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Relationship between calculated core-electron binding energy shifts and Hammett substituent (sigma) constants: I[†]

Yuji Takahata*

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-862 Campinas, São Paulo, Brazil

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ABSTRACT: For monosubstituted benzenes (Ph-Z), Linderberg *et al.* demonstrated the validity of the equation $\Delta\text{CEBE} \approx \kappa\sigma$, where ΔCEBE is the difference between the core-electron binding energies (CEBE) of a specific carbon in monosubstituted benzene derivatives (Ph-Z) and that of unsubstituted benzene (Ph-H), κ is related to the reaction constant and σ is the experimental Hammett sigma constant. CEBEs of carbon atoms for a series of Ph-Z were calculated using density functional theory (DFT) with the scheme ΔE_{KS}(PW86–PW91)/TZP+C_{rel}//HF/6–31G*. An average absolute deviation of 0.15 eV was obtained with respect to observed values. A linear regression analysis of the form $Y = A + BX$ of a plot of, for instance, Hammett σ_p-constants against *calculated* ΔCEBEs (in eV) at *para*-carbon for $n = 11$ produced a value of $A = -0.1310$ and $B = 1.056$ with a correlation coefficient $R = 0.983$, a standard deviation of 0.099 and a p-value <0.0001. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: core-electron binding energy difference; Hammett sigma-constant; density functional theory; monosubstituted benzenes

INTRODUCTION

Linderberg *et al.*[1] showed that the core-electron binding energy shift correlates linearly with the experimental Hammett sigma constant[2] (σ) in substituted benzene derivatives. Let us consider electrophilic aromatic substitution at the *para* position of monosubstituted benzenes, Ph-Z, as an example, where Z is a substituent such as NH_2 or NO_2. Linderberg *et al.*[1] demonstrated the validity of the equation

$$\Delta\text{CEBE} \approx \kappa\sigma_p \tag{1}$$

The left-hand side of Eqn (1) is called the CEBE shift and it is the difference between the core-electron binding energy (CEBE) of the *para*-carbon of Ph-Z and the CEBE of one carbon atom of benzene (Ph-H), which is the reference molecule:

$$\begin{aligned}\Delta\text{CEBE} \equiv\ & \text{CEBE}(\textit{para}\text{-carbon of Ph-Z}) \\ & - \text{CEBE}(\text{one carbon of Ph-H})\end{aligned} \tag{2}$$

The right-hand side of Eqn (1) is the product between the Hammett substituent (σ) constant[2] of Ph-Z (at the *para* position, σ_p) and the parameter κ, defined as

$$\kappa = 2.3kT(\rho - \rho*) \tag{3}$$

where ρ and ρ*, the reaction constants in the Hammett equation,[2] are specific for the reaction considered of a neutral molecule and core ionized molecule, respectively.[1] Equation (1) is an approximate equation, which was derived after a series of approximations and assumptions. There are equations similar to Eqn (1) at other carbon atoms in Ph-Z such as the *ortho* and *meta* positions in the molecule. The linear relationship between ΔCEBE and Hammett σ-constants is not limited to monosubstituted benzenes. There are corresponding equations for multiply substituted benzenes. Straight lines were obtained[1] by plotting experimentally observed CEBE values of Ph-Z with respect to corresponding Hammett σ-constants. This is a demonstration of the validity of Eqn (1).

The Hammett equation is one of the important examples of linear free energy relationships (LFERs). It has been widely used in studies of the chemical reactivity of substituted benzenes. It is worth investigating further the implications and application of Eqn (1). The object of the present work was to *calculate* the theoretical values of ΔCEBEs of the ring carbons in Ph-Z and see how they correlate with Hammett σ-constants. Recently, a

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**Correspondence to:* Y. Takahata, Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-862 Campinas, São Paulo, Brazil.
E-mail: taka@iqm.unicamp.br

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technique for calculating accurate CEBEs in molecules that contain atoms of the first and second rows of the periodic table was established[3] that uses density functional theory (DFT). This technique was used to investigate Eqn (1).

METHOD OF CALCULATION

The core-electron binding energies of carbon atoms in monosubstituted benzenes were calculated using DFT with the scheme[3] ΔE_{KS} (PW86–PW91)/TZP + C_{rel}//HF/6–31G*, where ΔE_{KS} is the difference of the total Kohn–Sham energies of the core-ionized cation and of the neutral parent molecule calculated by DFT, using the triple-zeta polarized (TZP) basis set. The functional combination is the Perdew–Wang 1986 exchange functional[4] and the Perdew–Wang 1991 correlation functional.[5] C_{rel} is a relativistic correction, which takes the value 0.05 eV in the case of a carbon atom. The geometry of molecules was optimized by *ab initio* HF/6–31G*. The Amsterdam Density Functional (ADF) package[6] was used for the calculation of CEBEs.

RESULTS AND DISCUSSION

Twelve monosubstituted benzenes, Ph-Z, were investigated, including benzene itself as the reference molecule. There are four distinguished ring carbon atoms, C1(*ipso*), C2(*ortho*), C3(*meta*) and C4(*para*) in Ph-Z (Fig. 1). Table 1 lists calculated and observed CEBEs in eV.

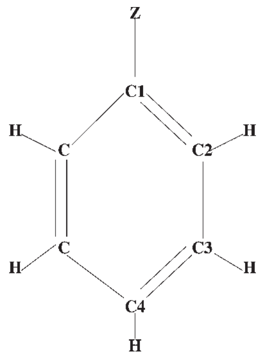

Figure 1. Distinguished ring carbon atoms, C1 (*ipso*), C2 (*ortho*), C3 (*meta*) and C4 (*para*) in Ph-Z

Twenty-five observed CEBEs are available in the literature for the seven molecules listed in the first column in Table 1. The average absolute deviation (AAD) of the calculated CEBEs for the present 25 cases with respect to the observed values is 0.13 eV, whereas 0.16 eV was obtained for 59 cases examined recently.[3] The AAD for the total of 83 cases is 0.15 eV. The maximum absolute deviation (MAD) in the present 25 cases is 0.48 eV. This value is for the C1 atom in Ph-CH_3.

The CEBE shifts (in eV) were calculated by Eqn (2) using calculated and observed CEBEs. They are listed in Table 2 together with Hammett σ-constants.

Table 1. Calculated and observed carbon CEBEs (eV) in the monosubstituted phenyl ring Ph-Z[a]

Molecule	Hole	Observed[b]	Theory	Molecule	Hole	Theory
Ph-H	C	290.41	290.44	Ph-OCH_3	C1	291.77
Ph-NH_2	C1	291.29	291.38		C2	290.05
	C2	289.95	289.99		C3	290.17
	C3	290.25	290.17		C4	289.88
	C4	289.85	289.83	Ph-OC_2H_5	C1	291.68
Ph-CH_3	C1	290.9	290.42		C2	289.97
	C2	290.2	290.10		C3	290.11
	C3	290.4	290.20		C4	289.82
	C4	290.1	290.13	Ph-$N(CH_3)_2$	C1	290.98
Ph-F	C1	292.9	292.75		C2	289.59
	C2	290.7	290.63		C3	289.83
	C3	290.9	290.69		C4	289.44
	C4	290.4	290.49	Ph-C_2H_5	C1	290.22
Ph-Cl	C1	292.0	291.84		C2	290.00
	C2	291.0	290.61		C3	290.11
	C3	290.5	290.65		C4	290.04
	C4	290.8	290.49	Ph-SCH_3	C1	290.70
Ph-NO_2	C1	292.1	292.06		C2	290.26
	C2	291.3	291.29		C3	290.35
	C3	291.0	291.19		C4	290.32
	C4	291.1	291.21			
Ph-CN	C1	291.85	291.86			
	C2	290.88	291.05			
	C3	290.88	291.01			
	C4	290.88	290.96			
AAD[c] (25 cases)		(0.00)	0.13			

[a] C1,C2, C3 and C4 are *ipso*, *ortho*, *meta* amd *para* carbons in Ph-Z, respectively.
[b] Ref. 7.
[c] Average absolute deviation.

Table 2. Hammett substituent (σ) constants vs calculated and observed ΔCEBEs (eV) for common groups at *para*, *meta* and *ortho* carbons in monosubstituted benzenes[a]

(a)	Substituent	Sigma-*para* (σ_p)[b]	Calculated ΔCEBE (eV)	Observed ΔCEBE (eV)
1	$N(CH_3)_2$	−0.83	−0.95	
2	NH_2	−0.57	−0.62	−0.56
3	OCH_3	−0.28	−0.51	
4	OCH_2CH_3	−0.24	−0.57	
5	CH_3	−0.16	−0.31	−0.16
6	C_2H_5	−0.15	−0.35	
7	SCH_3	0	−0.07	
8	F	0.06	0.05	−0.01
9	Cl	0.22	0.05	0.39
10	CN	0.65	0.52	
11	NO_2	0.78	0.77	0.69
(b)	Substituent	Sigma-*meta* (σ_m)[b]		
1	$N(CH_3)_2$	−0.15	−0.56	
2	NH_2	−0.16	−0.27	−0.16
3	OCH_3	0.11	−0.22	
4	OCH_2CH_3	0.1	−0.28	
5	CH_3	−0.05	−0.24	−0.05
6	C_2H_5	−0.07	−0.28	
7	SCH_3	0.15	−0.04	
8	F	0.34	0.25	0.49
9	Cl	0.37	0.21	0.09
10	CN	0.61	0.57	
11	NO_2	0.74	0.75	0.59
(c)	Substituent	Sigma-*ortho* (σ_o)[c]		
1	OCH_3	−0.39	−0.34	
2	CH_3	−0.17	−0.34	−0.21
3	F	0.24	0.19	0.29
4	Cl	0.2	0.17	0.59
5	NO_2	0.8	0.85	0.89
6	$N(CH_3)_2$	(−0.89)	−0.80	
7	NH_2	(−0.52)	−0.45	−0.46
8	OCH_2CH_3	(−0.48)	−0.42	
9	C_2H_5	(−0.45)	−0.39	
10	SCH_3	(−0.18)	−0.13	
11	CN	(0.61)	0.61	0.47

[a] The numerical values of Hammett substituent constants in parentheses are those estimated by substituting ΔCEBEs in the fitted line (Fig. 5).
[b] Ref. 8. Determined from the pK_as of substituted benzoic acids in water.
[c] Ref. 9.

Table 2 consists of three parts. In part (a), the entries are for C4, *para* to substituent Z. Parts (b) and (c) are corresponding entries for C3 and C2, *meta* and *ortho* to substituent Z, respectively. The numerical values and signs of ΔCEBEs agree with the Hammett σ-constants fairy well.

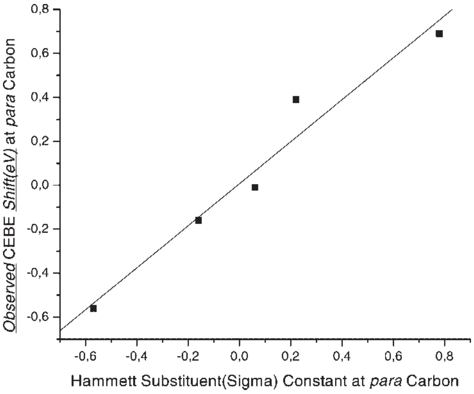

Figure 2. Plot of Hammett σ_p constants against *observed* ΔCEBEs at the C4 (*para*) atom for $n = 5$

Figure 2 shows a plot of *observed* ΔCEBEs [fifth column in part (a) of Table 2] of the C4 (*para*) atom versus Hammett σ_p constants. There are only five *observed* ΔCEBEs available in part (a) of Table 2 ($n = 5$). A linear regression analysis of the form $Y = A + BX$ resulted in $A = 0.0069$ and $B = 0.956$ with a correlation coefficient $R = 0.979$, a standard deviation of 0.115 and a p-value of 0.0038 (see regression 1 in Table 3).

The correlation coefficient of 0.979 is fairly high. The fitted line almost passes through the origin of the coordinates, with an intercept $A = 0.0069$, indicating the validity of Eqn (1). Both the standard deviation and p-value are sufficiently low, indicating satisfactory quality of the fit. The slope B of the fitted line corresponds to κ in Eqn (1). Hence we have $\kappa \approx 0.956$, which is close to unity. Figure 2 is just a reconfirmation of what Linderberg *et al.* demonstrated previously.[1] Regression 2 in Table 3 is the result of another regression analysis to be compared with regression 1. C*alculated* ΔCEBEs instead of *observed* ΔCEBEs were used in regression 2 for the same set of five samples ($n = 5$) as in Fig. 2.The quality of regression 2 is similar to that of 1. C*alculated* ΔCEBEs correlate with Hammett σ_p constants as well as the *observed* ΔCEBEs.

Figure 3 shows a plot of *calculated* ΔCEBEs of the C4 (*para*) atom for the whole set of data in part (a) of Table 2

Table 3. Summary of the linear regressions of the form $Y = A + BX$ corresponding to Figs 2–5[a]

Regression	Figure	A	B	R	SD	n	p
1	Fig. 2 (*para*-carbon)	0.0069	0.956	0.979	0.115	5	0.0038
2	Calculated ΔCEBE vs σ (*para*-carbon)	−0.0801	1.033	0.990	0.087	5	0.0013
3	Fig. 3 (*para*-carbon)	−0.131	1.056	0.983	0.099	11	<0.0001
4	Fig. 4 (*meta*-carbon)	−0.2452	1.300	0.968	0.107	11	<0.0001
5	Fig. 5 (*ortho*-carbon)	−0.0385	1.063	0.985	0.099	5	0.0023

[a] Regression 2, comparison with the regression of Fig. 2; X, Hammett substituent (σ) constant; Y, ΔCEBE in eV; R, correlation coefficient; SD, standard deviation; n, number of samples; p, p-value.

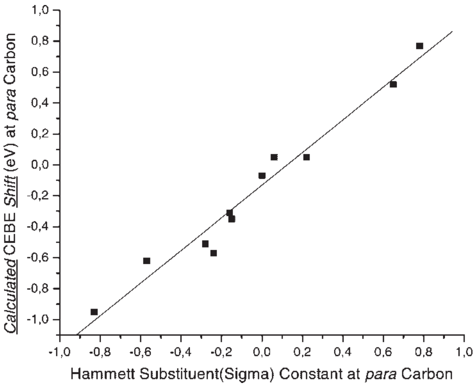

Figure 3. Plot of Hammett σ_p constants against *calculated* ΔCEBEs at the C4 (*para*) atom for $n = 11$

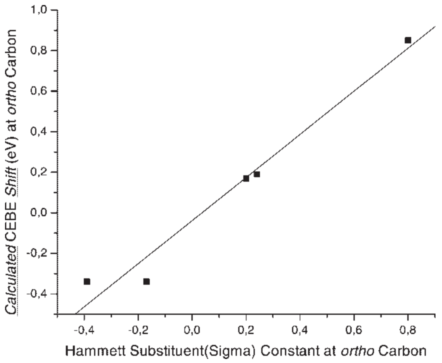

Figure 5. Plot of Hammett σ_o constants against *calculated* ΔCEBEs at the C2 (*ortho*) atom for $n = 5$

versus Hammett σ_p constants. It corresponds to a total of 11 samples ($n = 11$). The results of a linear regression analysis of the form $Y = A + BX$ are summarized in regression 3 in Table 3. Comparison between regressions 3, 2 and 1 in Table 3 reveals that the qualities of the fitted lines are similar. C*alculated* ΔCEBEs correlate with Hammett σ_p constants as well as the *observed* ΔCEBEs. The intercept A is -0.1310, which deviates slightly from zero. The value of B is 1.033, which is close to unity.

Figure 4 shows a plot of the data in part (b) of Table 2 for calculated ΔCEBEs of the C3 (*meta* to Z) atom versus Hammett σ_m constants. The quality of the fit in Fig. 4 (regression 4 in Table 3) is slightly worse than that in Fig. 3 (regression 3 in Table 3). The intercept A is -0.2452. Finally, Fig. 5 shows a plot of calculated ΔCEBEs of the C2 (*ortho* to Z) atom, from the data in part (c) of Table 2, versus Hammett σ_o constants. A linear regression analysis of the form $Y = A + BX$ produced the values $A = -0.0385$ and $B = 1.063$ with a correlation coefficient $R = 0.985$, a standard deviation of 0.099, and a p-value of 0.0023. Within the five samples treated, the correlation between Hammett σ_o constants and the calculated ΔCEBEs of the C2 (*ortho*) atom in the molecule is good. Since the number of samples is the same as in Fig. 2, the quality of the fits may be compared directly: one finds almost identical regression statistics. Since we have the fitted line (regression 5 in Table 3) and calculated values of ΔCEBEs, we can estimate unknown Hammett σ_o constants for some groups. The values in parentheses in Table 3 are such estimated Hammett σ_o constants.

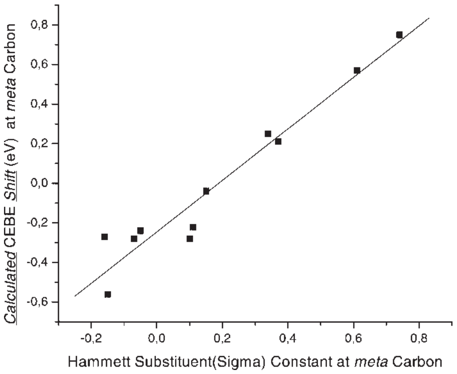

Figure 4. Plot of Hammett σ_m constants against *calculated* ΔCEBEs at the C3 (*meta*) atom for $n = 11$

In summary, when c*alculated* ΔCEBE is used, Eqn (1) should be modified to

$$\Delta\text{CEBE} \approx \kappa\sigma + C \tag{4}$$

where $\kappa \approx 1$, and the absolute value of C is approximately <0.25. We can see an approximate agreement, in numerical value and in sign, between the CEBE shifts (in eV) and the corresponding Hammett σ-constant. Finally, from the results of linear regression, we can also estimate the Hammett σ-constant of an unknown molecule by calculating ΔCEBE.

The maximum number of samples treated in this work was only 11, which is not sufficiently large to permit us to draw any definite conclusion regarding the form of Eqn (4). Therefore, the form of Eqn (4) is tentative. We are working with larger number of samples to verify which form of the equation might improve the relationship between ΔCEBE and σ. The numerical values corresponding to κ and C in Eqn (4) depend on the energy unit of ΔCEBE. The unit of eV was employed throughout this work. If other units such as kJ mol^{-1} were used for ΔCEBE in Eqn (4) κ and C would take completely different values from those given here.

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