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ARTICLES

Effects of Molecule Stabilization Energies on Radical Reactions: G3 and G3(MP2) Model Chemistries Applied to Benzylic Systems

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We have carried out G3 and G3(MP2) calculations of the molecule stabilization energies (MSEs) brought about by 11 common substituent groups in the meta and para positions of benzyl fluoride. We find that MSE is a function of the tendency of the substituent to donate or to withdraw electrons, such that a classic Hammett plot can be drawn. We propose that, in general, the direction of the benzylic Z−X dipole of YC_6H_4ZX is the major factor controlling the sign of the slope of Hammett plots of benzylic atom abstractions by radicals. When the Z−X dipole is pointed away from the substituted ring, electron withdrawing substituents destabilize the molecule, contributing to a decrease of the Z−X bond dissociation energy, and electron donating substituents stabilize it. The reverse is true when the dipole is reversed. This proposal is supported by ^{13}C NMR results and by a survey of relevant benzylic and quasi-benzylic hydrogen or halogen atom abstractions studied experimentally. Calculations at the G3 level of theory demonstrate an increase in the bond dissociation energy of p-$YC_6H_4CH_2$−H with increasing electron withdrawing ability of Y, contrary to results of previous lower level calculations. MSE values of substituted benzyl fluorides (p-$YC_6H_4CH_2F$) correlate well with allylic MSE (*trans*-YCH═$CHCH_2F$) and quantify the relative efficacy of transmission of electronic effects by vinylogy.

Introduction

Rates of benzylic atom abstractions by radicals depend upon the nature of para and meta substituents. Examples are benzylic hydrogen abstractions from *m*- and p-$YC_6H_4CH_2$−H by various radicals ($Br^\bullet$, $Cl^\bullet$, $Cl_3C^\bullet$, *tert*-$BuO^\bullet$, $ROO^\bullet$, $R_2N^\bullet$, $RS^\bullet$, $R_2NO^\bullet$, etc.) and abstractions of halogen by alkyltin, alkylgermanium, and alkylsilicon radicals from *m*- and p-$YC_6H_4CH_2$−X (X = Cl, Br, I). Rates of benzylic hydrogen abstractions by all studied radicals are retarded by electron withdrawing Y groups and enhanced by electron donating groups.[1] The opposite occurs for benzylic halogen abstractions by radicals of tin, germanium, and silicon.[2]

Considerable attention has been paid to stabilization or destabilization of the $YC_6H_4CH_2^\bullet$ radicals formed and to the strength of the benzylic bond being broken. Here, we focus on the transmission of electronic effects reflected in the molecule stabilization energy (MSE) of the parent molecule as a function of distance and molecular geometry. We use G3 and G3(MP2) model chemistry calculations and focus on MSE changes brought about by *m*- and *p*-Y substituents of benzyl fluorides. An earlier theoretical study of such effects was done with AM1 and DFT calculations, which may not be sufficiently accurate for the task. The conclusion was that the direction and magnitude of the effects of *p*-Y substituents on benzyl C−X bond dissociation energies (BDEs) do not depend on differences in the electronegativities of the benzyl C−X atoms, i.e., the C−X dipole of the bond being broken on abstraction by radicals.[3]

One is especially encouraged to study such molecules because of the volume and variety of experimental results that have been gathered on radical abstractions of benzylic atoms and the various and divergent rationalizations that have been advanced to explain them. Until recently, such molecules, which contain up to 11 “heavy” atoms, were near the limit of G3 and similar high level model chemistries. In this work, we have been able to carry out the first G3 and G3(MP2) calculations of MSE on 22 meta and para substituted benzyl fluorides, relative to benzyl fluoride. The substituents studied here are Y = $(CH_3)_2N$, H_2N, HO, CH_3O, H_3C, H_2C═CH, H, Cl, F_3C, NC, HC(O), and O_2N.

There is some disagreement in the literature on the importance of the benzyl C−X dipole as it relates to the dissociation energy of the bond in ring-substituted compounds, both for[4] and against.[5] The opposite directions of effects of ring substituents on radical abstractions of benzylic hydrogen and of benzylic halogen cannot depend on benzyl radical stabilization energies. This is because the same series of substituted benzyl radicals is produced in both reactions 1 and 2, where R denotes H-abstracting radicals that have been studied, X denotes Cl, Br, or I, and M denotes presumably nucleophilic (or electropositive) radicals of $^\bullet Sn(n\text{-}Bu)_3$, $^\bullet Ge(n\text{-}Bu)_3$, and $^\bullet Si(n\text{-}Bu)_3$.

$$YC_6H_4CH_2{-}H + {}^\bullet R \rightarrow YC_6H_4CH_2^\bullet + H{-}R \qquad (1)$$

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$$YC_6H_4CH_2{-}X + {}^{\bullet}M(n\text{-Bu})_3 \rightarrow YC_6H_4CH_2^{\bullet} + X{-}M(n\text{-Bu})_3 \quad (2)$$

Hence, there remain two possible explanations of ring substituent effects.

(1) Polar effects at the transition state (TS). For reaction 1, the TS would be $YC_6H_4CH_2^{\delta+}\cdots H\cdots{}^{\delta-}R$, and for reaction 2, it would be $YC_6H_4CH_2^{\delta-}\cdots X\cdots{}^{\delta+}M(n\text{-Bu})_3$.

(2) Molecule stabilization energies are the important factor in determining the direction of the effect, the sign of the Hammett slope,[6] because the effects of ring substituents would be in opposite directions depending on whether the dipole is $YC_6H_4CH_2 \leftarrow H$ or $YC_6H_4CH_2 \rightarrow X$. Electron withdrawing substituents would stabilize $YC_6H_4CH_2^{\delta-}{-}H^{\delta+}$ and destabilize $YC_6H_4CH_2^{\delta+}{-}X^{\delta-}$. Hammett correlations are linear free energy relations where $\log_{10}(k_Y/k_H)$ is plotted vs Hammett substituent constants, σ, which reflect the electron donating or withdrawing ability of the *meta*- or *para*-Y substituent.

A polar effect at the TS is unlikely. Benzylic hydrogen abstractions by primary, secondary, and tertiary alkyl radicals, which have been described as nucleophilic,[7] would have produced relative rate effects in directions similar to those of halogen abstractions by nucleophilic tin, germanium, or silicon radicals (positive Hammett slopes). Early claims[7] that the rates of alkyl radical abstractions of benzylic hydrogen from ring-substituted toluenes give positive Hammett slopes, as those of ${}^{\bullet}SnR_3$, ${}^{\bullet}GeR_3$, and ${}^{\bullet}SiR_3$, have been shown to be invalid because of unsuspected competing alkyl radical additions to the ring and extensive radical couplings.[8] If the rationalization of polar effects at the TS were valid with nucleophilic tertiary alkyl radicals, the dipole of the TS in reaction 1 should have reversed, as shown in brackets in reaction 3, and the effect of Y substituents on reaction rates would be in a direction similar to those of trialkyl-Sn, -Ge, and -Si radicals. It is not.

$$YC_6H_4CH_2{-}H + {}^{\bullet}CR_3 \rightarrow [YC_6H_4CH_2^{\delta-}\cdots H\cdots{}^{\delta+}CR_3] \rightarrow YC_6H_4CH_2^{\bullet} + H{-}CR_3 \quad (3)$$

Negative slopes are obtained in Hammett plots of benzylic hydrogen abstraction rates by primary, secondary, and tertiary alkyl radicals,[9] as found with all other H-abstracting radicals, the opposite of the positive slopes of halogen abstractions by ${}^{\bullet}Sn(n\text{-Bu})_3$, ${}^{\bullet}Ge(Et)_3$, and ${}^{\bullet}Si(n\text{-Bu})_3$.[2]

A recent, more thorough discussion of TS vs MSE effects is available.[9]

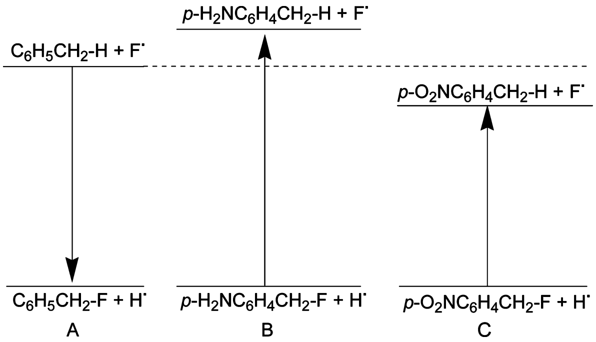
Theory

The enthalpy (frequently called energy) change of reaction 4 is the molecular stabilization or destabilization enthalpy MSE of *m*- and *p*-$YC_6H_4CH_2F$ relative to $C_6H_5CH_2F$.

$$Y{-}C_6H_4CH_2{-}F + H{-}C_6H_4CH_2{-}H \rightarrow Y{-}C_6H_4CH_2{-}H + H{-}C_6H_4CH_2{-}F \quad (4)$$

In isodesmic reaction 4, the enthalpy change in going from $YC_6H_4CH_2{-}F$ to $YC_6H_5CH_2{-}H$ is more or less compensated by the opposite reaction $C_6H_5CH_2{-}H$ to $C_6H_5CH_2{-}F$. We shall call the first reaction the "Y half reaction" and the second the "reference half reaction" (A in Scheme 1). If the enthalpy change of the Y half reaction is larger than that of the reference half reaction, reaction 4 is endothermic (for example, Y = *p*-NH_2, Y half reaction B in Scheme 1); if it is smaller, reaction 4 is exothermic (Y = *p*-NO_2, Y half reaction C in Scheme 1). The endothermic or exothermic nature of reaction 4 is determined by the electron donating or withdrawing ability of Y. Endothermic reactions, as defined by eq 4, have positive MSE values, which indicate greater stability of $YC_6H_4CH_2F$ relative to $C_6H_5CH_2F$ and contribute to an increase in BDE. The opposite is true for negative MSE. In Scheme 1, the baselines are arbitrarily drawn to the same level and the heights (enthalpies) are not drawn to scale.

SCHEME 1



Methods and Calculations

Input files were created using PCModel[10] and optimized by molecular mechanics within either the MM3[11] or MMX (PC-Model) parametrization. The input file was submitted to the National Center for Supercomputing Applications cluster[12] for computation within either the G3 or G3(MP2) model chemistry using the Gaussian 03 program.[13] The Y half reaction from a substituted benzyl fluoride to the corresponding substituted toluene is endothermic. The reference half reaction from toluene to benzyl fluoride is exothermic but not of exactly the same magnitude. The difference between the two reactions is the enthalpy change of the isodesmic reaction 4 (Table S2 in the Supporting Information provides the total enthalpy of each species examined). The total enthalpy is given by the G3 model chemistry,[13b,c] which approximates molecular enthalpy by utilizing the additivity principle in the convergence of basis sets and correlation energy. The energy is then corrected by a higher level correction to supplement the deficiency in slow convergence of the bonding electron pairs, and for thermal contributions from all degrees of freedom at a given temperature.

For example, for Y = *p*-$(CH_3)_2N$, the enthalpy change of reaction 4 is given in terms of the G3 output file (with no symmetry constraints) of total enthalpies H^{298} hartrees ($1\ E_h = 627.51$ kcal mol^{-1}), by $\Delta H^{298} = H^{298}[p\text{-}(CH_3)_2NC_6H_4CH_2{-}H] + H^{298}[C_6H_5CH_2{-}F] - H^{298}[p\text{-}(CH_3)_2NC_6H_4CH_2{-}F] - H^{298}[C_6H_5CH_2{-}H]$. With the G3 model, $\Delta H^{298} = -405.161579 - 370.519785 - (-504.361540 - 271.321033) = 0.001209\ E_h = 0.76$ kcal mol^{-1}, given at the top of the second column of Table 1. This is a measure of the stability, MSE, that replacement of Y = H by Y = *p*-$(CH_3)_2N$ brings about in benzyl fluoride. A similar calculation within the confines of the G3(MP2) model chemistry gives 0.70 kcal mol^{-1}, as shown in first line of the third column of Table 1. For *m*-$(CH_3)_2NC_6H_4CH_2F$, calculations within the G3 and G3(MP2) models give MSE values of 0.30 and 0.28 kcal mol^{-1}, respectively, and so on through Table 1. Predictably, G3 and G3(MP2) total enthalpies are different, but their differences mostly cancel in calculating MSE, so that the thermochemical results by G3(MP2) are about the same as those by G3.

TABLE 1: Calculated MSEs[a] of $YC_6H_4CH_2F$ by G3 and G3(MP2), Hammett σ Constants,[b] and MSEs of *trans*-YCH=CHCH$_2$F by G3(MP2)[c]

substituent	G3, benzylic	G3(MP2), benzylic	Hammett σ	G3(MP2), allylic
p-$(CH_3)_2N$	0.76	0.70	−0.83	2.79
m-$(CH_3)_2N$	0.30	0.28	−0.16	
p-H_2N	0.69	0.63	−0.66	2.57
m-H_2N	0.44	0.42	−0.16	
p-HO	0.35	0.33	−0.37	1.55
m-HO	−0.13	−0.12	0.12	
p-CH_3O	0.43	0.34	−0.27	1.87
m-CH_3O	0.02	0.02	0.12	
p-H_3C	0.24	0.23	−0.17	0.70
m-H_3C	0.21	0.20	−0.07	
p-$CH_2{=}CH$	0.01	−0.01	−0.04	0.11
m-$CH_2{=}CH$	0.01	0.00	0.06	
H (standard)	0.00	0.00	0.00	0.00
p-Cl	−0.25	−0.25	0.23	−0.59
m-Cl	−0.42	−0.41	0.37	
p-F_3C	...	−0.54	0.54	−0.75
m-F_3C	...	−0.60	0.43	
p-O=CH	−0.48	−0.44	0.42	−1.20
m-O=CH	−0.32	−0.31	0.35	
p-NC	−0.77	−0.74	0.66	−1.13
m-NC	−0.75	−0.74	0.56	
p-O_2N	−0.86	−0.82	0.78	−1.55
m-O_2N	−0.74	−0.71	0.71	

[a] Enthalpy values are in kcal mol^{-1}. [b] From the compilation of ref 14. [c] From ref 15a.

The calculations were performed to produce MSE results for the meta and para isomers of 11 substituents, each within the G3 and G3(MP2) model chemistries, plus two calculations for Y = H. The total number of calculations of H^{298} is 86, because two G3 calculations were not successful for Y = CF_3. Full output of total enthalpies in hartrees and geometries are given in the Supporting Information. Output files from both G3 and G3(MP2) calculations were checked for imaginary frequencies which would indicate a potential energy maximum encountered by the methyl or fluoromethyl group as it rotates from one stable conformation to another. Single imaginaries were not rare but could usually be eliminated merely by rotating the methyl or fluoromethyl group by 30° or some multiple thereof using the bond rotation option of the PCModel.[10] Similarly, the usual precautions regarding identifying local, as opposed to global, minima were taken.

Results

Table 1 lists the summary of MSE results of G3 and G3(MP2) model chemistries, leading to four entries for each substituent, two model chemistries for the para and two for the meta substituted isomers. Columns 2 and 3 give the MSE for each molecule in kcal mol^{-1}. These enthalpy differences are the result of replacing Y by H in $YC_6H_4CH_2{-}F$. Also given in Table 1 are Hammett substituent constants,[14] which are commonly used to quantify the propensity of various groups to withdraw or donate electrons in aromatic systems.[6] Previously reported MSE values by G3(MP2) of allylic fluorides, *trans*-YCH=CHCH$_2$−F, are also given in the table for comparison (see below).

Linear regressions of the G3 and G3(MP2) MSE results plotted against Hammett σ constants of the substituents are shown in Figure 1 for the *p*-$YC_6H_4CH_2F$ compounds. G3 (filled circles) and G3(MP2) (open circles) appear in vertical pairs; they are very close, and sometimes overlap. The correlation coefficient, *r*, for *p*-$YC_6H_4CH_2F$ is −0.99 for the G3 results and −0.99 for the G3(MP2) results. A plot of MSE values of *p*-$YC_6H_4CH_2F$ vs σ^+ substituent constants gave a slightly poorer correlation, $r = -0.97$.

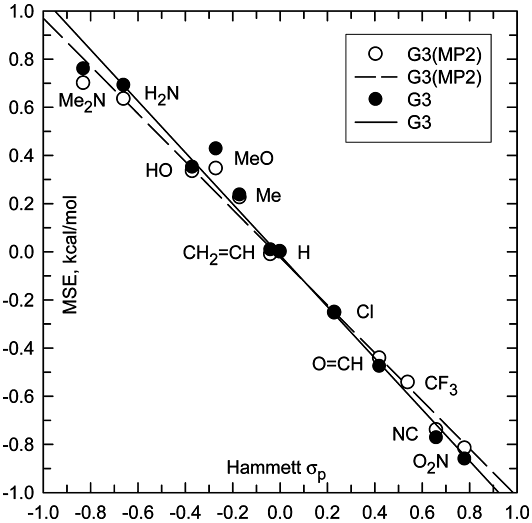


Figure 1. MSE values of *p*-$YC_6H_4CH_2F$ calculated by G3 (filled circles) and by G3(MP2) (open circles) vs Hammett σ constants. G3 points: MSE = $-1.07\sigma - 0.02$. G3(MP2) points: MSE = $-0.99\sigma - 0.02$. Positive MSE values contribute to an increase in BDE.

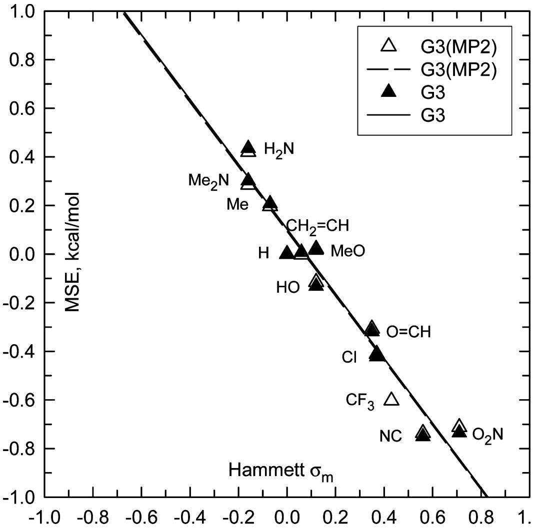


Figure 2. MSE values of *m*-$YC_6H_4CH_2F$ calculated by G3 (filled triangles) and by G3(MP2) (open triangles) vs Hammett σ constants. G3 points: MSE = $-1.33\sigma + 0.10$. G3(MP2) points: MSE = $-1.33\sigma + 0.09$. Positive MSE values contribute to an increase in BDE.

Figure 2 shows plots of G3 and G3(MP2) MSE data sets for *m*-$YC_6H_4CH_2F$ vs σ. The correlation coefficients are −0.98 and −0.98 for the G3 and G3(MP2) results, respectively. The two regression lines are almost coincident.

The G3 and G3(MP2) slopes are similar in each of the plots in Figures 1 and 2. The slope of the meta substituted compounds is more negative than that of the para. Statistically, the 95% confidence intervals of the plots of Figures 1 and 2 indicate a difference. However, there are factors that may make the slope differences insignificant: the σ range of the meta isomers is considerably smaller than that of the para, σ values derived from pK_a of benzoic acids may not be accurately applicable to the MSE values studied here, and somewhat different values of σ exist in the literature. In addition, the usual uncertainties of the theoretical calculations may not cancel out exactly in the molecules we compare, despite their general similarity.

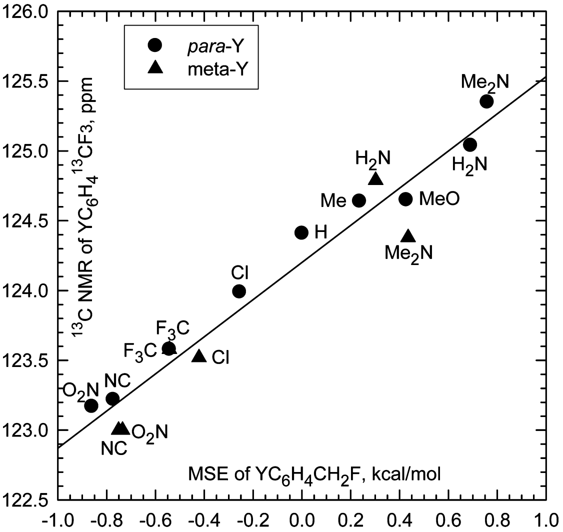


Figure 3. Benzylic ^{13}C NMR chemical shifts of *m*- and *p*-$YC_6H_4CF_3$ vs calculated MSE values (G3) of *m*- and *p*-$YC_6H_4CH_2F$; ppm = 2.34(MSE) + 118.69; $r = 0.97$.

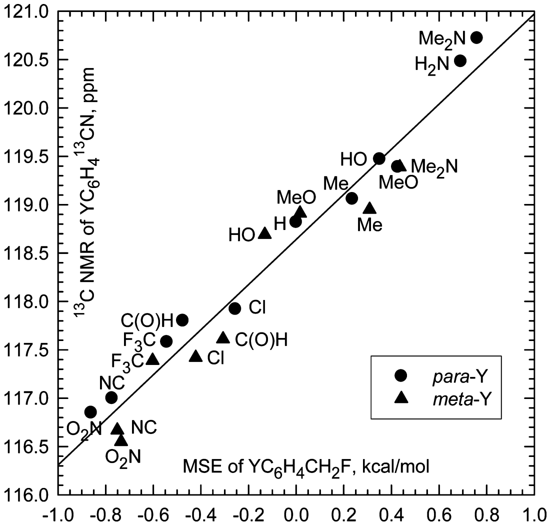


Figure 4. Benzylic ^{13}C NMR chemical shifts of *m*- and *p*-YC_6H_4CN vs calculated MSE values (G3) of *m*- and *p*-$YC_6H_4CH_2F$; ppm = 2.33(MSE) + 118.64; $r = 0.98$.

Discussion

Physical properties of the molecules studied should correlate with the calculated MSE values obtained for reaction 4. Alternative isodesmic reactions have been used to obtain MSE values, and they do not show such correlations, as will be discussed further below. The validity of the theoretical MSE values reported is established by comparison with experimentally determined NMR measurements of ^{13}C benzylic carbon chemical shifts of various related compounds. Figure 3 is a plot of available ^{13}C chemical shifts of the benzylic carbon[16] of various *m*- and *p*-$YC_6H_4CF_3$ vs corresponding MSE values from Table 1 (G3 calculation) for substituents in common.

The correlation is good between calculated MSE effects of *m*- and *p*-$YC_6H_4CH_2F$ and ^{13}C NMR data of similarly substituted α,α,α-trifluorobenzyl fluorides. Both have benzyl C → F bond dipoles pointed away from the ring. The direction of the bond dipole of the pertinent bonds discussed in this and subsequent sections is determined by the electronegativities, χ, of the bonded groups. The bond dipole in molecule A−B points in the direction of the more electronegative species.[15b]

Figure 4 is a plot of available ^{13}C chemical shifts[17] of the benzylic carbon of *m*- and *p*-$YC_6H_4C{\equiv}N$ vs corresponding MSE values from Table 1 (G3 calculation), indicating a good correlation. The benzyl C → N dipole of the benzyl cyanides is in the same direction as the corresponding C → F of benzyl fluorides.

Figure 5 is a plot of available ^{13}C NMR chemical shifts of the benzylic carbon of *p*-$YC_6H_4CH_3$ vs calculated MSE values of similarly substituted *p*-$C_6H_4CH_2F$ of Table 1 (G3 calculation). The ^{13}C NMR values are from two different sources.[16,17]

The benzyl C ← H dipole of $YC_6H_4CH_3$ is in the opposite direction from the benzyl C → F dipole of $YC_6H_4CH_2F$. In Figure 5, the slope is negative, a reversal of the positive slopes of Figures 3 and 4. The correlation in Figure 5 is not as good as that in Figures 3 and 4, because the ^{13}C NMR chemical shifts are small and the uncertainty of the measurements causes considerable scatter. This is shown by the difference between the two sets of data in Figure 5. For the meta substituted toluenes, the range of chemical shifts is even smaller and the uncertainty of the measurements results in very poor correlation, $r = -0.49$.

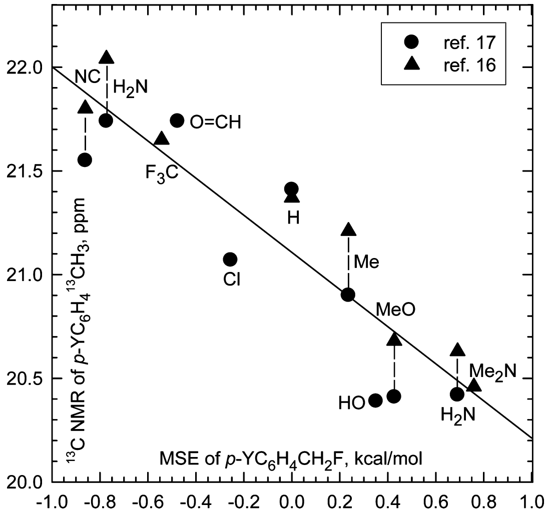


Figure 5. Benzylic ^{13}C NMR chemical shifts of *m*- and *p*-$YC_6H_4CH_3$ vs calculated MSE values (G3) of *p*-$YC_6H_4CH_2F$. Regression through all points: ppm = −0.89(MSE) + 21.11; $r = -0.92$.

The correlations with benzyl ^{13}C NMR chemical shifts in Figures 3−5 confirm that the theoretical MSE values constitute realistic descriptions of the molecules.

The principle of vinylogy assumes that electronic effects are transmitted through conjugated double bonds[18] and, therefore, electronic effects present in allylic compounds would reflect those of more complex conjugated systems, such as the para substituted benzyl fluorides. For the first time, we quantify the efficiency of transmission of such effects with increasing distance and geometry. Recently,[15] we reported a set of calculations of MSE values of *trans*-$YCH{=}CHCH_2F$ compounds with the same Y substituents as examined in this work. MSE was calculated on the basis of isodesmic reaction 5, which is of the same form as reaction 4.

$$YCH{=}CHCH_2{-}F + CH_2{=}CHCH_2{-}H \rightarrow YCH{=}CHCH_2{-}H + CH_2{=}CHCH_2{-}F \quad (5)$$

Figure 6 shows a plot of MSE of *p*-$YC_6H_4CH_2F$ vs MSE of *trans*-$YCH{=}CHCH_2F$. The correlation shows that the

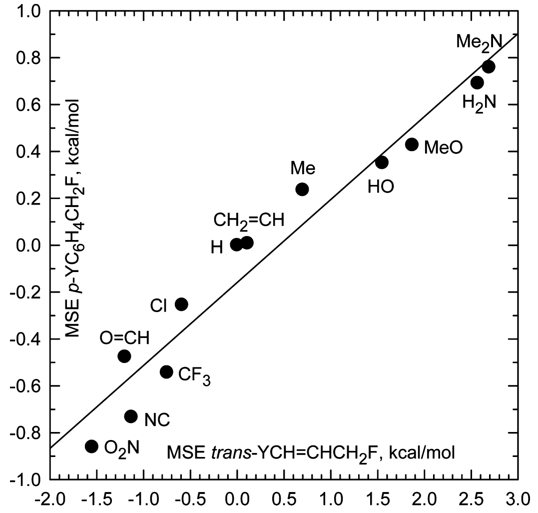


Figure 6. Plot of MSE of p-$YC_6H_4CH_2F$ vs MSE of *trans*-$YCH{=}CHCH_2F$. Linear regression: MSE(benzylic) = 0.35[MSE(allylic)] − 0.15, $r = 0.97$.

same type of electronic effects are present in the allylic and benzylic systems, but the slope is only 0.35. This indicates that electronic effects via transmission through one double bond in the allylic system are attenuated when transmitted through the aromatic system in the para substituted benzylic systems.

Isodesmic reactions equivalent to eq 4 have been used previously to obtain molecule stabilization energies.[3,19] However, the form of isodesmic reaction 4 is not the only one that has been used to calculate MSE. A widely used alternative is of the form of reaction 6.[20]

$$Y{-}C_6H_4Z{-}X + H{-}C_6H_4{-}H \rightarrow Y{-}C_6H_4{-}H + H{-}C_6H_4Z{-}X \quad (6)$$

Correlation of MSE values obtained by reaction 6 with physical properties (NMR spectra) is very poor, as is also true of the allyl fluorides.[15] The validity of MSE values obtained in this fashion and any conclusions drawn from them have also been questioned previously.[4d] Use of reaction 6 has led to plots of MSE of $YC_6H_4NH \leftarrow CH_3$ and $YC_6H_4NH \rightarrow F$ vs substituent constants that have positive slopes for both,[20e] even though the N−X dipoles are in opposite directions. Plots of MSE values calculated by the form of reaction 4 show a positive slope for $N \leftarrow CH_3$ and a negative slope for $N \leftarrow F$,[15] as expected from the reversal of the slope in Figure 5 as opposed to Figures 3 and 4. In reaction 6, the Y−X interaction is transmitted through $-C_6H_4Z-$ on the left and the Y−H interaction is transmitted through $-C_6H_4-$ on the right, whereas all interactions are through the same $-C_6H_4Z-$ group in the form of reaction 4.

Relative rates of benzylic atom abstractions, H or halogen, are a function of the direction of the dipole $C \leftarrow H$ or $C \rightarrow X$. The greater the electron donating ability of Y in *m*- and p-$YC_6H_4CH_2X$, the more the substrate molecule is stabilized when X is more electronegative than carbon. This contributes to strengthening of the benzyl C−halogen bonds and is consistent with the positive Hammett slopes for benzylic halogen abstractions by radicals.[2] The reversal of the sign of the slope in Figure 5 ($C \leftarrow H$), compared to Figures 3 and 4 ($C \rightarrow X$), supports the proposal that the direction of the dipole of the benzylic bond to be broken is a significant factor in the direction of the relative rates of benzylic atom abstractions by radicals.[4,21] Benzylic hydrogen abstractions and benzylic halogen abstractions, reactions 1 and 2, have negative and positive Hammett slopes, respectively. Because the same radicals are formed in both reactions, the stability of the benzyl radicals formed is not relevant in comparison with the *direction* of the slope, even though the exothermicities are different.

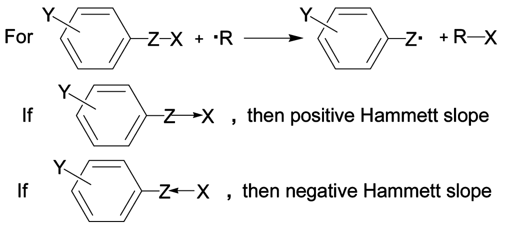
A study of hydrogen abstractions by alkylperoxy radicals from substituted toluenes[22] led to BDE[p-$O_2NC_6H_4CH_2{-}H$] greater than BDE[p-$CH_3OC_6H_4CH_2{-}H$] by 3.8 kcal mol^{-1}, consistent with the negative Hammett slopes obtained for all benzyl H-abstractions from toluenes. Electron withdrawing (EW) substituents strengthen the benzyl C−H bond, and electron donating (ED) substituents weaken it. Kinetic measurements of competitive brominations of toluenes found that BDE[m-$ClC_6H_4CH_2{-}H$] is about 2.2 kcal mol^{-1} greater than BDE[p-$CH_3C_6H_4CH_2{-}H$],[23] again indicating that Y = EW strengthens the benzyl C−H bond, leading to negative Hammett slopes for hydrogen abstractions. Measurements of equilibrium acidities and oxidation potentials also found that Y = ED weakens the benzyl C−H bond and Y = EW strengthens it in *m*- and p-$YC_6H_4CH(CN){-}H$[24a] and in *m*- and p-$YC_6H_4CH(SO_2Ph){-}H$,[24b] for example, by 2.6 and by 3.0 kcal mol^{-1} between p-CH_3O and m-CF_3 substituents, respectively. All *experimental* determinations of BDE-[$YC_6H_4CH_2{-}H$] have found weakening of the bond by 2−3 kcal mol^{-1} as the electron donating ability of Y increases, as opposed to lower level theoretical calculations.[3,20a] Reversals in the signs of the slopes of plots of benzylic BDEs vs σ have been reported by theoretical calculations of BDE[p-$YC_6H_4SiH_2{-}G$], for G = F, Cl, and Li. For bond dipoles $Si \rightarrow F$ and $Si \rightarrow Cl$, Y = ED strengthens the bonds and Y = EW weakens them. The reverse was found for $Si \leftarrow Li$.[20c]

Benzylic $YC_6H_4CH_2 \leftarrow H$ and quasi-benzylic BDEs of compounds with the dipole directed toward the substituted ring, such as $YC_6H_4O \leftarrow H$,[25] $YC_6H_4NH \leftarrow H$,[20d,26] $YC_6H_4O \leftarrow CH_3$,[19,20d,27] $YC_6H_4O \leftarrow CH_2C_6H_5$,[20d] and $YC_6H_4S \leftarrow H$,[28] have experimental BDEs that increase with increasing EW ability of Y. When the direction of the dipole reverses, as in $YC_6H_4C(R) \rightarrow ONR_2$ (alkoxyamines derived from TEMPO)[29] and $YC_6H_4S \rightarrow NO$,[30] effects of Y on BDE also reverse.

The differences in MSE of the benzyl fluorides found in this work are not large, spanning a range of 1.62 kcal mol^{-1}. However, if only one-half of this were to be reflected in the activation energy of a hypothetical exothermic benzyl−F atom abstraction, the Hammett slope would be 0.54 at 298 K. This is in line with experimentally determined relative rates of abstractions of Y-substituted benzyl−Cl and benzyl−Br by (n-$Bu)_3Sn^{\bullet}$ radicals, which gave Hammett slopes of $k_Y/k_H = 0.40\sigma$ for Cl and $k_Y/k_H = 0.22\sigma$ for Br.[2a] In this particular case, the sensitivity of the rates to substituent effects, or magnitude of the Hammett slopes, found experimentally follows the trend of the magnitude of the benzyl $C \rightarrow X$ dipole, with that of $C \rightarrow Cl$ being greater than that of $C \rightarrow Br$.

The direction of the benzyl C−X dipole appears to control the direction of rate changes (positive or negative Hammett slopes) in all *experimentally* studied benzyl−X atom abstractions, to our knowledge. However, the rate sensitivity to substituent effects (magnitude of the Hammett slope) must depend on the enthalpies of reaction.[21] If polar effects at the TS were to control the direction of the slope of Hammett plots, the rates of abstraction of hydrogen from a series of ring-substituted aromatic amines by primary alkyl radicals and by peroxyl radicals would show a dependence on the opposite directions of the TS dipoles, $Ar_2N^{\delta-}\cdots H\cdots {}^{\delta+}CH_2R$ and $Ar_2N^{\delta+}\cdots H\cdots {}^{\delta-}OOR$, respectively, based on Pauling's elec-

SCHEME 2



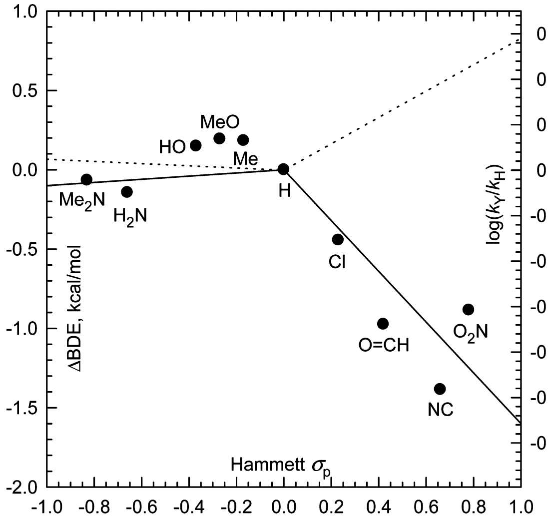


Figure 7. Points denote ΔBDE = BDE[$C_6H_5CH_2{-}F$] − BDE[p-$YC_6H_4CH_2{-}F$] vs Hammett σ_p (solid lines, left Y axis). The dotted lines are the Hammett slopes reported[2c] for $\log(k_Y/k_H)$ of the reaction $YC_6H_4CH_2{-}Br + {}^\bullet Sn(n\text{-}Bu)_3 \rightarrow YC_6H_4CH_2^\bullet + Br{-}Sn(n\text{-}Bu)_3$ (right Y axis) See text.

tronegativity values for N, C, and O. In fact, the ratio $k[p\text{-}CH_3O]/k[H]$ is greater than 1 for both H abstractions.[26b]

Scheme 2 outlines the behavior of benzylic and quasi-benzylic X atom abstractions.

Bond dissociation energies of the C−F bonds of p-$YC_6H_4CH_2F$ can be estimated from the MSE values reported here and the finding that electronic effects of p-Y are transmitted through the aromatic ring only 0.35 as efficiently as those transmitted through one double bond in *trans*-YCH=CHCH$_2$F. Multiplying the previously reported[15] radical stabilization energies, RSEs, of the allyl fluorides by 0.35 gives an estimate of the RSE for the corresponding p-$YC_6H_4CH_2^\bullet$: Y = $(CH_3)_2N$, 0.825; H_2N, 0.835; HO, 0.205; CH_3O, 0.233; H_3C, 0.052; H, 0.000; Cl, 0.188; HC(O), 0.498; NC, 0.612; O_2N, 0.024; and F_3C, −0.411 kcal mol^{-1}. All substituents larger than H (on either side of $\sigma = 0$) stabilize the benzyl radicals to a greater or lesser extent, except for F_3C, irrespective of the ED or EW ability of the substituent. This is in agreement with electron spin resonance measurements, E.S.R. (electron paramagnetic resonance), of the delocalization of the odd spin of substituted benzyl radicals, including the behavior of F_3C.[31] Evidently, the larger the molecular orbitals, the greater is the possible delocalization in addition to possible resonance effects. A reason for the different behavior of F_3C, and also F by E.S.R., has not been firmly established. From ΔBDE = MSE − RSE, we obtain the values plotted in Figure 7 vs σ_p, where negative values indicate C−F bonds weaker than those of $C_6H_5CH_2{-}F$. MSE and RSE effects on BDE are in opposite directions and tend to cancel in the domain $\sigma < 0$ and reinforce each other, weakening the bond in $\sigma > 0$. The scatter in ΔBDE is due to the fact that, while MSE correlates with σ, RSE does not. The resulting pattern is consistent with experimental relative reactivities reported by Menapace et al.[2c] for bromine abstractions by ${}^\bullet Sn(n\text{-}Bu)_3$ from para substituted benzyl bromides. They found a discontinuity in the Hammett slope at $\sigma = 0$. A plot of $\log_{10}(k_Y/k_H)$ vs σ_p gave a positive slope of 0.29 in the domain $\sigma_p > 0$ and a slightly negative slope of −0.024 in $\sigma_p < 0$ for this very exothermic reaction. This is exactly the pattern of behavior that is expected from Figure 7, with the values of $\log_{10}(k_Y/k_H)$ depending on ΔBDE. The weaker the bond, the faster is the rate of halogen abstraction.

We also performed some G3 calculations of BDE[p-$YC_6H_4CH_2{-}H$]. The values were obtained from $H^{298}[YC_6H_4CH_2^\bullet] + H^{298}[H^\bullet] - H^{298}[YC_6H_4CH_2{-}H]$, the result multiplied by 627.51 to convert to kcal mol^{-1}. The BDE for Y = H_2N is 89.53; for HO, 90.26; for H, 90.52; for Cl, 90.83; and for O_2N, 89.53 kcal mol^{-1}. The G3 value for toluene, BDE = 90.52, compares favorably with the experimental value of 89.7 ± 1 for its benzylic C−H.[32] The accuracy of this level of calculation for the types of molecules treated here is of the order of ±1 kcal mol^{-1}, but relative values of ΔBDE should be considerably more accurate. Assuming about equal pre-exponential terms of the rate constant for benzyl hydrogen abstraction by Br$^\bullet$, the difference of 1.42 kcal mol^{-1} between BDE[p-$H_2NC_6H_4CH_2{-}H$] and BDE[p-$O_2NC_6H_4CH_2{-}H$] must be reflected in the energy of activation, as a minimum, because the abstractions are endothermic. This would cause $k(H_2N)/k(O_2N) = e^{1420/(RT)} = 11.8$ faster at room temperature with the ED H_2N group relative to EW O_2N. This is consistent with the negative Hammett slopes that have been reported near room temperature for such H abstractions by Br$^\bullet$.[1a,23]

For any abstracting radical ${}^\bullet R$ in reactions $YC_6H_4Z{-}X + {}^\bullet R \rightarrow YC_6H_4Z^\bullet + X{-}R$, the Z•••R dipole at the TS does not appear to control the direction of Y substituent effects on relative rates (positive or negative Hammett slope). However, the sensitivity of relative reaction rates to substituent effects will be a function of the exothermicity of the reaction, the more exothermic reactions being less sensitive.

Conclusions

G3 and G3(MP2) calculations of molecule stabilization energies of meta and para substituted benzyl fluorides are correlated well with Hammett σ constants and with benzyl ^{13}C NMR chemical shifts. G3 calculations demonstrate an increase in BDE[p-$YC_6H_4CH_2{-}H$] with increasing electron withdrawing ability of Y. For radical abstractions of X from $YC_6H_4CH_2X$, the direction of the C−X dipole is the major factor determining the overall direction of the trends of relative rates, i.e., positive or negative Hammett slopes. Electronic effects of substituents transmitted through one double bond in allylic compounds are 2.9 times stronger than those transmitted from the para position of benzylic compounds. Some extensively used forms of isodesmic reactions for calculating MSE are not valid. Thermochemical results in calculating MSE by G3(MP2) are about the same as those by G3.

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Supporting Information Available: Complete Gaussian citation of ref 13, a summary of the conversion from H^{298} to relative MSE, a procedure for extracting an input geometry from a G3 or G3(MP2) output file, details of geometries, and energies and enthalpies H^{298} from all G3 and G3(MP2) calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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