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The Local HSAB Principle and Bond Dissociation Energy of *p*-Substituted Phenol

María de L. Romero and Francisco Méndez*

Departamento de Química, División de Ciencias Básicas e Ingeniería, Universidad Autónoma
Metropolitana-Iztapalapa, A.P. 55-534, México, D.F., 09340 México

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The calculation of the $XC_6H_4O{-}H$ bond dissociation energy (BDE) in a set of *p*-substituted phenols using the local hard and soft acids and basis principle (HSAB) is described. The expression for the interaction energy (ΔE_{int}) in terms of the chemical potentials of the reagents ($\mu_{XC_6H_4O}$, μ_H) and the atomic hardness fragments (η_O, η_H) provides good gas-phase BDE values.

I. Introduction

The Lewis generalized acid−base reaction $A + B \rightarrow A{:}B$ has an important role in the study of chemical reactivity of organic compounds. Several organic reactions begin with steps that involve the acid−base reaction.[1] In 1963, Pearson proposed the hard and soft acids and bases principle[2] (HSAB), "hard acids prefer to coordinate to hard bases". The principle refers to the bond dissociation energy (BDE) of the Lewis reaction. Therefore, the estimation of the BDE in terms of the chemical hardness and chemical potentials should be a topic of a great deal of attention.[3] However, the BDE in these terms has only been obtained for some diatomic and small polyatomic molecules.[4]

In this work, we have used the HSAB principle in its local version[5] and the density functional theory[6] (DFT) to investigate the O−H homolitic gas-phase BDE in a set of *p*-substituted phenols (XC_6H_4OH). Phenols are of special interest because their phenoxyl radicals are important intermediates in many biological and industrial processes.[7] Their experimental BDE values have been used to test ab initio calculations.[8a] In this respect, the energy differences should be calculated with high-level methods and corrections with the zero-point vibration and the superposition base error (BSSE) should be used to obtain good BDE values.[8b] The benefit of calculating the BDE via HSAB versus the traditional methods is that not such corrections need be considered when using HSAB. The interaction energy (ΔE_{int}) of the reaction $XC_6H_4OH \rightarrow XC_6H_4O + H$ is determined in terms of the chemical potentials[9] of the reagents and the atomic hardnesses[10] of the oxygen and hydrogen atoms involved in the O−H bond formation. In this study, we propose the ΔE_{int} is equal to the negative of the BDE. The results highlight the importance of the electrostatic contribution in the reaction in the determination of the BDE in the gas phase.

II. The Local HSAB Principle

According to the DFT, the ΔE_{int} for the reaction $XC_6H_4O + H \rightarrow XC_6H_4OH$ is given by[6] $\Delta E_{int} = E[\rho_{XC_6H_4OH}] - (E[\rho_H] + E[\rho_{XC_6H_4O}])$, where $\rho_{XC_6H_4O}$ and ρ_H are the ground-state electronic densities of the reagents and $\rho_{XC_6H_4OH}$ is the ground-state electronic density of the *p*-substituted phenol. The reaction can be divided into two successive steps:[11] (i) electron transfer (covalent interaction), and (ii) reshuffling of the electron density (electrostatic interaction), $XC_6H_4O + H \xrightarrow{i} (XC_6H_4O + H)^* \xrightarrow{ii} XC_6H_4OH$. The ΔE_{int} represents the energy involved in the two steps ($\Delta E_{int} = \Delta E_v + \Delta E_\mu$). ΔE_v is a consequence of the electronegativity equalization principle,[12] and ΔE_μ is a manifestation of the maximum hardness principle.[13] In a local viewpoint, the free hydrogen atom will interact with the oxygen atom of the *p*-substituted phenoxyl radical. The energy involved in the bond formation process is represented in the local HSAB principle by[5]

$$\Delta E_{int} = -\frac{(\mu_{XC_6H_4O} - \mu_H)^2}{2(\eta_H + \eta_O)} - \frac{\lambda(\eta_H \eta_O)}{2(\eta_H + \eta_O)} \qquad (1)$$

where μ_H and $\mu_{XC_6H_4O}$ are the chemical potentials of the free hydrogen atom and the *p*-substituted phenoxyl radical, respectively, and η_H and η_O are the atomic hardness of the free hydrogen atom and the oxygen atom in the *p*-substituted phenoxyl radical. The λ parameter is a constant related with an effective number of electrons.[5,14−16] The chemical potential[9] can be obtained from $\mu = -(1/2)(I + A)$, where I is the ionization potential and A is the electron affinity. The condensed hardness[5a] is obtained by $\eta_k = (\eta/f_k)$, where η is the global hardness obtained through $\eta = (1/2)(I - A)$ and f_k is the condensed fukui function[6,17] that measures the reactivity of the k atom toward an electrophilic (f_k^-), nucleophilic (f_k^+), or radical (f_k^0) attack. For the free H atom, $f_H^- = 1$ (it acts as a nucleophile and decreases its charge in the bond-forming process); for the oxygen atom (it acts as an electrophile and increases its charge), f_O^+ can be obtained from its gross charge in the *p*-phenoxyl neutral and in the anion evaluated at the geometry of the neutral, $f_O^+ = (q_O^{anion} - q_O^{neutral})$.[17] In general, a λ value equal to one has been used for the study of chemical reactivity in cycloadditions reactions,[16] and a λ value lower than one has been used for the study of weak interactions.[15]

III. The Bond Dissociation Energy of *p*-Substituted Phenol

The local HSAB principle, the chemical potential, and the condensed hardness parameters yield the BDE values in *p*-substituted phenols from eq 1. The DFT properties of *p*-substituted phenols, *p*-substituted phenoxyl radicals, and λ values were taken from ref 18. For the hydrogen atom, the

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* To whom correspondence to be addressed. E-mail: fm@xanum.uam.mx; phone: (52)55-58046417; fax: (52)55-58046415.

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TABLE 1: Calculated and Experimental O−H Homolitic BDE Values for the Reaction $XC_6H_4OH \rightarrow XC_6H_4O + H$[i]

				ΔBDE					
X	λ[a]	ΔE_ν[b]	ΔE_μ[b]	HSAB[b]	exp[c]	exp[d]	exp[e]	exp[f]	calc[g]
CF_3	1.2	0.03	−89.19	−3.5		−5.5		−3.2	−2.6
CH_2CH_3	1.2	0.12	−84.35	1.5					
CH_3	1.2	0.12	−83.85	2.0	2.2	1.1	2.1		1.8
CHO	1.4	0.05	−102.60	−16.8					
Cl	1.2	0.09	−86.25	−0.5		−0.4	0.6	−0.4	0.7
CN	1.3	0.05	−89.76	−4.0		−4.4	−4.7	−5	−2.3
$COOCH_3$	1.2	0.04	−87.58	−1.8					
COOH	1.3	0.04	−92.06	−6.3					
F	1.2	0.12	−85.56	0.3					
H	1.2	0.14	−85.84	0 (85.7)[h]	0 (88.3)[h]	0 (89.8)[h]	0 (88.2)[h]	0 (84.0)[h]	0 (89.5)[h]
i-Pr	1.2	0.10	−84.17	1.6					
NH_2	1.1	0.24	−77.77	8.2		12.6	12.7		8.6
NO_2	1.3	0.02	−92.05	−6.3		−4.5	−6		−4.4
OCH_3	1.1	0.17	−80.40	5.5	5.5	5.3	5.6	5.9	5.5
OH	1.1	0.18	−82.02	3.9		8.3	8		5.4
t-Bu	1.1	0.07	−83.77	2.0	3				

[a] λ values obtained from ref 18. [b] Calculated through eq 1. [c] Data from ref 20a. [d] Data from ref 20b. [e] Data from ref 20c. [f] Data from ref 20d. [g] Data from ref 8a. [h] Phenol's BDE. [i] The ΔBDE, ΔE_ν, and ΔE_μ values are in kcal/mol.

experimental μ_H and η_H values were used.[19] Table 1 shows the experimental and calculated ΔBDE values for a set of sixteen *p*-substituted phenols[8a,20] ($\Delta BDE = BDE_{HC_6H_4OH} - BDE_{XC_6H_4OH}$). Our calculated gas-phase BDE values are in close agreement with the experimental BDE values obtained in solution.[20] Many BDE values of interest to organic chemists have not been measured in the gas phase and, at least partly for this reason, a variety of techniques have been developed which purport to measure the BDE in solution. The agreement spans over 12 kcal/mol with $CH_3OC_6H_4OH$ and $O_2NC_6H_4OH$ at the two extremes. We can observe from Table 1 that in general the calculated BDE values in gas phase reproduce the experimental BDE values in solution within 0.1−2.6 kcal/mol (the experimental error is about 0.1−0.8 kcal/mol), except for hydroquinone (HOC_6H_4OH) and *p*-aminophenol ($H_2NC_6H_4OH$) for which the calculated values are lower by 4−5 kcal/mol. It seems reasonable to assume that stabilizing effects between the substituent (OH or NH_2) and the solvent are due to hydrogen bonding. The calculated ΔBDE values underestimate the calculated ΔBDE values obtained by Brinck et al.[8a] by 0.4−3.8 kcal/mol who computed the BDE values as differences in electronic energies (B3LYP/6-31G** level), without considering the zero point vibrational energy. Good linear correlations were obtained between our calculated BDE values in gas phase and the experimental BDE values in solution obtained by several techniques; $r^2 = 0.966$ for EPR spectrometry,[20a] $r^2 = 0.896$ for cyclic voltammetry,[20b] $r^2 = 0.941$ for pulse radiolysis,[20c] and $r^2 = 0.989$ for photoacoustic calorimetry.[20d] The results of the regression analysis show good agreement between photoacoustic calorimetry[20d] and our computed values. It is interesting to observe that there is a linear correlation between our calculated BDE values and the λ values, $BDE = 6.645 + 66.751\lambda$, $r^2 = 0.988$. When λ increases BDE also increases. This relationship suggests that the effective number of electrons increases when the stability of the O−H bond increases. From Table 1 we can see that the electrostatic contribution to the XC_6H_4O-H bond formation (and also to the bond dissociation) is higher than the covalent interaction, $|\Delta E_\mu| > |\Delta E_\nu|$. According to these results, we conclude that the expression for the ΔE_{int} between the hydrogen atom and the *p*-substituted phenoxyl radical in terms of the chemical potential ($\mu_{XC_6H_4O}$, μ_H) and the atomic hardness (η_O, η_H), provides good BDE values of *p*-substituted phenols in the gas phase. The methodology we propose is an alternative to the traditional ways of obtaining BDE.

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