performed in the 6-311++G** basis set (Binkley et al. 1980). The optimized structures were confirmed to be real minima by frequency analysis (no imaginary frequency). All enthalpies were calculated for 298.15 K. Hydrogen atom total enthalpy in the gas-phase, $H(H^\bullet)$, obtained by above mentioned approach reached the value of -1312.48 kJ mol⁻¹.

Results and discussion

Calculated values of Se—H BDE are summarized in the first column of Table 1. As it was mentioned above, no experimental or theoretical BDE values of studied structures are available, only the Se—H bond dissociation enthalpy for the benzeneselenol has been found in range of 318–335 kJ mol⁻¹ (Leeck et al. 1996). As it can be seen in the Table 1, our calculated value is in the middle of the experimentally found range (first row). All studied substituents cause the decrease in the Se—H BDE values. The electron-donating groups decrease Se—H BDE values more than weak electron-withdrawing groups (Table 1). This trend can be observed also in the case of O—H BDEs of phenols and S—H BDEs of thiophenols, but in the case of benzeneselenols, the drop in BDEs, induced by the relatively weak electron-withdrawing groups, is significantly higher in comparison to phenols and thiophenols. No uniform shift has been found between the Se—H BDE values and O—H BDEs or Se—H BDE values and S—H BDEs.

When we do not take the values obtained for non-substituted phenol, thiophenol and benzeneselenol into account, found BDEs for *para*-substituted phenols, thiophenols and benzeneselenols are in 37 kJ mol⁻¹, 22 kJ mol⁻¹ and 16 kJ mol⁻¹ ranges, respectively. Therefore, it can be established for oxygen, sulphur and selenium that the larger the atom is, the weaker the substituent induced changes in corresponding BDE values are. It can be also seen that the larger the atom, the smaller corresponding BDEs.

The Hammett equation (and its extended forms) 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 substituent in *meta* position) and σ_p (for substituent in *para* position) are able to predict equilibrium and rate constants for a variety of families of reactions successfully (Hansch et al. 1991; Krygowski and Stepień 2005). They correlate very well with the changes in BDE in the case of *para*-substituted phenols and thiophenols (Klein and Lukeš 2006; Rimarčík et al. 2011). Figure 2 presents the correlation between Hammett constants σ_p and calculated gas-phase Se—H BDEs for ten studied *para*-substituted benzeneselenols. The equation obtained from the linear regression is as follows

$$\text{BDE/kJ mol}^{-1} = 291.97 + 13.6 \times \sigma_p \quad (\text{benzeneselenols, gas-phase}) \quad (3)$$

The correlation coefficient, R , reached the value of 0.924. For the correct comparison, we have performed also the correlations between Hammett constants σ_p and gas-phase O—H BDEs and the

Tab. 1. Calculated gas-phase B3LYP/6-311++G** bond dissociation enthalpies (BDE) of the *para*-substituted benzeneselenols, phenols and thiophenols in kJ mol⁻¹ and Hammett constants σ_p .

| Substituent | Benzeneselenols | Phenols ^a | Thiophenols ^b | σ_p^c |
|----------------------------|-----------------|----------------------|--------------------------|--------------|
| non-substituted | 326 | 347 | 316 | |
| <i>p</i> -NMe ₂ | 279 | 306 | 292 | -0.83 |
| <i>p</i> -NH ₂ | 282 | 308 | 296 | -0.66 |
| <i>p</i> -O- <i>i</i> -Pr | 286 | 321 ^d | 301 ^d | -0.45 |
| <i>p</i> -OMe | 288 | 323 | 303 | -0.27 |
| <i>p</i> -OH | 289 | 325 | 304 | -0.37 |
| <i>p</i> - <i>t</i> -Bu | 293 | 339 | 311 | -0.20 |
| <i>p</i> -SH | 290 | 331 ^d | 305 ^d | 0.15 |
| <i>p</i> -F | 294 | 340 | 311 | 0.06 |
| <i>p</i> -Br | 295 | 343 | 314 | 0.23 |
| <i>p</i> -Cl | 295 | 342 | 314 | 0.23 |

^aData taken from Ref. Klein and Lukeš 2006,

^bData taken from Ref. Rimarčík et al. 2011,

^cData taken from Ref. Hansch et al. 1991,

^dData calculated by B3LYP/6-311++G** approach.

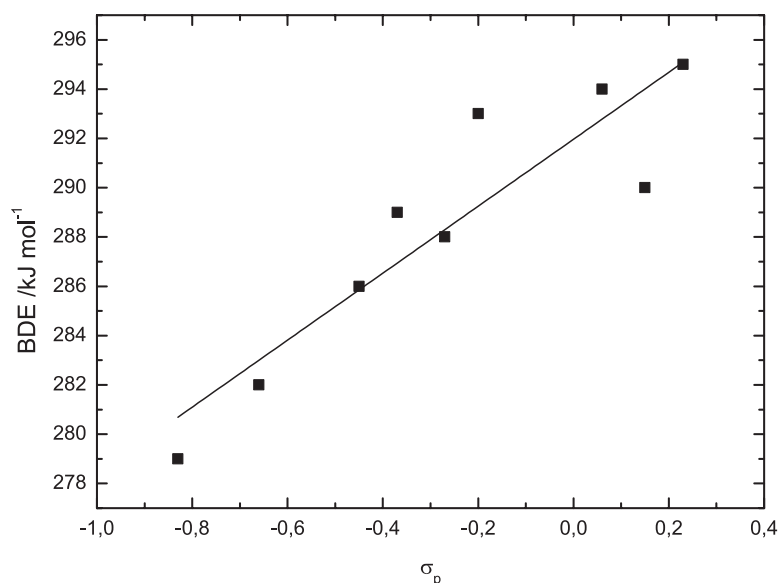


Fig. 2. Dependence of gas-phase Se—H BDE (kJ mol^{-1}) on Hammett constants σ_p .

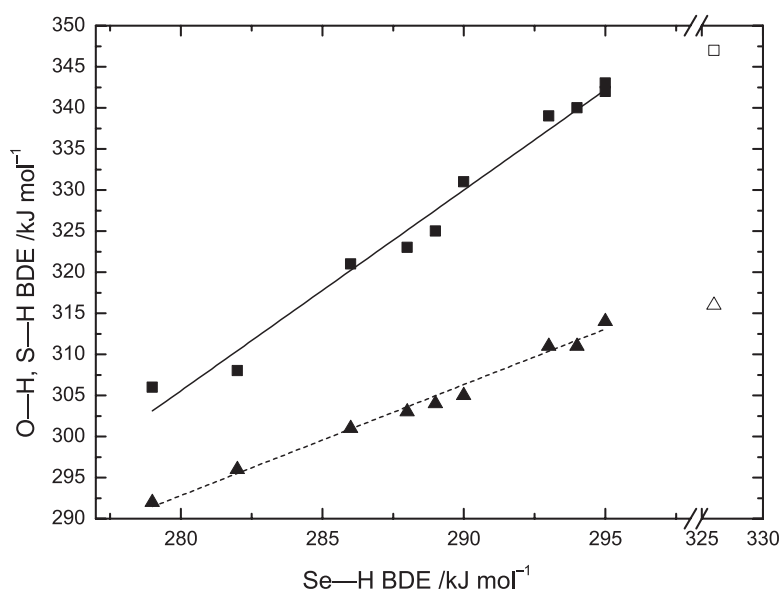


Fig. 3. Correlation of S—H BDEs with Se—H BDEs (triangles, dashed line) and correlation of O—H BDEs with Se—H BDEs (squares, solid line).

same one for gas-phase S—H BDEs for the same set of substituents.

These equations have been obtained

$$\text{BDE}/\text{kJ mol}^{-1} = 335.3 + 36.2 \times \sigma_p \quad (4)$$

(phenols, gas-phase)

$$\text{BDE}/\text{kJ mol}^{-1} = 309.60 + 20.30 \times \sigma_p \quad (5)$$

(thiophenols, gas-phase)

Correlation coefficients, R , achieved following values: 0.986 (phenols) and 0.993 (thiophenols). It should be noted that in the case of phenols and thiophenols, the BDE values for *para*-SH- and *para*-*t*-Bu-substituted phenols and thiophenols were excluded from the linear regression. While the

linearity of dependences $\text{BDE} = f(\sigma_p)$ for phenols and thiophenols can be considered very good also in this smaller set of substituents, the linearity of equation 3 is rather poor.

In the Figure 3, the dependences O—H BDE = $f(\text{Se—H BDE})$ and S—H BDE = $f(\text{Se—H BDE})$ are depicted. The following equations have been obtained

$$\begin{aligned} \text{O—H BDE}/\text{kJ mol}^{-1} &= \\ &= -379 + 2.44 \times \text{Se—H BDE}/\text{kJ mol}^{-1} \quad (\text{phenols}) \quad (6) \end{aligned}$$

$$\begin{aligned} \text{S—H BDE}/\text{kJ mol}^{-1} &= \\ &= -86 + 1.352 \times \text{Se—H BDE}/\text{kJ mol}^{-1} \quad (7) \\ &\quad (\text{thiophenols}) \end{aligned}$$

Both equations show very good linearity with correlation coefficients 0.991 and 0.994 respectively. The open square and open triangle denote the values not included in the linear regressions (non-substituted structures). Slopes in the equations (6) and (7) are higher than 1 and the slope of dependence O—H BDE = $f(\text{Se—H BDE})$ is higher than that of the S—H BDE = $f(\text{Se—H BDE})$ one. Therefore, in the case of *para*-substituted phenols, the substituent effect on the BDE values is larger than that for the *para*-substituted thiophenols and the substituent induced changes in BDEs are weakest in the case of benzeneselenols. Figure 3 also shows that the substituent effect on BDE values is strongest in the case of stronger electron-withdrawing substituents and weaker for stronger electron-donating substituents (within the frame of chosen substituents set).

Conclusion

In this paper, the gas-phase bond dissociation enthalpies of *para*-substituted benzeneselenols were investigated using DFT/B3LYP/6-311++G** approach. Observed trends were compared with the trends obtained for *para*-substituted phenols and thiophenols using the same theoretical approach. The electron-donating substituents decrease Se—H BDE values more than the weak electron-withdrawing substituents. This trend can be observed also in the case of O—H BDEs of phenols and S—H BDEs of thiophenols. While the linearity of dependences BDE = $f(\sigma_p)$ for phenols and thiophenols have been found very good, benzeneselenols exhibit relatively poor linearity. For oxygen, sulphur and selenium, it has been found that the larger the atom is, the weaker the substituent induced changes in corresponding BDEs are. It has been also observed

that the larger the atom, the smaller corresponding BDEs.

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