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An AM1 study of the effect of substituents on the bond dissociation energies of anilines, phenols, and α-substituted toluenes

Gerritt P. Bean*

Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, CO 80309-0215, USA

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Abstract—Two isodesmic equations (see Graphical Abstract) were used to separate the ground state and radical effect of *para*-substituents, Y, on the bond dissociation energies (BDEs) of $YC_6H_4Z{-}H$ (Z=CHX, NX, or O). In all cases, the ground state is destabilized by electron-donating groups (*p*-EDGs), while stabilized by electron-withdrawing groups (*p*-EWGs). The radicals are stabilized by *p*-EDGs, the 'captodative effect', but the effect of *p*-EWGs depends upon the electronegativity of Z, which can be modified by an adjacent substituent, X. When Z is polarized by a strong EWG (e.g. NO_2) or when Z is NH or O, the radicals are destabilized by *p*-EWGs, an 'anti-captodative effect'. Relative to $C_6H_5Z{-}H$, the *p*-EWGs may either increase or decrease the BDE depending upon the 'apparent electronegativity' of Z. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

It was long assumed that relative bond dissociation energies (BDEs) were a measure of the stabilization energy of the corresponding radical, i.e. a stronger R–H bond will produce a less stable R radical.[1] This also assumed that substituents had little effect upon the stability of the ground state molecule. It is now recognized that the stability of both the ground state molecule and the radical must be considered.[2] A well-studied example is the different effect that *para*-substituents have on the BDEs of toluenes and phenols.[3] It has often been noted that both electron-donating (EDGs) and electron-withdrawing groups (EWGs) slightly decrease the homolytic BDEs of the *p*-substituted toluenes.[4] This is contrary to their effect on the BDEs of phenols (or anilines) where EDGs decrease the BDEs while EWGs increase the BDEs. It is apparent that *para*-substituents on the toluenes have a different effect on the ground state and/or the radical energies than that observed for the phenols.[5] A number of approaches have been used in attempts to separate the 'ground-state' or 'polar effects' and the 'radical effects'.[6] Wu and co-workers have used two isodesmic reactions to evaluate the effect that substituents have on the ground state and on the benzyl radicals of *para*-substituted toluenes.[7] The heats of formation were obtained from density functional theory (DFT) calculations.

For the ground-state effect (GE)

$$YC_6H_4CH_3 + C_6H_6 \rightarrow YC_6H_5 + C_6H_5CH_3$$

Radical effect (RE)

$$YC_6H_4CH_2^{\bullet} + C_6H_6 \rightarrow YC_6H_5 + C_6H_5CH_2^{\bullet}$$

The total effect (TE) is TE=RE−GE.

From their results, they concluded that EDGs destabilize the ground state of toluenes but stabilize the benzyl radicals; both effects decrease the BDE. However, EWGs stabilize both the ground state and the radical. Because the magnitude of the RE is greater than the GE, the BDEs are also decreased, although to a lesser extent than by EDGs. (Substituents that stabilize the ground state increase the BDE while stabilization of the radical lowers the BDE.) Relative to toluene itself, both EDGs and EWGs decrease the BDE as is observed experimentally. More recently, Wu and Lai have calculated the GE and RE for a series of *p*-substituted phenols.[8] As with the toluenes, EDGs destabilize the ground state and stabilize the radical, which results in the lowering of the BDEs. In contrast to the toluenes, EWGs on the phenols destabilize the radical but stabilize the ground state. This increases the gap between the ground state and the radical so that the BDE increases.

Ingold and co-workers have recently reported a study of the BDEs of *p*-substituted benzyl halides (F, Cl, and Br) in an investigation to determine if there were 'purely polar effects' (GEs) affecting the BDEs.[9] Using photoacoustic calorimetry, Clark and Wayner had reported that, contrary to toluene, EWGs decrease the C–Br BDE in benzyl bromides.[10] Using DFT to calculate the heats of formation, Ingold et al. found that, as for the toluenes, both *p*-EDGs and *p*-EWGs decrease the BDEs, but within a range of

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*E-mail: tahosa@infi.net

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<2.3 kcal/mol. To observe if there were any polar effects with the benzyl halides, they corrected for the stabilizing effect that Y has on the benzyl radicals by using the isodesmic reaction

$$C_6H_5CH_2{-}X + YC_6H_4CH_2{-}H \rightarrow YC_6H_4CH_2{-}X + C_6H_5CH_2{-}H$$

They calculated the change in the BDEs, relative to the toluenes (ΔΔBDE), as

$$\Delta\Delta\mathrm{BDE}(X{-}H) = [\Delta\mathrm{BDE}(YC_6H_4CH_2{-}X - C_6H_5CH_2{-}X)] - [\Delta\mathrm{BDE}(YC_6H_4CH_2{-}H - C_6H_5CH_2{-}H)]$$

Plotting the values of ΔΔBDE (X–H) against the σ^+ values for the Y substituents gave a linear relationship for X=F, Cl, and Br (r^2>0.98). The ρ^+ values were −0.90, −1.36, and −1.43, respectively. From this, they concluded that there were purely polar effects on the BDEs of the benzyl halides and that *p*-EDGs strengthen the carbon-halogen bond while *p*-EWGs weaken these bonds.[11]

Because the effect of *para*-substituents on the BDEs of toluenes, α-substituted toluenes, anilines, and phenols depends upon the stabilizing or destabilizing effect on both the ground state and their radicals it was of interest to investigate the effect that substituents, both on the aromatic ring and the side-chain, have on the energy of the ground state and the radical. For this study, we chose a series of *p*-substituted toluenes, anilines, phenols, and α-substituted toluenes that may also have substituents on CH_2, NH or O, which we have symbolized as YC_6H_4ZH, where Z=CHX, NX, or O.

2. Computational methodology

The heats of formation (ΔH_f) of the neutral molecules, YC_6H_4ZH, where Z is CHX, NX, or O, and their radicals were calculated using the semi-empirical AM1 MO method which directly provides the heats of formation and has been shown to give reasonable values for neutral compounds, ions, and radicals.[12] A representative set of EDGs and EWGs on the aromatic ring and the X groups were chosen. The large number of compounds and their radicals (>300) precluded the use of more sophisticated methods such as density functional theory.[13,14] The calculations were performed using the MOPAC 97 program from Fujitsu Ltd. All of the calculations were made with full optimization of the geometry.[15] The ΔH_f, spin density on the C, N, or O atom, and energy of the singly occupied molecular orbital (SOMO) of the radicals were calculated at the unrestricted Hartree–Fock (UHF) level. Although the restricted Hartree–Fock (RHF) or 'half-electron' calculations give better agreement with the experimental ΔH_fs for the radicals, there is a better correlation of the spin density and SOMO values of the radicals from the UHF calculations with the ΔH_fs of the radicals and the BDEs.[3b,12b]

3. Results

3.1. Separation of the ground state and radical effects on toluenes, anilines, and phenols

To investigate the different behavior of the toluenes as compared to the anilines and phenols, we combined the approaches of the Ingold and Wu groups. In this manner, we adjusted the ΔH_fs of the toluenes, anilines, and phenols ($\Delta\Delta H_f$RH) and their radicals ($\Delta\Delta H_f\mathrm{R}^{\cdot}$) using the ΔH_fs of the corresponding benzenes and phenyl radicals. These correspond to the following isodesmic reactions.

For $\Delta\Delta H_f$RH, where Z=CH_2, NH, or O

$$YC_6H_4ZH + C_6H_6 \rightarrow YC_6H_5 + C_6H_5ZH \qquad (1)$$

And for $\Delta\Delta H_f\mathrm{R}^{\cdot}$,

$$YC_6H_4Z^{\cdot} + C_6H_5^{\cdot} \rightarrow YC_6H_4^{\cdot} + C_6H_5Z^{\cdot} \qquad (2)$$

Our $\Delta\Delta H_f$RH is the same as the GE of Wu and co-workers but $\Delta\Delta H_f\mathrm{R}^{\cdot}$ differs from their RE.[16,17] Similar to Wu's TE, our ΔΔBDE is equal to $\Delta\Delta H_f\mathrm{R}^{\cdot}-\Delta\Delta H_f\mathrm{RH}$. It is also the difference between the BDE and an 'Adj BDE' calculated using the adjusted ΔH_f values for the molecules and their radicals.

$$\mathrm{Adj}\ \Delta H_f\mathrm{RH}[YC_6H_4ZH] = \Delta H_f\mathrm{RH}[YC_6H_5] - [\Delta H_f\mathrm{RH}[C_6H_6] - \Delta H_f\mathrm{HR}[C_6H_5ZH]] \qquad (3a)$$

$$\Delta\Delta H_f\mathrm{RH} = \mathrm{Adj}\ \Delta H_f\mathrm{RH}[YC_6H_4ZH] - \Delta H_f\mathrm{RH}[YC_6H_4ZH] \qquad (3b)$$

$$\mathrm{Adj}\ \Delta H_f\mathrm{R}^{\cdot}[YC_6H_4Z^{\cdot}] = \Delta H_f\mathrm{R}^{\cdot}[YC_6H_4^{\cdot}] - [\Delta H_f\mathrm{R}^{\cdot}[C_6H_5^{\cdot}] - \Delta H_f\mathrm{R}^{\cdot}[C_6H_5Z^{\cdot}]] \qquad (4a)$$

$$\Delta\Delta H_f\mathrm{R}^{\cdot} = \mathrm{Adj}\ \Delta H_f\mathrm{R}^{\cdot}[YC_6H_4Z^{\cdot}] - \Delta H_f\mathrm{R}^{\cdot}[YC_6H_4Z^{\cdot}] \qquad (4b)$$

$$\mathrm{Adj\ BDE} = [\mathrm{Adj}\ \Delta H_f\mathrm{R}^{\cdot}[YC_6H_4Z^{\cdot}] + \Delta H_f[H^{\cdot}]] - \mathrm{Adj}\ \Delta H_f\mathrm{RH}[YC_6H_4ZH] \qquad (5)$$

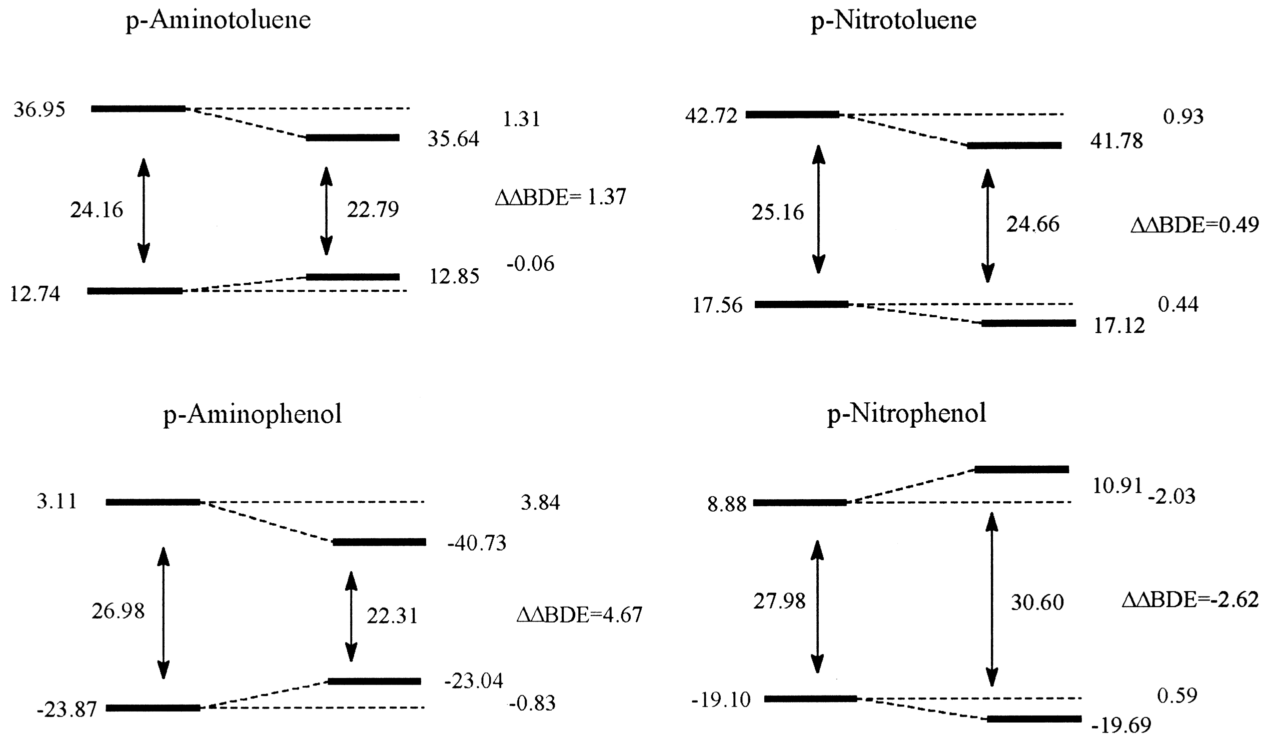
In addition to calculating the values of ΔΔBDE, $\Delta\Delta H_f$RH, and $\Delta\Delta H_f\mathrm{R}^{\cdot}$, we also examined the energy of the odd electron (designated as SOMO for 'singly occupied molecular orbital') and the spin density on the C, N, or O atoms of the benzyl, anilino or phenoxy radicals. These data are tabulated in Table 1.

We see that the ground state ($\Delta\Delta H_f$RH) of the toluenes, anilines, and phenols are destabilized by EDGs while being stabilized by EWGs. This is opposite to the behavior of the anilino and phenoxy radicals ($\Delta\Delta H_f\mathrm{R}^{\cdot}$) which are stabilized by EDGs but destabilized by EWGs. The benzyl radicals, however, are stabilized by both EDGs and EWGs. This agrees with the findings of Wu and co-workers.[7,8] Both EDGs and EWGs weaken the BDEs of the toluenes while the BDEs of the anilines and phenols are weakened by EDGs but strengthened by EWGs. This can be visualized as

Table 1. BDEs, changes in ΔH_f for toluenes, anilines, and phenols and their radicals, SOMO, and spin of their radicals. Energies are in kcal/mol, unless otherwise indicated

	BDE	Adj. BDE	ΔΔBDE	$\Delta\Delta H_f\mathrm{RH}^a$	$\Delta\Delta H_f\mathrm{R}^{\cdot a}$	SOMO[b]	Spin density[c]
Toluenes							
H	76.25	76.25	0	0	0	−8.682	0.9114
p-Me	75.82	76.19	0.37	0.01	0.38	−8.526	0.9050
p-HO	75.41	76.41	1.00	−0.06	0.93	−8.399	0.8993
p-MeO	75.49	76.43	0.94	−0.06	0.87	−8.318	0.9007
p-NH$_2$	74.89	76.26	1.37	−0.06	1.30	−7.995	0.8928
p-CN	76.18	76.62	0.44	0.23	0.67	−9.107	0.9000
p-CHO	76.40	76.51	0.11	0.24	0.35	−9.056	0.9024
p-CF$_3$	76.68	76.91	0.22	0.25	0.48	−9.283	0.9056
p-NO$_2$	76.76	77.26	0.50	0.43	0.93	−9.546	0.8980
Anilines							
H	81.50	81.50	0	0	0	−9.289	0.7172
p-Me	80.77	81.45	0.68	−0.06	0.62	−9.050	0.7067
p-HO	79.51	81.67	2.16	−0.84	1.33	−8.849	0.6969
p-MeO	79.52	81.68	2.16	−0.82	1.33	−8.743	0.6981
p-NH$_2$	78.49	81.51	3.02	−0.83	2.18	−8.327	0.6825
p-CN	82.99	81.88	−1.12	1.08	−0.03	−9.712	0.7097
p-CHO	83.32	81.77	−1.55	1.35	−0.20	−9.688	0.7120
p-CF$_3$	83.97	82.16	−1.80	1.28	−0.52	−9.975	0.7199
p-NO$_2$	85.29	82.52	−2.78	2.21	−0.57	−10.254	0.7163
Phenols							
H	79.07	79.07	0	0	0	−9.665	0.3747
p-Me	77.94	79.02	1.08	−0.06	1.01	−9.375	0.3613
p-HO	76.33	79.23	2.91	−0.81	2.10	−9.137	0.3501
p-MeO	76.31	79.25	2.94	−0.77	2.17	−9.015	0.3506
p-NH$_2$	74.40	79.08	4.68	−0.84	3.84	−8.511	0.3286
p-CN	80.34	79.45	−0.89	0.28	−0.61	−10.078	0.3668
p-CHO	80.86	79.34	−1.18	0.33	−0.85	−10.070	0.3691
p-CF$_3$	81.64	79.73	−1.91	0.34	−1.57	−10.394	0.3798
p-NO>$_2$	82.69	80.09	−2.61	0.58	−2.03	−10.681	0.3768

[a] Positive sign indicates stabilization.
[b] SOMO.
[c] In e.v.s.



Scheme 1.

Table 2. $\Delta\Delta H_f$RH, $\Delta\Delta H_f$R$^{\cdot}$, and $\Delta\Delta$BDE for $YC_6H_4CH_2X$, Y=p-NH_2 and p-NO_2

X	Loss of X				Loss of H			
	$\Delta\Delta H_f$RH		$\Delta\Delta$BDE^{a,b}		$\Delta\Delta H_f$R$^{\cdot c}$		$\Delta\Delta$BDE^{d}	
	p-NH_2	pNO_2	p-NH_2	p-NO_2	p-NH_2	p-NO_2	p-NH_2	p-NO_2
NHMe	0.17	0.12	1.13	0.81	0.74	2.35	0.57	2.24
H	−0.06	0.43	1.36	0.50	1.30	0.93	1.36	0.50
F	0.26	−0.61	1.04	1.54	1.22	0.30	0.96	0.92
Cl	0.38	−0.90	0.92	1.83	1.37	0.27	0.99	1.18
Br	0.35	−0.84	0.95	1.77	1.50	0.03	1.15	0.87
CN	0.34	−1.19	0.96	2.12	1.75	−0.76	1.42	0.43
CF_3	0.53	−1.52	0.77	2.47	2.01	−1.20	1.48	0.32
NO_2	1.01	−2.59	0.29	3.52	2.50	−2.17	1.49	0.42
SO_2CN	0.70	−1.97	0.60	2.90	3.06	−2.35	2.36	-0.38

Positive values indicates stabilization or weaker bond.

[a] For breaking the $YC_6H_4CH_2{-}X$ bond.

[b] $\Delta\Delta H_f$R$^{\cdot}$ for the benzyl radicals are in Table 1.

[c] For the YC_6H_4CHX radical.

[d] For breaking the $YC_6H_4CHX{-}H$ bond.

diagrammed in Scheme 1 where the energies of the ground-state and radicals on the left are the 'adjusted' heats of formation and those on the right are the AM1 heats of formation of the p-amino and p-nitro toluenes and phenols.[18]

It has often been noted that there is a good correlation of BDEs with Brown's σ^+ values.[3a,b,5,8,9] Plots of $\Delta\Delta$BDE for the anilines and phenols versus σ^+ give straight lines (r^2>0.96) with ρ^+ values of −2.55 and −3.17, respectively. Because the $\Delta\Delta$BDE values for both EDGs and EWGs are positive for the toluenes, a plot of $\Delta\Delta$BDE versus σ^+ is 'V shaped'. However, the values of $\Delta\Delta$BDE for EDGs on toluene give a good correlation with the σ^+ values (r^2=0.99 and ρ^+=−1.05). For the EWGs there is a better correlation with σ_p values (r^2=0.88 and ρ_p=0.66) than with σ^+ (r^2=0.50). This is also true for the values of $\Delta\Delta H_f$R$^{\cdot}$ for benzyl radicals where σ^+ had r^2=0.99 for EDGs but for EWGs, r^2=0.69 for σ^+ while for σ_p, r^2=0.95. In contrast to the anilines and phenol, the effect of the p-EWGs on both the ground state and the radicals of toluenes appears to be inductive rather than resonance. This may be related to the smaller effect that *para*-substituents have on both $\Delta\Delta H_f$RH and $\Delta\Delta H_f$R$^{\cdot}$.

Although plots of $\Delta\Delta H_f$RH of the toluenes versus the anilines or phenols, or the anilines versus the phenols give fairly straight lines, with a correlation of r^2>0.81, the correlation is much better when the separate EDGs or EWGs are plotted against each other (r^2>0.98). Thus, the effect of the substituents on the heats of formation of the neutral molecules is proportional for the different families. There is a good correlation of the $\Delta\Delta$BDEs of the toluenes, anilines, and phenols with the energy of their SOMOs, r^2>0.91, indicating that the strength of the bonds depends upon the gap between the SOMOs of the $YC_6H_4Z^{\cdot}$ and $H^{\cdot}$ radicals; i.e.the 'hardness'.[13,19]

A plot of the $\Delta\Delta H_f$R$^{\cdot}$s of the anilines versus the phenols is a straight line with r^2=0.98. Although plots of the $\Delta\Delta H_f$R$^{\cdot}$s of the toluenes versus either the anilines or phenols are V shaped, when only the EDGs of the toluenes are plotted against the anilines or phenols, r^2>0.96, but for the EWGs the correlation is much poorer, r^2>0.63.

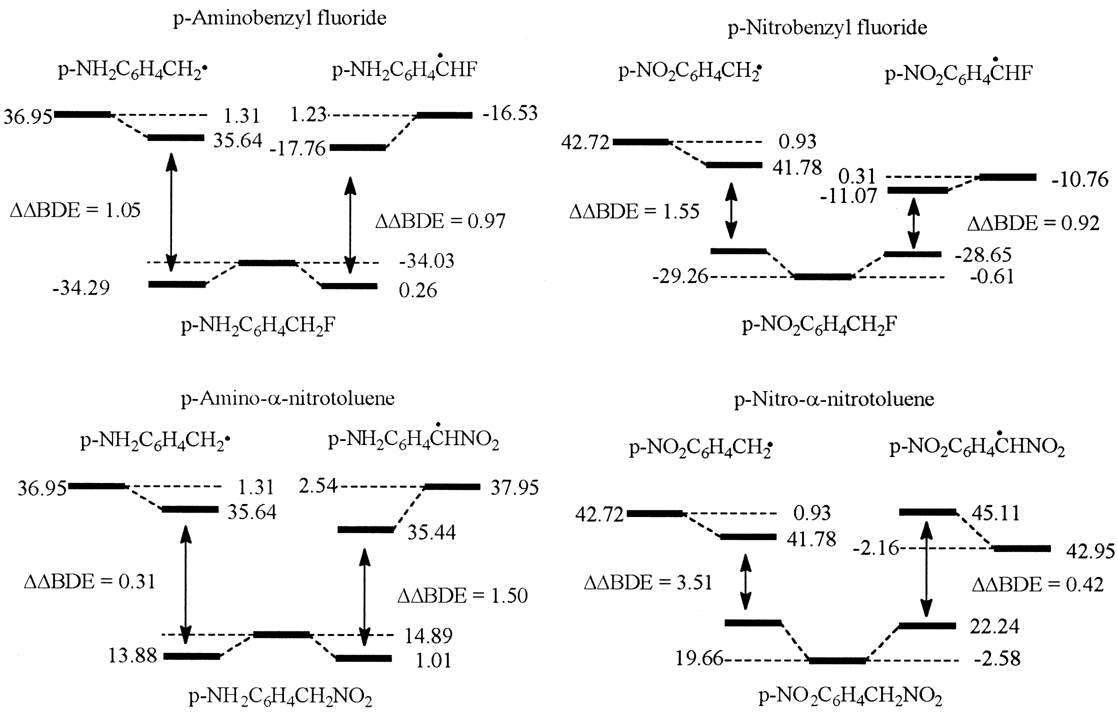
The RE is considered to be due to the stabilization of the radicals by spin delocalization and there is a fair correlation of the spin density on the N or O atom of the anilino and phenoxy radicals with the $\Delta\Delta H_f$R$^{\cdot}$ values, r^2>0.91.[3b] Although, both the spin density and the $\Delta\Delta H_f$R$^{\cdot}$ of the substituted benzyl radicals are lower than that of the benzyl radical itself, their correlation is still fair, r^2=0.90. It is much better if the EDGs are separated from the EWGs, r^2=0.98 and 0.86, respectively.[20]

We examined the relationship between the charges on the C, N, or O atoms, both on the ground state, ΔQ_{GS}, and radicals, ΔQ_{Rad}, with their $\Delta\Delta H_f$RH and $\Delta\Delta H_f$R$^{\cdot}$ values. Although the correlation overall for $\Delta\Delta H_f$RH versus ΔQ_{GS} for the toluenes and anilines (r^2>0.93) was good, it was much poorer for the phenols (r^2=0.70) because the EDGs and EWGs had quite different slopes. The separate correlation for the EDGs and EWGs was much better (r^2>0.91). Although the correlation for $\Delta\Delta H_f$R$^{\cdot}$ versus ΔQ_{Rad}, for the anilino and phenyl radicals was fair (r^2>0.85), again the correlation for the separate EDGs and EWGs was better than 0.93 because the EDGs and EWGs had different slopes. For the benzyl radicals, the separate correlations were 0.80 and 0.90, respectively.

It is obvious from these results that it is the effect that EWGs have on the benzyl radicals which produces the anomalous lowering of the BDEs. Later we will discuss the reason why, contrary to the anilines and phenols, the $\Delta\Delta H_f$R$^{\cdot}$ values for the benzyl radicals are all positive.

3.2. Application of the separation of ground state and REs to α-substituted toluenes

Nau has suggested that GEs become important only when a polar bond is being broken.[6a] We have therefore applied the same analysis to a series of α-substituted toluenes ($YC_6H_4CH_2X$, X=F, Cl, Br, CN, CF_3, and NO_2) and have calculated $\Delta\Delta H_f$RH and $\Delta\Delta$BDE for the loss of X.[21] The



Scheme 2.

values for the *p*-amino and *p*-nitro compounds are tabulated at the left side of Table 2. In a similar manner, we have calculated the $\Delta\Delta H_f\text{R}^{\cdot}$ for the radicals, $\text{YC}_6\text{H}_4\text{CHX}$, produced by the loss of hydrogen from $\text{YC}_6\text{H}_4\text{CH}_2\text{X}$, and the ΔΔBDE values for that process. These data are at the right of Table 2.

As X increases, the electron-withdrawal from the methylene carbon atom, the ground state becomes more stabilized by *p*-EDGs and destabilized by *p*-EWGs. Because the nature of X has no effect on $\Delta\Delta H_f\text{R}^{\cdot}$ for the resulting $\text{YC}_6\text{H}_4\text{CH}_2$ radicals, the effect of X on the BDEs for breaking the $\text{YC}_6\text{H}_4\text{CH}_2\text{–X}$ bond depends only upon the effect that X has on the ground-state energies. An increase in the electron-withdrawal from the methylene carbon atom has the opposite effect on the ΔΔBDEs; for *p*-EDGs the BDEs are weakened while for *p*-EWGs the BDEs are strengthened (left side of Table 2).

As observed for the toluenes, plots of ΔΔBDE for the $\text{YC}_6\text{H}_4\text{CH}_2\text{–X}$ versus σ^+ or σ_p have the characteristic V-Shape but the slope of the 'legs' change as X is varied. Plots of $\Delta\Delta H_f\text{RH}$ for the $\text{YC}_6\text{H}_4\text{CH}_2\text{X}$ families versus σ_p give better correlations than with σ^+ (average r^2=0.85 versus 0.75). This again indicates that inductive rather than resonance effects of the substituents affect the heats of formation of the ground state. There is an excellent correlation, r^2>0.99, between the $\Delta\Delta H_f\text{RH}$ values for $\text{YC}_6\text{H}_4\text{CH}_2\text{X}$ families, which indicates that the effect of the substituents, both electron-donating and withdrawing, have the same relative effect on the ΔH_fs of the ground state. As X becomes more electron-withdrawing, the slope of ΔΔBDE versus σ^+ for the *p*-EWGs (ρ^+) for each family ranges from 0.7 to 3.9 while for the *p*-EDGs ρ^+ is only −0.3 to −1.1. In addition, the range of values for the slope of $\Delta\Delta H_f\text{RH}$ versus σ_p for the *p*-EWGs is wider (0.5 to −2.8) than for the *p*-EDGs (0.1 to −1.5). This indicates that electron-withdrawal by X affects the sensitivity of $\Delta\Delta H_f\text{RH}$ (and also ΔΔBDE) to the *p*-EWGs more than to the *p*-EDGs. Our results are in agreement with the conclusions of Ingold and co-workers that substituents do exert a polar effect on the BDE of toluenes having α-substituents such as the benzyl halides. They found that the sensitivity to the substituents, ρ^+, is proportional to the dipole moment rather than the C–X electronegativity difference. We note that this is also true (r^2=0.94) for the slope (ρ^+) of ΔΔBDE for the six $\text{YC}_6\text{H}_5\text{CH}_2\text{X}$ compounds versus σ^+ and the AM1 dipole moments of $\text{C}_6\text{H}_5\text{CH}_2\text{X}$.

When the leaving group is a hydrogen atom, the nature of X affects the stability of both the ground state and the radical. We see in Table 2 that as X becomes more electron-withdrawing the stabilization of the resulting $\text{YC}_6\text{H}_4\text{CHX}$ radicals ($\Delta\Delta H_f\text{R}^{\cdot}$) by *p*-EDGs increases, while the stabilization by the *p*-EWGs decreases. This results in $\Delta\Delta H_f\text{R}^{\cdot}$ for the *p*-EWGs becoming negative (destabilized) when X=CN, CF_3, or NO_2, similar to the anilino or phenoxy radicals. Moreover, as electron-withdrawal by X increases, the *p*-EWGs have a greater effect on the values of $\Delta\Delta H_f\text{R}^{\cdot}$ than do the *p*-EDGs.[22] This is illustrated in Scheme 2 for the dissociation of the *p*-amino and *p*-nitrobenzyl fluorides and α-nitrotoluenes for the loss of X and of H.

When X is the very strong electron-withdrawing SO_2CN group, the $\Delta\Delta H_f\text{R}^{\cdot}$ values for the *p*-EWGs are so negative, e.g. −2.35 for the *p*-NO_2 group, that the ΔΔBDEs are also negative (−0.38 for *p*-$\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{CN}$) as is observed for the anilines and phenols. When there are *p*-EWGs, sufficient electron-withdrawal from the methylene group can destabilize the $\text{YC}_6\text{H}_4\text{CHX}$ radical so that the BDEs become stronger than that of $\text{C}_6\text{H}_5\text{CH}_2\text{X}$.

3.3. A rational for the different effect of substituents on the BDEs of toluenes and anilines or phenols

The question remains, why do both *p*-EDGs and *p*-EWGs stabilize the benzyl radicals while *p*-EWGs destabilize the radicals of anilines and phenols? As suggested by Walter some years ago, an obvious distinction is that the anilino and phenoxy radicals have an unshared pair of electrons that might interact with the single radical electron, while this is not possible for the benzyl radicals.[23] As we have noted in the previous section, an increase in electron pulling by an α-substituent enhances the effect that *para*-substituents have on both the ground state and the radical although the effect on the ground state is smaller. Plots of the resulting ΔΔBDEs for the loss of H from $YC_6H_4CH_2X$ versus σ^+ or σ_p are V shaped, but as X becomes more 'electron pulling', the ΔΔBDEs for the *p*-EDGs become more positive (weaker BDEs) while for the *p*-EWGs the ΔΔBDEs approach zero (close to the BDE of $C_6H_5CH_2X$) as the bonds become stronger. Indeed, when X is the very strong electron-withdrawing SO_2CN group, the ΔΔBDEs for the *p*-EWGs actually become negative (i.e. stronger BDEs than $C_6H_5CH_2X$) as is observed for the anilines and phenols.

In a recent paper, Cheng and co-workers, have presented experimental evidence that it is the enhanced electronegativity, or as they suggested 'the apparent electronegativity', of the methylene carbon atom, rather than the lack of a non-bonding electron pair that governs the direction of radical substituent effects.[24] For a series of α-onium toluenes, they found that *p*-EDGs decrease the BDE, while they are increased by *p*-EWGs as found for anilines and phenols.[25] They attributed this to the enhanced electronegativity of the benzyl carbon atom, which resulted from the adjacent electron-pulling group. These workers suggested that it is the low electronegativity of the methylene group of the $YC_6H_4CH_2$ radicals, not the lack of an unshared pair of electrons, which is responsible for the 'anomalous' weakening of the BDEs of toluenes by *p*-EWGs as compared to the more electronegative NH and O of the anilino and phenoxy radicals.

We examined the $YC_6H_4CH_2X$ series, where X=OH, OMe, NH_2, or NHMe, and found that electron releasing α-substituents also enhance the effect that *para*-substituents have on the energy of the ground state; *p*-EDGs slightly increase the stabilization while *p*-EWGs are slightly destabilizing (Table 2). For the ground state, either electron-withdrawal or donation to the methylene carbon atom amplifies the effect of the *para*-substituents. For the YC_6H_4CHX radicals, the effect of electron-donating α-substituents is opposite to that for the ground state energies; *p*-EDGs slightly decrease the stabilization while *p*-EWGs appreciably stabilize the radicals. Therefore, a perturbation of the charge on the methylene carbon atom by either increasing or decreasing the electronegativity of the methylene group (Cheng's apparent electronegativity) by an adjacent electron-pulling or pushing group enhances the effect of the *para*-substituents, in the same direction for the ground state but in the opposite direction for the radicals.[26]

A similar examination of the *N*-substituted anilines, YC_6H_4NHX, where X is H, Me, OH, NH_2, CN, or NO_2, indicated that in the case of $YC_6H_4NHNH_2$, the $YC_6H_4NNH_2$ radical is stabilized by both *p*-EDGs and *p*-EWGs as is found for the toluenes. We also observed that there is a narrower range for the charge on the N atom in this radical than when X is either a hydrogen atom or and electron-withdrawing group. This is despite a much larger range, particularly for *p*-EWGs, for the charge on the *ipso*-carbon atom adjacent to the nitrogen atom. It appears that electron release by the N-amino group 'dampens' the effect that *p*-substituents have on the charge on the nitrogen atom of the radical. Thus, due to electron release to the nitrogen atom of the radical, it behaves in a manner similar to that of the CH of the benzyl radicals. For the *p*-EDGs, there is only a small electron release by the N-amino group to the nitrogen atom of the radical. When there are *p*-EWGs, there is a much greater electron release to the nitrogen atom because of increased conjugation or the 'captodative (pull–push) effect' on the radical (e.g. $NO_2C_6H_4NNH_2$).[27]

From these observations, it is apparent that when X is a very strong electron-withdrawing group, the YC_6H_4CHX radical behaves as if the CHX were the more electronegative NH, or O group, while when X is a strong electron-releasing group, the YC_6H_4NX radical behaves as if the NX were the less electronegative CH_2 group. The stability of the radicals are enhanced when the *p*-substituent is electron releasing and the α-substituent is electron-withdrawing; the push–pull or captodative effect. This effect stabilizes the radical by increasing the conjugation and results in a decrease of the BDE. Conversely, when the *p*-substituent is electron-withdrawing, the radical is destabilized (due to less conjugation) and because this is a 'pull–pull' or 'anti-captodative' situation, the BDE increases. The electron-withdrawal strength of the α-substituent determines the magnitude that these effects have through the enhancement of the electronegativity of the methylene group. In the case of the *N*-substituted anilines, when X is an electron-releasing group, it is the *p*-EWGs that increase the stability of the radical so that the BDE is decreased by the captodative effect; in this case pull–push. For the *p*-EDGs, it is a push–push situation so the anti-captodative effect is to decrease the stability of the $YC_6H_4NNH_2$ radical.

Cheng and co-workers have stated that "it must be the electron demanding property (i.e. apparent electronegativity) of the radical center, rather than the existence of a non-bonding electron pair, that plays the critical role in controlling the directions of radical substituent effects". We add however, that the apparent electronegativity of the radical center determines the magnitude of the effect that *p*-substituents have on the stabilization or destabilization of the radical. In addition, the apparent electronegativity of the radical center determines if anti-captodative effect of *p*-EWGs is to stabilize or destabilize the radical. For the benzyl radicals, the pi–pi bond order between the *ipso* and the methylene carbon atoms of the $YC_6H_4CH_2$ radicals is increased by both *p*-EDGs and *p*-EWGs, as is the stabilization of the radicals. However, when X is a strong electron-withdrawing group, the pi–pi bond order for the YC_6H_4CHX radical is increased by *p*-EDGs and the increased conjugation, or the captodative effect, stabilizes the radical. Conversely, the pi–pi bond order is lowered by *p*-EWGs and the anti-captodative effect is to decrease the stability of the radical. Regardless of whether X is H or a strong electron-withdrawing group, the pi–pi bond order for the ortho-meta bonds is increased by either *p*-EDGs or *p*-EWGs. Therefore, it is the effect that X has on the bond between the *ipso* and methylene carbon atom that controls the conjugation (or captodative–anti-captodative effect) between the *para*-substituent and the radical center.

In the case of the anilines and phenols, the greater electronegativity of the NH or O of the radicals, relative to the CH_2 of the benzyl radical, increases the stabilization–destabilization by the *para*-substituents as captodative or anti-captodative.

4. Conclusions

When the separation of the ground state and the REs on the BDEs was applied to the *p*-substituted toluenes, anilines, and phenols there was a clear distinction between the effect that *p*-EWGs have on the sign of $\Delta\Delta H_f R^{\cdot}$ (the RE) for the toluenes and those of the anilines and phenols. Whereas *p*-EDGs stabilize the radicals of toluenes, anilines, and phenols, *p*-EWGs destabilize the radicals of the anilines and phenols, but stabilize the benzyl radicals. The different effect that *para* substituents have on the benzyl radicals is responsible for the BDEs of the toluenes to be lowered by both EDGs and EWGs. This is contrary to the BDEs of anilines and phenols, which are lowered by EDGs but increased by EWGs. It is also noted that the magnitude of the effect of the substituents is much smaller for the toluenes. When the *p*-EDGs and *p*-EWGs are separated, there is a good correlation between the $\Delta\Delta H_f R^{\cdot}$ values and the spin density for all three series.

Nau's suggestion that ground state effects become important only when a polar bond is broken is substantiated. In the case of $YC_6H_4CH_2X$, as X becomes more electron-withdrawing, the effect that *p*-substituents have on the ground state energy is increased. When X is a strong electron pulling group and the *p*-substituent is electron pushing (*p*-EDG) the push–pull or captodative effect stabilizes the YC_6H_4CHX radical, but when the *p*-substituent is also electron pulling (*p*-EWG) the radical is destabilized, an anti-captodative effect, because it is a pull–pull system with less conjugation. This causes $\Delta\Delta H_f R^{\cdot}$ to becoming negative, as is found for the anilines and phenols. Therefore, it is the electron pulling power of X that determines whether the BDEs of $YC_6H_4CH_2X$ are increased or decreased by *p*-EWGs.

When there are electron-releasing N-substituents on anilines (e.g. an NH_2 group), *p*-EWGs stabilize the $YC_6H_4NNH_2$ radicals, a captodative effect, so that so that the N–H bond is weakened as is found for the toluenes. It appears that electron release by the X substituent 'attenuates' the effect that *p*-substituents have on the radicals because the apparent electronegativity of nitrogen atom is decreased.

The *p*-EDGs produce a regular pattern for affecting the values of $\Delta\Delta H_f RH$, $\Delta\Delta H_f R^{\cdot}$, spin density, and the charges on the radical center of the anilines, phenols, and α-substituted toluenes. However, the effect that *p*-EWGs have depends upon the electron-withdrawing or releasing strength of the X substituent, which determines whether $\Delta\Delta H_f R^{\cdot}$ is stabilized (captodative effect) or destabilized (anti-captodative effect). An increase in the electronegativity of the radical center has two affects on the BDEs; the magnitude of the effect produced by *p*-EDGs is increased and for *p*-EWGs, there is a change from stabilization to destabilization of the radicals.

It has been shown that the different behavior of the toluenes from that of the anilines and phenols is not due to the latter having a lone pair of electrons but, as stated by Cheng et al. it is "the electron demanding property (i.e. apparent electronegativity) of the radical center, rather than the existence of a non-bonding electron pair, that plays the critical role in controlling the directions of radical substituent effects". However, we modify this to include that the stabilization or destabilization of the radicals depends upon the relationship between the *para*-substituents and the electronegativity of the radical center. When there is a strong push–pull system produced by a *p*-EDG and a strong electron-withdrawing X group that produces a strong apparent electronegativity for the methylene carbon atom, the increased conjugation (captodative effect) stabilizes the radical. With a *p*-EWG, destabilization of the radical occurs due to the pull–pull system in which conjugation is decreased; an anti-captodative effect. However, if the apparent electronegativity of the methyl carbon atom is low, there is essentially no conjugation so both *p*-EDGs and *p*-EWGs stabilize the radical, as found in the toluenes.

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14. The AM1 BDEs of the phenols were compared with both experimental data[3d] and those calculated by DFT.[8] The correlation with the experimental data was r^2=0.93 with an average deviation of the AM1 data from the least square line of 0.61±0.21 kcal/mol. For the DFT data, r^2=0.96 and the deviation was 0.44±0.21 kcal/mol. Plots of the AM1, the experimental, and DFT BDE data versus Brown's σ^+ values had a correlation of 0.96, 0.96, and 0.97, respectively, with an average deviation of 0.48±0.31, 1.06±0.49, and 0.59±0.32 kcal/mol, respectively. Although the AM1 BDEs at the UHF level are lower than the experimental or DFT values, the relative effect of the substituents is as good as either the experimental or DFT data.
15. The keywords used in these calculations included LET, PRECISE, DDMIN=0.0 and GNORM=0.001 which tighten the gradient norm and trust radius. For the radicals, the additional keywords were SPIN, DENSITY, and PI. Where conformers are possible (e.g. HOC_6H_4CHF radical), the conformer of the lower energy was used.
16. There is less than a 0.17 kcal/mol difference between the values of RE, calculated from the AM1 ΔH_fs and $\Delta\Delta H_f R^{\cdot}$ for *p*-EDGs. However, the difference increases with *p*-EWGs up to 1.01 kcal/mol due to the greater effect that *p*-EWGs have on the AM1 ΔH_f of the phenyl radicals than on the benzenes that were used by Wu. However, this difference $[\Delta H_f(YC_6H_4^{\cdot}) - \Delta H_f(YC_6H_5)]$ is constant for all YC_6H_4ZH systems.
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20. There is a good correlation, r^2=0.97, between the AM1 $\Delta\Delta H_f R^{\cdot}$ values for the phenoxy radicals with Wu's DFT RE values but it is much poorer for the benzyl radicals, r^2=0.58.[7,8]
21. As reported by Ingold et al.[9] 'the preferred conformations of the benzyl halides have the C–F bond lying in the aromatic plane, whereas the C–Cl and C–Br bonds are perpendicular to this plane'.
22. In most cases, there is a linear relationship (r^2>0.97) between the values of $\Delta\Delta H_f$RH, $\Delta\Delta H_f R^{\cdot}$, ΔQ_{GS}, ΔQ_{Rad}, spin density, σ^+ and σ_p for the *p*-EDGs on the α-substituted toluenes. However, there is much poorer relationship (r^2>0.75) for the *p*-EWGs.
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26. There is a fair correlation (r^2>0.90) for the values of $\Delta\Delta H_f$RH versus the charge on the carbon atom of the methylene group of the $YC_6H_4CH_2X$, where X is an electron-withdrawing group. However, for the radicals, only when X=CN, CF_3, NO_2 and SO_2CN is there a correlation (r^2>0.88) for $\Delta\Delta H_f R^{\cdot}$ versus the charge on the carbon atom of the CHX group. When X=H, F, Cl, or Br, plots of $\Delta\Delta H_f R^{\cdot}$ versus the charge are 'V shaped'.
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