Bond Strengths of Toluenes, Anilines, and Phenols: To Hammett or Not

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ABSTRACT

The Hammett equation correlates the effects of Y on many different chemical properties of YC_6H_4ZX families of compounds. One of the most surprising is that the $Z–X$ bond dissociation enthalpy (BDE), a homolytic property, can be correlated for some $4\text{-}YC_6H_4\text{-}ZX$ families with electrophilic substituent constants, $\sigma_p^+(Y)$, which were largely derived from the rates of the heterolytic S_N1 solvolyses of para-substituted cumyl chlorides. Although there is no Hammett correlation of the $C–X$ BDEs in $4\text{-}YC_6H_4CH_2X$ (X = H, halide, OPh) families, there are good correlations of $N–X$ BDEs with $\sigma_p^+(Y)$ in $4\text{-}YC_6H_4NHX$ (X = H, CH_3, OH, F) and excellent correlations of $O–X$ BDEs with $\sigma_p^+(Y)$ in $4\text{-}YC_6H_4OX$ (X = H, CH_3, CH_2Ph) families. The reasons for this varied behavior are discussed.

Introduction

Free radical chemists have a strong and abiding interest in the bond dissociation enthalpies, BDEs (commonly referred to as bond strengths or bond energies), of organic molecules. This is because the overall enthalpy change in a homolytic reaction is determined by the BDEs of the bonds being made and broken and it is the overall enthalpy change that determines whether the reaction will be exothermic (and probably fast) or endothermic (and

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definitely slow). This Account describes the resolution, thanks to a combination of experimental measurements and theoretical calculations, of controversies regarding the influence, or lack of influence, of para-substituents, Y, on $Z–X$ BDEs in compounds having the general formula $4\text{-}YC_6H_4Z–X$.

The view that had become well established by the mid-1990s was that $Z–X$ BDEs in $4\text{-}YC_6H_4Z–X$ gave Hammett-type linear free energy correlations with the substituent constant of Y, either the Hammett constants, $\sigma_p(Y)$ (based on $4\text{-}YC_6H_4CO_2H$ pK_as) or the Brown and Okamoto[1] electrophilic substituent constants, $\sigma_p^+(Y)$ (largely based on $4\text{-}YC_6H_4C(CH_3)_2Cl$ rates of S_N1 solvolysis). However, the evidence favoring a correlation of $\{BDE(4\text{-}YC_6H_4Z–X)$ − $BDE(C_6H_5Z–X)\} = \Delta BDE(Z–X)$ with $\sigma_p(Y)$ or $\sigma_p^+(Y)$, varied from "overwhelming" for $Z–X = O–H(\sigma^+)$, through "reasonably good" for $Z–X = NH–H(\sigma^+)$ to "unconvincing" for $Z–X = CH_2–H(\sigma)$. Nevertheless, we will start this Account with discussions of various $Z = C(H_2)$ families of compounds because it was here that a controversy erupted that piqued our interest and initiated the work described herein.

To set the stage, in 1963, the logarithms of the rate constants for reaction 1 were shown to correlate linearly

$$ROO^\bullet + YC_6H_4OH \rightarrow ROOH + YC_6H_4O^\bullet \quad (1)$$

with σ^+, a result that was attributed to an electronic effect of Y, which might favor or disfavor the polar transition state shown:[2]

$$[YC_6H_4O^{\delta+}\cdots H\cdots O^{\delta-}OR]^\ddagger$$

Then in 1970, Mahoney and DaRooge[3] showed that a phenol with an electron-donating (ED) Y substituent (4-MeO) had an O–H BDE that was weaker by several kilocalories per mole than a phenol with an electron-withdrawing (EW) Y substituent (3-EtOC(O)). These workers concluded[3] that the effects of Y on the rates of H-atom abstraction from YC_6H_4OH by radicals were primarily due to Y-induced changes in O–H BDEs and not to the polar effects of Y on the transition state. This conclusion has received overwhelming support from experimental measurements[4–6] and by theoretical methods.[7]

C–X ΔBDEs for $4\text{-}YC_6H_4CH_2$–X

By 1991, it was firmly established that EW Ys increased and ED Ys decreased the O–H BDEs in $4\text{-}YC_6H_4O–H^{3,4}$ and the O–C BDEs in $4\text{-}YC_6H_4O–CH_3^8$ and that the EW/ED character of Y had little effect on C–C BDEs in $4\text{-}YC_6H_4CH_2–CH_3^{9,10}$ and C–H BDEs in $4\text{-}YC_6H_4CH_2–H.^{12}$ It was therefore rather exciting when Clark and Wayner (CW)[14] reported that C–Br BDEs in $4\text{-}YC_6H_4CH_2–Br$ were *decreased* by EW Ys. These BDEs were measured by

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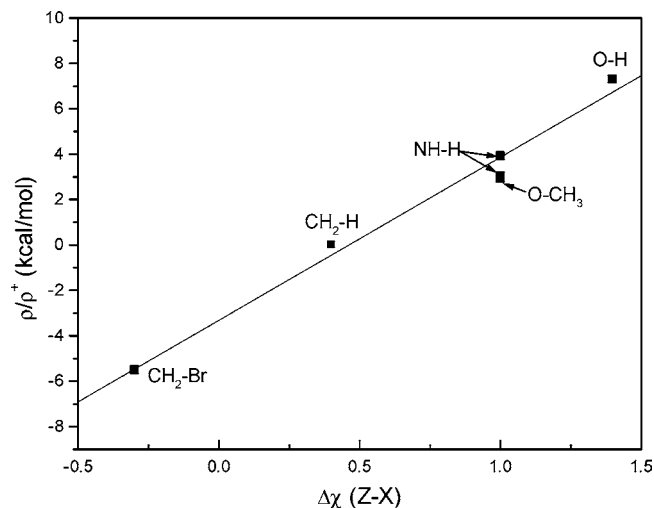**FIGURE 1.** Purported correlation of ρ/ρ^+ with $\Delta\chi(Z-X)$, adapted from ref 19.

Table 1. Calculated Gas-Phase C−X ΔBDE = {BDE(4-YC$_6$H$_4$CH$_2$X) − BDE(C$_6$H$_5$CH$_2$-X)} in kcal/mol[a]

Y[b] (C−X $\Delta\chi$)	X = H (0.4)	X = Br (−0.3)	X = Cl (−0.5)	X = F (−1.5)
NH$_2$	−1.7	−0.2	−0.2	−0.5
OCH$_3$	−0.9	0.1	0.0	−0.4
CH$_3$	−0.4	0.1	0.0	−0.4
H	0.0[c]	0.0[c]	0.0[c]	0.0[c]
CF$_3$	0.5	−0.8	−0.5	−0.2
CN	−0.5	−1.6	−1.6	−1.3
NO$_2$	−0.1	−1.5	−1.6	−1.0

[a] Reference 24. [b] Values of the substituent constants for Y (σ_p and σ_p^+) increase monotonically from NH$_2$ through to NO$_2$, see Table 2. [c] BDE CH$_2$−H = 90.4, CH$_2$−Br = 57.1, CH$_2$−Cl = 68.6, and CH$_2$−F = 97.2 kcal/mol.

photoacoustic calorimetry (PAC) and a plot of C−Br BDEs vs σ_p(Y) gave a reasonably good straight line with a ρ value equal to −5.5 kcal/mol. CW believed[14] that since the then-accepted correlation of 4-YC$_6$H$_4$CH$_2$−H BDEs with σ had a small but positive slope, their C−Br BDE results could not be attributed to the stabilizing effects of Y on the 4-YC$_6$H$_4$CH$_2$• radicals. Instead, the substituent must exert its "important (i.e., greater) effect on the ground state of the parent" bromide.[14] An EW Y was presumed to decrease the C−Br BDE because it destabilized 4-YC$_6$H$_4$CH$_2$Br relative to C$_6$H$_5$CH$_2$Br by the interaction of Y with the C−Br bond's dipole. CW[14] also pointed out that "the magnitude of this effect will depend on the electronegativity difference of the atoms or groups in the bond being broken." Furthermore, the then-available ρ/ρ^+ values for Z−X = CH$_2$−Br, CH$_2$−H, O−CH$_3$, and O−H gave a reasonable straight line when plotted against (Pauling)[15] electronegativity differences for the bonding atoms, $\Delta\chi$. However, it should be noted that the atomic χ value for carbon (2.5) is not identical to the χ value for carbon-centered groups because of interactions within the group, for example,[16] χ(CH$_3$) = 2.525 and χ(C(CH$_3$)$_3$) = 2.378. Thus, χ(4-YC$_6$H$_4$CH$_2$) will not be constant but will vary as the ED/EW character of Y varies.

The correlation between ρ/ρ^+ and atomic $\Delta\chi$ received additional support within 2−3 years from two sources. First, some electrochemical measurements provided additional evidence that EW Ys weakened C−Br bonds in 4-YC$_6$H$_4$CH$_2$Br.[17] Second, measurements of N−H BDEs for 4-YC$_6$H$_4$NH$_2$ gave fair linear correlations when plotted against σ_p^+(Y),[18,19] and the slopes of these plots[20] were of a sign and magnitude fully consistent with CW's suggested linear correlation of ρ/ρ^+ with $\Delta\chi$[Z−X], see Figure 1.

By 1995, the BDEs measured over the preceding decade gave the dipole interaction model description of the origin of the effects of Y on Z−X BDEs in 4-YC$_6$H$_4$Z−X every appearance of being an unassailable fact when Z was from the first row of the periodic table,[21] see Figure 1. Furthermore, with the assumption that the covalent term in Pauling's equation was more or less invariant, a first-order

treatment had been presented indicating that ρ^+ should be related to $\Delta\chi$[Z−X];[22] a comprehensive discussion pertaining to the precise physical foundation of this correlation is, however, beyond the scope of this Account. Unfortunately, a 1951 study of the unimolecular decomposition rates of benzyl bromides in the gas phase[23] appears to have been overlooked. This early work failed to reveal any substantial effect of ring substituents on C−Br BDEs.[23] More devastating for the dipole interaction model was a 1997 report by Laarhoven et al.[11] in which the same PAC technique was used as had earlier been employed by CW with no substituent effect on YC$_6$H$_4$CH$_2$−Br BDEs being detected for Y = 4-CN, 4-C(CH$_3$)$_3$ or 3-CF$_3$.[11] Furthermore, competitive thermolysis of benzyl bromides in the gas phase indicated that any variation in YC$_6$H$_4$-CH$_2$−Br BDEs (Y = H, 4-CN, 4-CF$_3$, 4-C(CH$_3$)$_3$, 4-Br, 4-CH$_3$O and 3-CF$_3$) was less than 1 kcal/mol.[11]

Since experimental approaches gave conflicting YC$_6$H$_4$-CH$_2$−Br BDEs, we turned to theory. The calculation of *reliable gas-phase BDEs* (298 K) requires an extremely high level of theory and enormous computing power. In contrast, and thanks to the cancellation of errors, the calculation of gas-phase BDEs that will yield *reliable differences in BDEs (ΔBDEs) within a closely related family of compounds* can be carried out quickly and cheaply using density functional theory (DFT) to calculate electronic energies for AM1-optimized structures.[7] Some C−X ΔBDE = [BDE(4-YC$_6$H$_4$CH$_2$−X) − BDE(C$_6$H$_5$CH$_2$−X)] for X = H, Br, Cl, and F are given in Table 1.[24] In agreement with earlier[25−28] and later[29] work, the polar effects of Y on 4-YC$_6$H$_4$CH$_2$−H BDEs are much less important than the abilities of Y to delocalize the unpaired electron in 4-YC$_6$H$_4$CH$_2$•,[30] only CF$_3$ being bond-strengthening. Despite the large decrease in $\Delta\chi$ along the C−H, C−Br, C−Cl, C−F series, the effects of Y on CH$_2$-X BDEs are *small* (<2.0 kcal/mol) *and roughly equal for each Y for the three halides* (Table 1). We therefore recommended[24,31] that CW's[14] "intriguing hypothesis that the direction and magnitude of the effects of Y-substituents on 4-YC$_6$H$_4$Z−X BDEs depends on the difference in the electronegativities of the bonding atoms in Z and X *should be discarded.*" We continued "However, this does not mean that Y has no "purely polar" effect on carbon−halogen BDEs in benzyl halides. To "see" this purely polar effect it is, of course, necessary to correct for the major...stabilizing effect of

Table 2. Calculated Gas-Phase RSEs, MSEs, and TSEs ($= RSE - MSE = \Delta BDE$) for 4-$YC_6H_4CH_2^{\bullet}$ and 4-$YC_6H_4CH_3$ in kcal/mol[a]

Y	σ^{+b}	RSE	MSE	TSE[c]
$(CH_3)_2N$	−1.70	−1.3	0.7	−2.0
H_2N	−1.30	−0.9	0.8	−1.7
CH_3O	−0.78	−0.1	0.6	−0.7
CH_3	−0.31	−0.2	0.3	−0.5
H	0.0	0.0	0.0	0.0
CF_3	0.61	−0.3	−0.6	0.3
CN	0.66	−1.2	−0.8	−0.4
NO_2	0.79	−1.2	−0.9	−0.3

[a] Reference 20. [b] Reference 1. [c] Slight differences from Table 1 are due to the higher level of theory employed in this work.

each Y on the 4-$YC_6H_4CH_2^{\bullet}$ radicals" arising from electron delocalization into Y. This can be accomplished from the data in Table 1 via

$$\Delta\Delta BDE = [\Delta BDE(4\text{-}YC_6H_4CH_2\text{-}X - C_6H_5CH_2\text{-}X)] - [\Delta BDE(4\text{-}YC_6H_4CH_2\text{-}H - C_6H_5CH_2\text{-}H)] \quad (2)$$

and $\Delta\Delta BDE$ (C−Br, C−Cl, and C−F) correlates well with $\sigma_p^{+}(Y)$, $\rho^{+} = -1.43$, -1.36, and -0.90 kcal/mol, respectively. Note that the signs of ρ^{+} are in the direction suggested by CW,[14] namely, ED Ys strengthen and EW Ys weaken the C−X bonds. Nau[33] had earlier drawn rather similar conclusions regarding his "polar ground-state stabilization energy" effect of Y on 4-$YC_6H_4CH_2$−Br BDEs. Our calculations[24] and Nau's[33] indicate that substituents do exert a *purely polar* effect on the BDEs of benzyl halides. However, the magnitudes of these effects are remarkably similar and ρ^{+} correlates with the dipole moments of the benzyl halides—namely, $C_6H_5CH_2Br$, 2.03 D; $C_6H_5CH_2Cl$, 1.94 D; $C_6H_5CH_2F$, 1.66 D—and not with $\Delta\chi$ (C−X).[24]

Molecule and Radical Stabilization/Destabilization. Like other workers in this field,[26,27,33,34] we have also separated the effects of Y on 4-$YC_6H_4CH_3$ from its effect on 4-$YC_6H_4CH_2^{\bullet}$.[20] We refer to the interaction enthalpies between Y and the CH_3 group as the *molecule stabilization enthalpies* (MSE),[35] which were determined using the isodesmic reaction

$$C_6H_5CH_3 + YC_6H_5 \xrightarrow{MSE} 4\text{-}YC_6H_4CH_3 + C_6H_6 \quad (3)$$
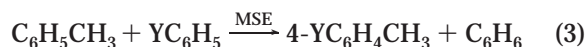
The interaction enthalpies between Y and the $CH_2^{\bullet}$ group, which we refer to as the *radical stabilization enthalpies* (RSE), were determined using the isodesmic reaction

$$C_6H_5CH_2^{\bullet} + YC_6H_5 \xrightarrow{RSE} 4\text{-}YC_6H_4CH_2^{\bullet} + C_6H_6 \quad (4)$$
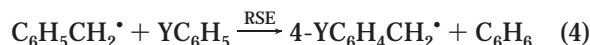
The *total stabilization (destabilization) enthalpy* (TSE) is equal to ΔBDE and is comprised of both the MSE and RSE, that is,

$$TSE = RSE - MSE = \Delta BDE \quad (5)$$

Some results[20] are given in Table 2. All ED and EW Ys slightly stabilize the radical, indicating that polar effects are unimportant in stabilizing/destabilizing 4-$YC_6H_4CH_2^{\bullet}$ (contrast 4-$YC_6H_4O^{\bullet}$ and 4-$YC_6H_4NH^{\bullet}$, vide infra). However, ED Ys destabilize and EW Ys stabilize 4-$YC_6H_4CH_3$. This

Table 3. Homolyses of Benzyl Phenyl Ethers and Anisoles, Differences in E_a and BDE from the Unsubstituted Compounds (kcal/mol)[a]

	4-YC_6H_4O−CH_2Ph		4-YC_6H_4O−CH_3	
Y	ΔE_a	ΔBDE (calcd)	ΔE_a	ΔBDE (calcd)
CH_3O	−5.5	−6.1	−3.1	−6.1
CF_3	3.2	3.0	2.2	3.0

[a] Reference 13.

indicates that two ED groups, Y and CH_3, interact to destabilize the molecule (a push−push effect), increasing the MSE and hence decreasing the TSE and ΔBDE, whereas an EW Y and the CH_3 group interact to stabilize 4-$YC_6H_4CH_3$ (a pull (Y)−push (CH_3) effect), decreasing the MSE and hence increasing the TSE and ΔBDE, the latter to a positive value for 4-CF_3. Toluene RSEs and TSEs do not correlate with $\sigma^{+}(Y)$. However, MSEs for toluenes, like those for phenols and anilines, do correlate with σ^{+}, but poorly.[20] This is because the push−push destabilizing effects of ED Ys are smaller for all three families than the pull−push stabilizing effects of EW Ys having comparable $|\sigma^{+}|$ ($|\sigma|$). Presumably push−push effects rapidly "saturate" the electron-accepting capacity of the aromatic ring (vide infra).

O−X $\Delta BDEs$ for 4-YC_6H_4O−X

Experiment and theory agree that O−H $\Delta BDEs$ in 4-YC_6H_4-OH give excellent linear correlations with $\sigma^{+}(Y)$.[4−7,13,20,29] Our work on 4-$YC_6H_4CH_2$−X BDEs (X = H, halogen) led us to believe that "differences in BDEs for 4-YC_6H_4O−X compounds caused by changes in Y should be *largely independent* of X."[13] This forced us to address one glaring inconsistency, namely, Suryan et al.'s[8] experimental determination of 4-YC_6H_4O−CH_3 BDEs for which ρ^{+} was only 3.0 kcal/mol[13] consistent with $\Delta\chi(O−C)$, see Figure 1, but less than half of the value we expected. It is also inconsistent with Wu and Lai's[34] conclusion that the effects of Y on 4-YC_6H_4O−H and O−CH_3 BDEs were "nearly identical".

As is our custom, this inconsistency was examined by experiment and theory.[13] Rates of O−C bond cleavage were measured for substituted anisoles in the gas phase at ca. 1000 K and for substituted benzyl phenyl ethers in the liquid phase at ca. 550 K in the presence of a radical scavenger, 9,10-dihydroanthracene. The effect of Y on 4-YC_6H_4O−$CH_2C_6H_5$ was, as expected, much greater than that on 4-$YC_6H_4CH_2$−OC_6H_5 BDEs.

The O−H and O−C BDEs were calculated for phenols and phenyl ethers for two ED (NH_2, CH_3O) Ys, two EW (CF_3, NO_2) Ys, and Y = H and gave essentially identical ρ^{+} values (6.7 kcal/mol) for O−H, O−CH_3, and O−CH_2Ph BDEs. The 4-$YC_6H_4CH_2$−OC_6H_5 $\Delta BDEs$ did not correlate with σ^{+}, and BDEs were weaker for the four substituents than for Y = H as found previously for other 4-YC_6H_4-CH_2−X (Table 1). Differences in the experimental activation enthalpies for 4-YC_6H_4O−CH_2Ph bond cleavage, ΔE_a, were in remarkably good agreement with calculated $\Delta BDEs$, see Table 3. For the anisoles, the E_a's (and the
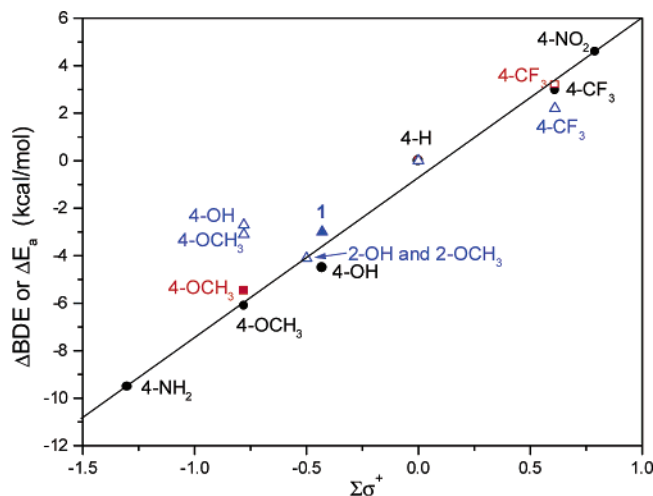
FIGURE 2. Correlation of calculated ΔBDE(O−C) in 4-Y$_6$H$_4$OCH$_3$ (●) and of ΔE$_a$ from the thermolysis of benzyl phenyl ethers (□) and pyrolysis of anisoles (△) with Σσ$^+$.

ΔBDEs) were in excellent agreement[36] with those obtained by Suryan et al.[8] who employed the same experimental technique, reinforcing the ρ$^+$ = 3.0 kcal/mol anomaly.[13] Theoretical and experimental values of O−C ΔBDEs and ΔE$_a$'s are in good agreement for all anisoles *except* 4-HOC$_6$H$_4$OCH$_3$ and 4-CH$_3$OC$_6$H$_4$OCH$_3$ (Figure 2).

Temperature-Dependent Substituent Effects. Two literature "explanations" for the difference between computational and experimental 4-YC$_6$H$_4$O−CH$_3$ ΔBDEs were inconsistent with certain facts and were discarded.[13] The experimental temperatures remained the only possible source of the discrepancies in the effects of substituents on 4-YC$_6$H$_4$O−H (∼300 K) and 4-YC$_6$H$_4$O−CH$_3$ (∼1000 K) ΔBDEs. The OH and OCH$_3$ groups exert their maximum substituent effects when their conjugating oxygen 2p-type lone pair is perpendicular to the aromatic ring plane. At ambient temperatures, these groups lie in the aromatic plane and have significant Ph-OX rotation barriers, for example, ∼3.5 kcal/mol for X = H. Consider 4-ROC$_6$H$_4$-OCH$_3$: Out-of-plane rotation of RO will increase the O−CH$_3$ BDE because nonplanar 4-ROC$_6$H$_4$O$^\bullet$ will be less stabilized than its planar conformer and because ED conjugating substituents (RO) have a larger effect on RSE than on MSE, vide infra. At high temperatures, conformational changes are expected, and the rotational configuration of both the substituent and dissociating group become important. To ensure that the substituent exerts its maximum effect at elevated temperatures, it must be "held" in the coplanar position. This was achieved with the disubstituted anisole **1**.

1
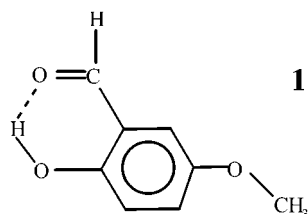
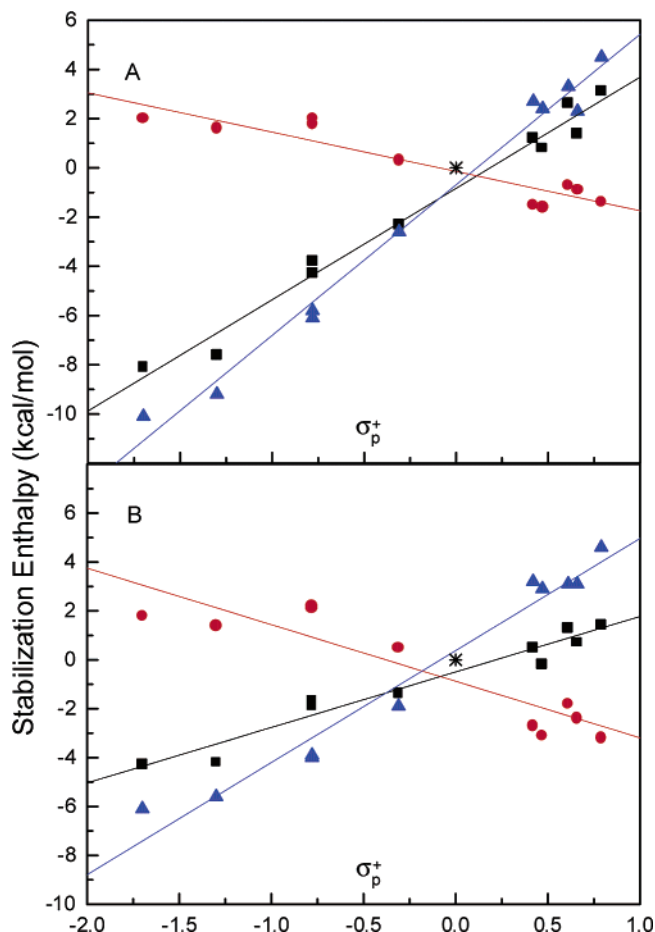The strong intramolecular H-bond in **1** (∼10 kcal/mol)[37]

FIGURE 3. Correlation of stabilization enthalpies in (A) 4-YC$_6$H$_4$OH and 4-YC$_6$H$_4$O$^\bullet$ and in (B) 4-YC$_6$H$_4$NH$_2$ and 4-YC$_6$H$_4$NH$^\bullet$ (●, MSE; ■, RSE; ▲, TSE). The asterisks indicate the (0,0) point.

ensured that both the HO and CHO substituents remained in-plane even at 1000 K and its experimental high-temperature ΔBDE (the filled blue triangle in Figure 2) does, indeed, lie close to the line drawn through the (298 K) calculated ΔBDEs for all the other anisoles. Experimental 4-ROC$_6$H$_4$O−CH$_3$ ΔBDEs for R = H and CH$_3$ are only about half their calculated values (Figure 2), which, to a first approximation, implies that HO and CH$_3$O rotate freely at 1000 K. However, the ΔE$_a$ point for 4-CH$_3$-OC$_6$H$_4$O−CH$_2$Ph (a filled red square in Figure 2) lies essentially on the line implying that the CH$_3$O and PhCH$_2$O groups are not free rotors at 500 K.

Calculated RSE, MSE, and TSE for 4-YC$_6$H$_4$O−H.[20] The RSEs and TSEs give excellent linear correlations with σ$^+$-(Y) for 10 substituents ranging from the strong ED Me$_2$N to the strong EW NO$_2$ (see Figure 3A). The MSEs are not really well correlated by σ$^+$ or σ. However, for phenols, the RSEs (ρ$^+$ = 4.5) make a 3-fold greater contribution to the TSEs than do MSEs (ρ$^+$ ≈ −1.6), and hence, the TSEs are still well correlated by σ$^+$ (ρ$^+$ = 6.1 kcal/mol).

Another method for calculating 4-YC$_6$H$_4$O−H BDEs is to use DFT-computed ionization and reduction potentials for 4-YC$_6$H$_4$O$^\bullet$ in combination with the (local) hard and soft acids and bases (HSAB) principle.[22,28] Although this "hardness" approach may be useful in predicting substituent effects on heterolytic bond cleavage and has had

some success with homolytic BDEs,[22,28] recent work is not encouraging.[38] Further theoretical development is required.

N−X ΔBDEs for 4-YC₆H₄NH−X

X = H. Measurements of a number of $4YC_6H_4NH-H$ BDEs using three different experimental techniques[18,19,39] showed disturbing inconsistencies.[20] That is, one procedure[20] was certainly unreliable because N−H BDEs were calculated from oxidation potentials of anilinyl radicals *estimated* by *irreversible* cyclic voltametry in DMSO combined with the aniline's DMSO pK_a's (which lie far above the normal pK_a range). Another procedure,[19] which involved combining the reduction potentials of anilinyl radical cations (generated in water by pulse radiolysis) with their pK_a's (which lie in the normal range), should provide fairly reliable N−H BDEs. There were also a very few PAC measurements.[39] Additional measurements by PAC and by the radical equilibrium electron paramagnetic resonance (REqEPR) technique were unsuccessful.[20] REqEPR measurements could, however, be made on 3,7-disubstituted phenothiazines, **2**, and 4,4′-disubstituted diphenylamines, **3**,

2   **3**
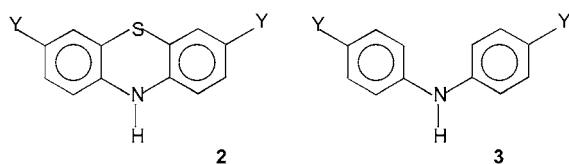
and ΔBDEs were calculated for some of these compounds.[20] Good agreement between theory and experiment for several **2** and **3** compounds gave us the confidence to calculate 4-YC₆H₄NH−H ΔBDEs using the same substituents as those employed in the 4-YC₆H₄O−H calculations. For 4-YC₆H₄NH₂, the correlations with σ^+ of the RSEs and TSEs (see Figure 3B) are not quite as good as those for 4-YC₆H₄OH. The TSEs (ΔBDEs) with EW Ys are remarkably similar for anilines and phenols, although the MSE/RSE mix differs. The MSE contributions for EW Ys are larger in anilines than phenols because the NH₂ group is a stronger π-ED and a weaker σ-EW than the OH group. Hence, NH₂ interacts more strongly than OH with both π- and σ-EW Ys. The MSEs for anilines and phenols with ED Ys are very similar, and there is essentially no difference in their magnitudes for Y = CH₃O, HO, H₂N, and Me₂N despite the large differences in ED abilities of Y. Thus, the law of diminishing returns sets in for destabilization of anilines and phenols when the already electron-rich aromatic ring is substituted with an ED group.

The RSEs are smaller for the anilines than for the phenols because the unpaired electron is more localized on the heteroatom in anilinyls than in phenoxyls. This has been demonstrated by electron spin resonance (ESR) spectroscopy and is due to smaller 2p−π orbital overlap in anilinyl, which arises because the C−N bond in C₆H₅-NH• is longer (1.34 Å) than the C−O bond in C₆H₅O• (1.25 Å), though shorter than the C−C• bond in C₆H₅CH₂• (1.40

Table 4. Calculated Gas-Phase N−X ΔBDEs for 4-YC₆H₄NH-X in kcal/mol[a]

Y	X = CH₃	X = H	X = OH	X = F
(CH₃)₂N	−6.4	−6.1	−5.9	−5.0
H₂N	−5.9	−5.6	−5.5	−4.8
CH₃O	−3.6	−4.1	−3.3	−2.9
CH₃	−1.5	−1.9	−1.6	−1.3
H	0[b]	0[b]	0[b]	0[b]
CF₃	3.7	3.1	2.6	1.5
CN	3.7	3.1	2.3	1.0
NO₂	5.6	4.7	3.7	2.0
ρ^+ [c]	5.0 ± 0.3	4.6 ± 0.3	4.0 ± 0.2	3.0 ± 0.2
R^2 [c]	0.974	0.967	0.983	0.977

[a] Reference 20. [b] BDE N−CH₃ = 66.6, N−H = 91.5, N−OH = 43.5, and N−F = 53.6 kcal/mol. [c] With three additional substituents (HO, COOH, and CHO).

Å).[40] These differences in C−Z• bond lengths explain why there is no monotonic change in the Z−H BDEs of toluene (90.4),[24] aniline (91.5),[20] and phenol (87.2 kcal/mol).[13,41] Another consequence is that the unpaired electron in anilinyls interacts less strongly with π-ED and EW Ys than that in phenoxyls.

X = CH₃, OH, and F. The strong ED character of the NH₂ group and strong EW character of the NH• moiety cause the effects of Y on MSEs and RSEs to be of comparable magnitude. This contrasts with the role of Y on O−X[13] and CH₂−X[13,24] ΔBDEs in 4-YC₆H₄ZX. In these two families, MSEs are small relative to RSEs, which therefore dominate, and for molecules of practical interest to organic chemists, the effects of Y are essentially independent of X (≤1.5 kcal/mol for the examined X, see, for example, Table 1). However, substitution by X of one H in NH₂ could substantially modify the ED effect of the amino group, which would influence MSEs and hence N−X ΔBDEs. Our original proposal[24] that the effect of Y on Z−X ΔBDEs in 4-YC₆H₄Z−X would be independent of X, while essentially true for Z = O and CH₂, seemed unlikely to be true for Z = NH. Since dissociation of the N−X bond yields the same 4-YC₆H₄NH• radical, N−X ΔBDEs reflect MSE differences, which can be substantial for EW Ys, see Table 4. Nevertheless, despite large changes in the magnitude and direction of bond polarity, namely, $N^{\delta-}-C^{\delta+}$ (Δχ = 0.6), $N^{\delta-}-H^{\delta+}$ (Δχ = 1.0), $N^{\delta+}-O^{\delta-}$ (Δχ = −0.4), and $N^{\delta+}-F^{\delta-}$ (Δχ = −0.9), the signs of ρ^+ are all the same (Table 4) and lie between those for 4-YC₆H₄O−X (6−7 kcal/mol) and 4-YC₆H₄CH₂−X (∼0). This provides additional evidence that Z−X bond polarity (even in the favorable N−X case) has no more than a minor effect on the magnitude of ρ^+, not the major effect once advocated.[14]

Conclusion and Why Only Some 4-YC₆H₄Z−X ΔBDEs Correlate with σ_p^+

The constants $\sigma_p^+(Y)$ describe the relative abilities of Y to stabilize the positive charge in the carbocation, 4-YC₆H₄C-(CH₃)₂⁺, formed in the S_N1 solvolysis of 4-YC₆H₄C(CH₃)₂-Cl.[1] The RSEs of 4-YC₆H₄O• and 4-YC₆H₄NH• correlate well with σ_p^+ because O• and NH• are, like a positive charge, strong EW moieties (estimated[20] σ_p^+ or σ_p ≈ 2 and 1,

respectively, vs 0.79 for NO_2). The O–H and N–H ΔBDEs (the TSEs) in phenols and anilines also correlate very well and well, respectively, with σ_p^+ because the RSE, relative to the MSE, makes the major (OH) or an equal (NH) contribution to the TSE. The MSEs for $4\text{-}YC_6H_4OH$, $4\text{-}YC_6H_4NH_2$, and $4\text{-}YC_6H_4CH_3$ correlate poorly with σ_p^+ and σ_p because the "push–push" interactions of ED Ys readily "saturate". The C–H ΔBDEs do not correlate with σ_p^+ or σ_p because $CH_2^\bullet$ is neither EW nor ED and $4\text{-}YC_6H_4\text{-}CH_2^\bullet$ radicals are stabilized by any group that can delocalize the unpaired electron. Hence, RSEs (and TSEs) in toluenes do not correlate with $\sigma_p^+(Y)$ or $\sigma_p(Y)$.

Two Directions for Future Work

First, calculations yield gas-phase BDEs, but many experimental measurements are made in solution, and liquid-phase BDEs can differ from gas-phase values by several kilocalories per mole largely as a consequence of hydrogen bonding with solvent molecules. This is usually H-bonding by the substrate, for example, phenol, which increases the measured O–H BDE,[42] but in some solvents, H-bonding of the radical is more important,[43] which would decrease the measured O–H BDE. An understanding of solvent effects on (readily calculated or already known) gas-phase BDEs would be of immense help in synthetic planning and in mechanistic organic chemistry.

Second, compared with first row elements, elements in the next row have lower electronegativities (viz., C/Si 2.5/1.8; N/P 3.0/2.1; O/S 3.5/2.5), form longer bonds, and have poorer ($3p$–2π) orbital overlap in $C_6H_5Z^\bullet$. Substituent effects on second row Z–H BDEs are therefore expected to have a negligible effect on RSEs for $4\text{-}YC_6H_4Z^\bullet$. For Z = SiH_2[32] and PH[44] substituent effects on MSEs will be negligible because SiH_3 and PH_2 must be weak EDs. In contrast, substituent effects on MSEs for Z = S are expected to be nonnegligible because SH must be a fairly strong ED group ($\sigma_p^+(CH_3S) = -0.60$ vs $\sigma_p^+(CH_3) = -0.31$ and $\sigma_p^+(CH_3O) = -0.78$). If RSEs could be ignored, TSE would equal $-$MSE (eq 5) and a plot of S–H ΔBDEs for $4\text{-}YC_6H_4SH$ vs σ_p^+ would be expected to yield a ρ^+ value of 1.6, comparable to the phenol and anisole $-$MSE ρ^+ values with the usual relatively poor correlation coefficients found for MSE plots because of saturation effects. The experimental S–H ΔBDEs in $4\text{-}YC_6H_4SH$[45,46] are consistent with this analysis. However, calculations[47] on $4\text{-}YC_6H_4SH$ (which, at the same level of theory, we have confirmed) indicate that substituents exert a larger effect on RSEs than on MSEs. This disagreement between our present understanding of substituent effects on S–H BDEs for $4\text{-}YC_6H_4\text{-}SH$ (which lead us to expect large MSEs and small RSEs) and calculations (which indicate the reverse) will have to be resolved by careful measurements of the heats of formation of these compounds.

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