Computational Assessment of Polar Ground-State Effects on the Bond Dissociation Energies of Benzylic and Related Bonds

Werner M. Nau*

Institut für Physikalische Chemie, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

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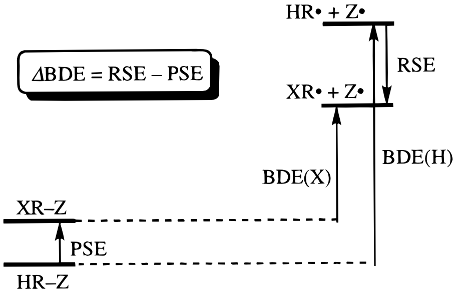
Introduction

It is well known that aryl substituents cause significant variations in the homolytic bond dissociation energies (BDEs) of benzylic and related bonds, e.g., for toluenes, phenols, and anilines.[1−8] These effects of remote aryl substituents are of prominent interest in radical chemistry,[9] since steric substituent interactions, which are well known to affect the BDEs in proximately substituted alkanes,[10] should be negligible. As a consequence, the substituent effects in benzenoid systems have often been related to substituent-dependent changes in radical stabilization energy (RSE). However, over the years, a number of experimental results have revealed significant contributions of the polar ground-state stabilization energy (PSE) in addition to radical effects.[1−8] Thus, a decrease in BDE caused by a substituent X can either be due to a stabilization of the resulting radical XR• or to a polar destabilization of the undissociated molecule XR−Z as shown in Scheme 1.

Scheme 1



Since substituent effects on the PSE cannot be measured directly, their assessment requires the use of two-parameter linear energy relationships or quantum-mechanical calculations. The two-parameter method can succeed only in a few cases[7] since it warrants reliable sets of radical substituent parameters, which are hardly accessible, e.g., for phenoxy radicals.[4] Hence, there is a substantial interest for the computational analysis of polar ground-state effects, since their knowledge allows a better understanding of substituent effects on the BDEs.

In a previous publication, the use of 1,2-diarylethanes or related symmetrical derivatives as reference molecules for the calculation of polar ground-state effects on benzylic bonds was suggested,[7] but no detailed rationalization was given. This method yields the PSE as the reaction enthalpy of the isodesmic reaction 1 ($Y = CH_2$, O, S, NH, BH, etc.). More recently, the isodesmic reaction 2 has been employed to calculate polar ground-state contributions to the BDEs of toluenes,[8] a method that had been previously applied to anisoles.[4] In view of the contrasting computational procedures for assessing polar ground-state effects on benzylic and related bonds, it appears timely to demonstrate that the use of the isodesmic reaction 1 is more appropriate. Semiempirical calculations are employed to expose significant differences between the results obtained from the isodesmic reactions 1 and 2.

$$XC_6H_4Y{-}YC_6H_4X + 2\ C_6H_5Y{-}Z \rightarrow C_6H_5Y{-}YC_6H_5 + 2\ XC_6H_4Y{-}Z \quad (1)$$

$$XC_6H_5 + C_6H_5Y{-}Z \rightarrow XC_6H_4Y{-}Z + C_6H_6 \quad (2)$$

Results and Discussion

According to Pauling's original bonding theory,[11] the conversion of two homonuclear molecules AA and BB to the corresponding heteronuclear species AB is exothermic on account of the additional "ionic resonance energy" E_i of the A−B bond (eq 3a), which is equal to the square of the difference in electronegativity of the atoms forming the bond. The relevant BDE of A−B is thus obtained from the BDEs of the homosymmetric molecules plus E_i (eq 3b).

$$A{-}A + B{-}B \rightarrow 2\ A{-}B + E_i \quad (3a)$$

$$\mathrm{BDE}(A{-}B) = 1/2\ \mathrm{BDE}(A{-}A) + 1/2\ \mathrm{BDE}(B{-}B) + E_i(A{-}B) \quad (3b)$$

This simple definition can be directly transferred to the situation in polyatomic molecules, e.g., for benzylic and related bonds XR−Z (eq 4a), where the ionic resonance energy contribution to the BDE is now actually a composite ($\Sigma\Delta E_i$) of E_i for the R−Z bond and the differences in E_i for the remaining bonds in XRZ relative to ZZ and XRRX (eq 4b).

$$XR{-}RX + Z{-}Z \rightarrow 2\ XR{-}Z \quad (4a)$$

$$\mathrm{BDE}(XR{-}Z) = 1/2\ \mathrm{BDE}(XR{-}RX) + 1/2\ \mathrm{BDE}(Z{-}Z) + \Sigma\Delta E_i(XR{-}Z) \quad (4b)$$

The effects of aryl substituents X on the BDEs of benzylic and related bonds are measured relative to the unsubstituted system HR−Z (eq 5), i.e., ΔBDE = BDE(XR−Z) − BDE(HR−Z). Here, the covalent and ionic contributions correspond to the radical stabilization

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* To whom correspondence should be addressed. Fax: +41-61-267-3855. E-mail: nau@ubaclu.unibas.ch.

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energy and the polar ground-state stabilization energy of the substituent X (eqs 6 and 7). The opposite signs

$$\Delta BDE = 1/2\ BDE(XR-RX) - 1/2\ BDE(HR-RH) + \Sigma\Delta E_i(XR-Z) - \Sigma\Delta E_i(HR-Z) \quad (5)$$

$$RSE = 1/2\ BDE(XR-RX) - 1/2\ BDE(HR-RH) \quad (6)$$

$$PSE = -[\Sigma\Delta E_i(XR-Z) - \Sigma\Delta E_i(HR-Z)] \quad (7)$$

for RSE and PSE account for their contrary effects on the BDE (Scheme 1). Accordingly, the RSE of a substituent X is given as the relative BDE of the symmetrically substituted molecule (eq 6). The advantages of this definition for RSE have been previously addressed.[3,12,13]

The PSE, on the other hand, is obtained as the difference in ionic resonance energies (eq 7), which themselves are a function of the group electronegativities in XRZ. Although reliable values for the group electronegativities of substituted benzyl groups are hardly available, the PSE can still be quantified indirectly according to eq 8, *cf.* PSE = RSE − ΔBDE. Using the definition for the BDE as the difference in enthalpies (ΔH_f) of the resulting radicals and the molecule, one obtains eq 9, which allows the calculation of PSEs through computationally accessible enthalpies. The PSE in eq 9, however, corresponds to the reaction enthalpy for the isodesmic reaction 10.

$$PSE = 1/2[BDE(XR-RX) - BDE(HR-RH)] - [BDE(XR-Z) - BDE(HR-Z)] \quad (8)$$

$$PSE = [\Delta H_f(XR-Z) - \Delta H_f(HR-Z)] - 1/2[\Delta H_f(XR-RX) - \Delta H_f(HR-RH)] \quad (9)$$

$$XR-RX + 2\ HR-Z \rightarrow HR-RH + 2\ XR-Z \quad (10)$$

For benzylic systems, reaction 10 transforms to reaction 1, which has been previously employed for the calculation of PSEs.[7] As can be seen, the isodesmic reaction 1 follows directly from theoretical considerations and is compatible with a recommended definition of RSE (eq 6),[3,12,13] while reaction 2 receives no such support. There are several conceptual advantages of using reaction 1 instead of reaction 2 for the calculation of polar ground-state effects in benzylic bond cleavages. Most importantly, the PSE should refer to that portion of polar stabilization energy that is lost or gained upon homolytic cleavage of the benzylic bond ArY−Z as is the case in reaction 1, and not to that portion that is due to the removal of the whole group YZ as in reaction 2. For example, homolytic cleavage of the N−H bond in anilines according to reaction 1 does not affect, to a first approximation, the resonance interaction of the nitrogen lone pair with the aryl group, yet this interaction is entirely removed upon cleavage of the aniline C−N bond according to reaction 2. Secondly, since the polar ground-state effect is inherently related to the polarity of the broken bond, a nonpolar bond should serve as reference. This condition is only met for the symmetrical molecules with nonpolar Y−Y bonds in reaction 1 but not for the substituted benzenes with polar Ar−H bonds in reaction 2.

In summary, the isodesmic reaction 1 describes exclusively the mutual interaction between a benzyl group XR and a substituent Z, which is relevant in the homolysis of benzylic bonds. The isodesmic reaction 2, however, provides a method of quantification for the synergetic or antagonistic interaction between two aryl substituents,[14,15] which includes among others, but not exclusively, the effects of the aryl substituents X on the benzylic bonds R−Z. Hence, the isodesmic energy of reaction 1 contributes to the isodesmic energy of reaction 2.

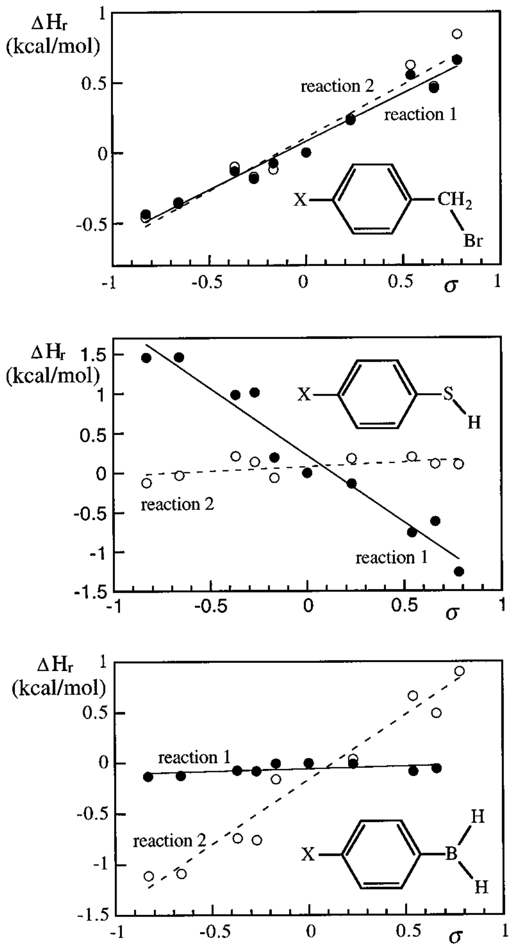

Figure 1. Isodesmic energies (ΔH_r) for reaction 1 (●) and reaction 2 (○) calculated by the semiempirical AM1 method and plotted against the Hammett σ values. The results are shown for benzyl bromides, thiophenols, and phenylboranes employing various *para*-substituents (NMe_2, NH_2, OH, OMe, Me, H, Cl, CF_3, CN, NO_2). The energies for the isodesmic reaction 1 provide the polar ground-state stabilization energies (PSEs), which contribute to the bond dissociation energies (BDEs) of benzylic and related bonds according to Scheme 1.

Semiempirical AM1 calculations[7,15] were performed to contrast the enthalpies of the isodesmic reactions 1 and 2. The PSEs were calculated from the isodesmic reaction 1 for benzyl bromides, thiophenols, and phenylboranes with reference to the symmetrical 1,2-diarylethanes, 1,2-diaryl disulfides, and 1,2-diaryldiboranes.[16] These examples cover bonds with different polarization, namely $ArH_2C^{\delta+}-^{\delta-}Br$, $ArS^{\delta-}-^{\delta+}H$, and approximately nonpolar for ArHB−H, *cf.* Pauling electronegativities for carbon

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(2.5), bromine (2.8), sulfur (2.5), hydrogen (2.1), and boron (2.0).[11] For each case, a representative set of electron-donating and -accepting aryl substituents (NMe_2, NH_2, OH, OMe, Me, H, Cl, CF_3, CN, NO_2) was examined, and the calculated PSEs were plotted against the Hammett σ constants[17] (Figure 1).

Linear regression analysis of the PSEs calculated from the isodesmic reaction 1 provides a positive ρ constant for benzyl bromides (+0.68, $r = 0.99$), a negative value for thiophenols (−1.69, $r = 0.97$), and no significant slope for phenylboranes (+0.05, $r = 0.50$). Electron-donating substituents should decrease the group electronegativity of the benzyl group, while electron-accepting substituents should increase it. Hence, electron donors increase the electronegativity difference in the C−Br bond of benzyl bromides but decrease it in the S−H bond of thiophenols, resulting in a polar ground-state stabilization or destabilization, and in the calculated positive and negative ρ values. For electron donors, the calculated ρ values correspond to higher BDEs in the case of benzyl bromides and to lower BDEs in the case of thiophenols, *cf.* Scheme 1. For the approximately nonpolar B−H bond in phenylborane both electron-donating and -accepting substituents appear to introduce some ionic character, since a slight stabilization is calculated for both types of substituents (resulting in a parabolic curvature and a poor correlation coefficient).

The isodesmic energies calculated for reaction 2 differ from the PSEs obtained for reaction 1 (Figure 1). This variation, as judged by the ρ constants, is minor for benzyl bromide (+0.76, $r = 0.97$), but much larger or even opposite substituent effects are predicted for phenylborane (+1.28, $r = 0.98$) and thiophenol (+0.12, $r = 0.55$). The positive ρ constants obtained from reaction 2 for all three systems appear to be related to the slight electron-accepting nature of the *p*-bromomethyl, *p*-mercapto, and *p*-borano groups.[17] Despite the very similar σ values of the *p*-bromomethyl and *p*-mercapto groups ($\sigma = +0.14$ and +0.15),[17] the stabilizing interaction with electron donors is less pronounced for thiophenols. This might reflect the concomitant destabilization of the S−H bond, which is expected from the negative ρ value according to reaction 1. Conversely, since the ρ values obtained for benzyl bromide from reactions 1 and 2 are very similar, the substituent effect on the C−Br bond, which is obtained from reaction 1, appears to be also the major denominator of the isodesmic energy for reaction 2. This special situation leads to a reasonable description of PSEs on the benzylic bond even by the less appropriate isodesmic reaction 2. Nevertheless, as exposed for phenylboranes and thiophenols (Figure 1) the differences between the isodesmic reactions 1 and 2 for assessing polar substituent effects are by no means semantic, but may lead to quantitative and qualitative discrepancies, which question some of the conclusions drawn in the previous studies.[4,8] In particular, since the difference between calculated BDEs and PSEs has been used to assess RSEs (Scheme 1), the latter quantity is subject to the same systematic deviations.

The calculated positive and negative ρ values for benzyl bromides and thiophenols are in qualitative agreement with experimental data.[5,6] Moreover, although no experimental BDE data are accessible for phenylboranes, the small calculated ρ value is indeed expected from experimental data for the homolysis of a nonpolar bond.[5,6] Hence, the assessment of the isodesmic reaction 1 by the AM1 method can be regarded as a useful tool for the interpretation of experimental data. From a quantitative view, the ρ values obtained from the AM1 calculated PSEs for reaction 1 (Figure 1) are smaller than those from the experimental BDEs for benzyl bromides[5] and thiophenols.[6] Although the scatter in the Hammett σ plots obtained from other semiempirical methods (MNDO, PM3) was more severe than for AM1, the ρ values were within ±30% of the AM1 values. The differences between the computed and experimental ρ values might reflect significant contributions of radical stabilizing effects to the experimental BDEs (Scheme 1) and the inaccuracy of the semiempirical methods. While it would be desirable to employ more sophisticated computational methods, the use of high level *ab initio* methodology is discouraged by the large diarylethane and related molecules. Moreover, the presently available experimental data on polar ground-state effects[4−7] are too limited to allow a reliable calibration of the calculated data or even an unambiguous decision as to which level of theory would be best suited to predict the absolute magnitude of polar ground-state effects.

In conclusion, polar ground-state effects, which according to Scheme 1 affect the BDEs, can be evaluated by means of Pauling's classical bonding theory and by semiempirical calculations. The energies obtained for both isodesmic reactions 1 and 2 represent interesting quantities, but only the former is a meaningful measure of the PSE relevant for the homolytic cleavage of benzylic bonds. Hence, the isodesmic reaction 2 is not recommended for the evaluation and discussion of the polar ground-state effects on benzylic bonds,[4,8] since it may lead to incorrect predictions.

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(16) In the calculated minimum conformations, the S−H, B−H, S−S, and B−B bonds were equatorial in relation to the aryl group, while the C−Br and C−C bonds were axial. The relative conformation of the aryl groups was *anti* in $Ar-CH_2-CH_2-Ar$ and *gauche* in Ar−S−S−Ar and Ar−BH−BH−Ar. The values were not corrected for zero-point energy contributions.

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