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Geometry, solvent, and polar effects on the relationship between calculated core-electron binding energy shifts (ΔCEBE) and Hammett substituent (σ) constants

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Abstract

According to Lindberg et al. there exists an equation ΔCEBE $=\kappa\sigma$ for substituted benzene derivatives. Core-electron binding energy shift (ΔCEBE) is the difference between the CEBE of a specific carbon in monosubstituted benzene derivatives (C_6H_5–Z) and in benzene (C_6H_5–H); κ is related to a reaction constant and σ is the experimental Hammett substituent constant. The object of the present work is to investigate geometry, solvent, and polar effects on Lindberg's equation using theoretically calculated ΔCEBE. The CEBEs were calculated using DFT within the scheme ΔE_{KS} (PW86x-PW91c/TZP+C_{rel}). The geometry has only little effect on the CEBE values. A regression relation between ΔCEBE and σ takes the form ΔCEBE $=\kappa\sigma-C$ with $\kappa\cong 1.17$ and $C\cong 0.17$. We estimated 69 σ constants in water that have not been presented in the literature. Theoretical resonance (σ_R) and inductive (σ_I) effects were calculated using Taft equations. ΔCEBE (R) and ΔCEBE (I) effects on ΔCEBE were also calculated using Taft-like equations. The quality of the correlation to the resonance is better than that to the inductive effect, in water. The regression quality in aqueous organic solvent is poorer than in water in both Lindberg and Taft equations. The solvent effect is greater on the resonance than on the inductive effect.

Keywords: CEBE shift; Hammett σ; DFT; LFER; Benzenes

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1. Introduction

Eq. (1) shows the basic form of the Hammett equation [1]:

$$\log\frac{K}{K_0}=\rho\sigma \qquad (1)$$

in which K is an equilibrium or rate constant for a side chain reaction of a benzene derivative where a substituent is in *para* or *meta* position with respect to the side chain and K_0 is the corresponding quantity for the unsubstituted compound; σ is a Hammett substituent constant, which, in principle, is characteristic of the substituent, and ρ is a reaction constant, which is dependent on the nature of the reaction. The Hammett equation is one of the important examples of linear free energy relationships (LFERs) and it has been widely used in studies of the chemical reactivity of substituted benzenes.

Lindberg et al. [2] showed that the core-electron binding energy (CEBE) shift for an aromatic carbon atom correlates linearly to the experimental Hammett substituent constant (σ) in substituted benzene derivatives, C_6H_5–Z (Fig. 1), as described in Eq. (2):

$$\Delta\text{CEBE}=\kappa\sigma. \qquad (2)$$

The left hand side of Eq. (2) is called CEBE shift, defined by Eq. (3). It is the difference between the CEBE of a ring carbon of C_6H_5–Z and of benzene (C_6H_5–H), which is the reference molecule.

$$\Delta\text{CEBE}\equiv\text{CEBE(ring carbon of }C_6H_5\text{–Z)}$$
$$-\text{CEBE(carbon of }C_6H_5\text{–H)} \qquad (3)$$

The right hand side of Eq. (2) is the product of the Hammett substituent constant σ for Z and a parameter κ, defined by Eq. (4):

$$\kappa=2.3kT(\rho-\rho*), \qquad (4)$$

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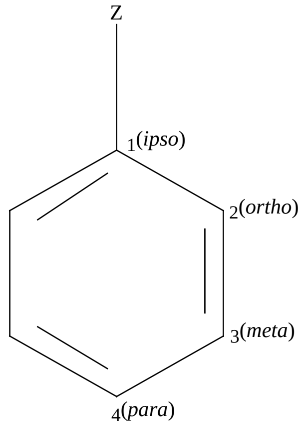

Fig. 1. Monosubstituted benzene, C_6H_5–Z, and its numbering system.

where ρ and ρ^* are the reaction constants in the Hammett equation for a neutral and a core-ionized molecule, respectively.

Preliminary investigation of the validity of Eq. (2) using *calculated* ΔCEBE of a specific carbon in about a dozen monosubstituted benzene derivatives (C_6H_5–Z) resulted in a regression equation $\Delta\text{CEBE}=\kappa\sigma-C$ with $\kappa=1.056$ and $C=0.1310$ [3]. A dozen of *para* fluoro disubstituted benzenes p-F–C_6H_4–Z, instead of monosubstituted benzenes C_6H_5–Z, were also employed to test the validity of Eq. (2) using *calculated* ΔCEBE [4]. A regression equation $\Delta\text{CEBE}=\kappa\sigma-C$ with $\kappa=1.01$ and $C=0.08$ was obtained. The object of the present work is to carry out a thorough investigation on the nature of Eq. (2), extending the previous work by using a much larger number of monosubstituted benzenes C_6H_5–Z and studying aspects that were not treated previously. Aspects such as geometry, solvent, and polar effects on the equation are investigated.

The International Union of Pure and Applied Chemistry (IUPAC) published two technical reports that compiled values of Hammett constants at *para* (σ_p) and *meta* (σ_m) positions based on the ionization of substituted benzoic acids in water [5] and in aqueous organic solvent (1:1 EtOH–H_2O) [6], both at 25 °C. In this work, we use three groups of experimental data: (i) values of σ_m and σ_p, measured in water, for 34 compounds (let us call the group as IUPAC-1) [5]; (ii) values of σ_m and σ_p, measured in aqueous organic solvent, for 30 compounds (IUPAC-2) [6]; (iii) values of σ_0 (*ortho*) from diverse sources [7,8]. We shall use the published values of σ_o, σ_m, and σ_p, and to investigate Eq. (2). The substituent constants σ_m and σ_p can be related to inductive (σ_I) and resonance (σ_R) effects, for instance, through Taft equations [9], and this aspect is explored. In this work, we used a technique to calculate accurate CEBEs in molecules formed by atoms of the first and second rows of the periodic table [10]. It used density functional theory (DFT) and provided average absolute deviations (AAD, between our calculations and experimental data) < 0.16 eV for a variety of small and medium size molecules.

2. Method of calculation

Consider the core-ionization process:

$$M \rightarrow M^+ + e^- \tag{5}$$

where M is a neutral substituted benzene C_6H_5–Z and M^+ is the molecular ion produced by the removal of an electron from a 1s core level of a carbon in M. The CEBE for e^- in Eq. (5) can be calculated as the difference, ΔE, between $E(M^+)$, the total energy of the cation M^+, and E(M), the total energy of the neutral molecule M, as given in Eq. (6);

$$\Delta E = E(M^+) - E(M) = \text{CEBE} \tag{6}$$

The total energy (E_{KS}) calculated with DFT includes correlation energy, among others energies, and is called Kohn–Sham (KS) total energy. If DFT provides accurate total energies, $E_{KS}(M^+)$ and $E_{KS}(M)$, one can calculate accurate ΔE_{KS}, which is CEBE, using Eq. (6). ΔCEBE is, then, calculated with Eq. (3). The CEBEs of carbon atoms in C_6H_4–Z were calculated using DFT within the scheme ΔE_{KS} (PW86x-PW91c/TZP + C_{rel}) [10]. In the shorthand notation, ΔE_{KS} is the difference in the total Kohn–Sham energies calculated by DFT for the core-ionized cation and for the neutral parent molecule (Eq. (6)) using a triple-zeta polarized (TZP) basis set. The functional combination is the Perdew–Wang 1986 exchange functional [11] and the Perdew–Wang 1991 correlation functional [12]. The relativistic corrections [13] can be estimated using empirical Eq. (7):

$$C_{rel} = KI_{nr}^{N}, \tag{7}$$

where I_{nr} is the nonrelativistic CEBE and C_{rel} is the relativistic correction. When both C_{rel} and I_{nr} are in eV units, $K=2.198\times10^{-7}$ and $N=2.178$. For the carbon atom, C_{rel} takes the average value of 0.051 eV. The geometry of the molecules was optimized using the same functional and basis employed for the calculation of CEBEs. We used the Amsterdam Density Functional (ADF) package [14] to calculate CEBEs in this study. For linear regression analyses, we used a Fortran program [15,16] that provides least-squares (LSQ) fits with error estimates in both coordinates.

3. Results and discussion

3.1. Core-electron binding energies

In order to study the effect of molecular geometry on calculated CEBEs, we adopted three different sets of molecular geometries. The first set was calculated using DFT(PW86x-PW91c)/TZP, the second set using HF/6-31G(d) [3], and the third set is experimental geometry obtained from the literature for benzene [17] and its derivatives, Z = Me [18], NO_2 [18], F [18], Cl [18], and NH_2 [19]. The resulting AADs are 0.13, 0.14, and 0.16 eV, respectively. The AADs are approximately equal to each other; the two calculated sets yielded slightly better CEBEs than the experimental set. All results are listed in