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Remote Substituent Effects on Allylic and Benzylic Bond Dissociation Energies. Effects on Stabilization of Parent Molecules and Radicals

Andreas A. Zavitsas,* Donald W. Rogers, and Nikita Matsunaga

Department of Chemistry and Biochemistry, Long Island University, University Plaza, Brooklyn, New York 11201

zavitsas@liu.edu

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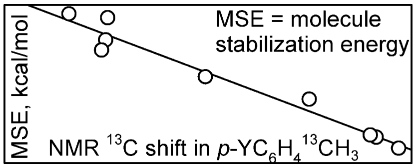
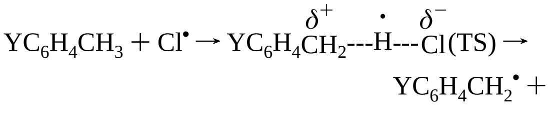


The effect of remote substituents on bond dissociation energies (BDE) is examined by investigating allylic C−F and C−H BDE, as influenced by Y substituents in *trans*-$YCH{=}CHCH_2{-}F$ and *trans*-$YCH{=}CHCH_2{-}H$. Theoretical calculations at the full G3 level model chemistry are reported. The interplay of *stabilization energies* of the parent *molecules* (MSE) and of the *radicals* formed by homolytic bond cleavage (RSE) and their effect on BDE are established. MSE values of allyl fluorides yield an excellent linear free energy relationship with the electron-donating or -withdrawing ability of Y and decrease by 4.2 kcal mol^{-1} from Y = $(CH_3)_2N$ to O_2N. RSE values do not follow a consistent pattern and are of the order of 1−2 kcal mol^{-1}. A decrease of 4.1 kcal mol^{-1} is found in BDE[C−F] from Y = CH_3O to NC. BDE[$YCH{=}CHCH_2{-}H$] generally increases with decreasing electron-donating ability of Y for electron-donating groups and does not follow a consistent pattern with electron-withdrawing groups, the largest change being an increase of 3.6 kcal mol^{-1} from Y = $(CH_3)_2N$ to CF_3. The G3 results are an indicator of benzylic BDE in p-$YC_6H_4CH_2{-}F$ and p-$YC_6H_4CH_2{-}H$, via the principle of vinylogy, demonstrated by correlating MSE of the allylic compounds with physical properties of their benzylic analogues.

Introduction

The effect of remote substituents on bond dissociation energies (BDE) has been a topic of much interest in the chemical literature as, for example, the effect of meta or para substituents on benzylic BDE[$YC_6H_4CH_2{-}X$]. Because BDE is the energy required for homolytic bond cleavage, properties of the free radicals formed must be studied. Relative reactivities of benzyl hydrogen abstraction by radicals from substituted toluenes give linear free energy plots of the Hammett type[1] vs the electron-donating or -withdrawing ability of the substituent as measured by its substituent constant, σ. In the expression $\log(k_Y/k_H) = \rho\sigma$, ρ denotes the slope, negative σ or σ^+ indicate higher electron-donating ability than H, and positive σ or σ^+ higher electron-withdrawing ability of Y. The Hammett correlation for benzyl hydrogen abstractions from substituted toluenes by chlorine atoms, for example, would be explained by postulating that dipolar structures at the transition state (TS) are causing the observed negative Hammett slope ρ, in reaction 1. Y electron donors stabilize the partial positive charge on the benzyl carbon at the TS, lowering the TS energy and enhancing the rate of abstraction, while electron-withdrawing groups destabilize it.[2]



$$YC_6H_4CH_3 + Cl^\bullet \rightarrow YC_6H_4\overset{\delta^+}{C}H_2\text{---}\overset{\bullet}{H}\text{---}\overset{\delta^-}{Cl}(TS) \rightarrow YC_6H_4CH_2^\bullet + HCl \quad (1)$$

A proposal was made in 1972 that the effects of substituents

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[1] Hammett's σ_p and σ_m values were derived from the pK_a of para- and meta-substituted benzoic acids: Hammett, L. P. *J. Am. Chem. Soc.* **1937**, *59*, 96−103. Hammett, L. P. *Physical Organic Chemistry*; McGraw Hill: New York, 1940. Substituent σ^+ values are from the logarithms of the rate constants for solvolysis of cumyl chlorides and reflect resonance effects better: Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957**, *79*, 1913−1917. Okamoto, Y.; Brown, H. C. *J. Org. Chem.* **1957**, *22*, 485−494. The σ^+ values used in this work are from the following compilation: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

[2] (a) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957; pp 365−369. (b) Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, pp 275−331.

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on the rates of benzyl hydrogen abstractions by free radicals from meta- and para-substituted toluenes, $YC_6H_4CH_3$, may not always be due solely to polar effects at the TS, as was the prevalent explanation at the time, but also to the effect of substituents on the BDE of the C−H bond, with electron-donating substituents weakening the bond and electron-withdrawing substituents strengthening it.[3] The explanation of observed Hammett correlations by invoking polar effects at the TS requires a reversal in the sign of ρ when the abstracting radical is less electronegative than a benzyl carbon. The BDE explanation, on the other hand, requires negative ρ, irrespective of the abstracting radical. The BDE postulate prompted several examinations of abstractions from substituted toluenes, with mixed results. Some supported the BDE argument and others did not.[4] Negative ρ values are observed in benzylic hydrogen abstractions from meta- and para-substituted toluenes, ethylbenzenes, cumenes (isopropylbenzenes), benzaldehydes, benzyl ethers, etc. by radicals such as $Br^\bullet$, $Cl^\bullet$, $(CH_3)_3CO^\bullet$, $Cl_3C^\bullet$, $ROO^\bullet$, $R_2N^\bullet$, etc.[2b] Subsequent reports of positive ρ values with alkyl radicals as the H-abstracting species from toluenes seemed to invalidate the BDE proposal, but these reports were subsequently shown to have been the result of experimental difficulties[4j,k,p] or were caused by competing radical additions to the aromatic ring, as alkyl radicals added with positive ρ.[5]

Strong support for the BDE postulate came from the work of Mahoney and DaRooge, who demonstrated that the quasi-benzylic BDE[O−H] of phenols is a function of ring substituents, decreasing by as much as 8 kcal mol^{-1} in proceeding from the electron-withdrawing *m*-COOEt to the electron-donating *p*-MeO substituent.[6] Several subsequent investigations confirmed BDE changes caused by ring substituents. Substituent effects on benzyl BDE[C−H] values were reported[7] in the direction predicted by the BDE postulate. Several additional measurements of BDE[ArO−H] were reported.[8] In anilines, electron-withdrawing substituents strengthen the N−H bond and electron donors weaken it, in the direction originally suggested,[3] by an increase of about 6 kcal mol^{-1} in going from *p*-NO_2− to *p*-CH_3O− substituents.[9] Substituent effects on BDE were also reported for the quasibenzylic bonds of anisoles $ArO-CH_3$ and similar ethers,[10] ArS−H of thiophenols[11a−c] and $ArS-CH_2C_6H_5$ of aryl thioethers,[11d] ArS−NO bonds,[12] $ArSiH_2-X$ bonds,[13] $ArN(CONR_2)-NO$,[14] $ArCH(R)-ONR_2$,[15] etc.

These findings prompted research on the question as to whether the observed BDE effects were due primarily to stabilization or destabilization of parent molecules, *m*- or *p*-YC_6H_4G-X, or to radical stabilization or destabilization of the resulting benzylic or quasibenzylic radicals $YC_6H_4G^\bullet$.[4bb,9e,11c,16] On various grounds, proposals were made that the direction of

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the G−X dipole, dependent on electronegativity differences between G and X, would have a significant effect on the stability of the parent molecule.[17] The molecule would be stabilized by electron-donor substituents in the case of ArG$\rightarrow$X, lowering its energy and tending to increase BDE, and the reverse for ArG$\leftarrow$X. The magnitude of the effect would increase with the strength of the dipole. One such proposal arose from photoacoustic calorimetry measurements of BDE[p-$YC_6H_4CH_2$−Br] that showed significant BDE decreases with increasingly electron-withdrawing Y's.[17a] This finding, combined with the slopes of Hammett correlations of BDEs of phenols, anisoles, and toluenes, led to the suggestion that G−X dipoles influence BDE values: Y substituents would stabilize or destabilize the molecule depending on the electronegativity difference between G and X; hence, BDEs do not reflect only stabilization energies of the radicals formed by homolytic cleavage.

The same conclusion was reached on the basis of Hammett slopes of BDEs of ArO−H, ArNH−H, ArS−H, ArO−CH_3, $ArCH_2$−H, $ArCH_2$−Br, and Ar−Cl.[11a] The same conclusion was also reached on the basis of AM1 calculations of BDEs of $ArCH_2$−Br, ArS−H, and ArBH−H and arguments based on Pauling's electronegativity equation.[17b−d] In the experimental studies cited,[6−15] results adhere to the parent molecule dipole argument. The effect of substituents on benzylic C$\rightarrow$halogen bonds would be opposite to that on C$\leftarrow$H bonds. Consistent with this, rates of abstractions of halogen atoms from ring-substituted benzyl halides by $R_3Si^\bullet$ and $R_3Sn^\bullet$ radicals show a substituent dependence that is the reverse of benzyl hydrogen abstractions.[4n,18]

A later experimental determination of BDE[p-$YC_6H_4CH_2$−Br] by photoacoustic calorimetry and gas phase thermolyses found no significant effect of Y on BDE.[19a] This led to calculations of BDE[p-$YC_6H_4CH_2$−X] (X = F, Cl, Br), where the effects of Y substituents on BDEs were found to be minor and scattered even with the large electronegativity difference of C and F.[19b] The large size of the molecules precluded a full G3 ab initio calculation,[20] and the methods used were the semiempirical AM1[21] and ab initio, but less computer intensive, density functional theory (DFT). The conclusion was reached that proposals "that the direction and magnitude of the effects of Y-substituents on 4-YC_6H_4Z−X BDEs depends on the differences in the electronegativities of the bonding atoms in Z and X *should be discarded*." The arguments are summarized in a recent account.[22] However, the arguments[11a,17] of the importance of Z and X electronegativities were made in regards to *stabilization of the molecules as they contribute to BDEs and not on BDEs alone* that are dependent on both molecule and radical stabilization effects that may add or cancel each other out. Calculated molecule stabilization effects were actually reported in the direction postulated by the dipole arguments.[19b] Extensive similar (AM1 and PM3) calculations on 48 p-YC_6H_4G−X molecules supported the G−X dipole argument.[19c]

In the current work, we examine smaller analogues of benzylic systems to elucidate the effects of Y on YCH$=$$CHCH_2$−F and YCH$=$$CHCH_2$−H, using the more accurate full G3 model chemistry to obtain bond dissociation energies and stabilization energies of the parent molecule and of the radicals formed by bond homolysis.

Results and Discussion

We studied remote substituent effects by applying the G3 model chemistry to allyl fluorides and propenes, with various Y substituents on C1, YCH$=$$CHCH_2$−F and YCH$=$$CHCH_2$−H. We focused on the fluorides YCH$=$$CHCH_2$−F because they have the largest C−F dipole of the halides. Results with the higher level of theoretical methodology, G3 vs AM1 or DFT, provide a firmer foundation for our understanding of the transmission of the effects of remote substituents through −CH$=$CH−. Via the principle of vinylogy,[23] the results should also reflect the behavior of benzyl analogues, p-$YC_6H_4CH_2$−F and p-$YC_6H_4CH_2$−H, where substituent effects are transmitted through −C_6H_4−. Vinylogy operates because electronic effects are transmitted through the double bond as, for example, in α,β unsaturated carbonyl compounds $RCH_2CH$$=$$CHCOR_1$, where γ hydrogens assume the acidity normally associated with the position α to the carbonyl. Effects found with the allyl fluorides should reflect similar effects in the corresponding benzyl fluorides and we demonstrate below that this is the case.

Enthalpies of formation at 298 K, $\Delta_f H°$, in kcal mol^{-1}, were obtained from the G3 energy values in atomic units (au, also called hartrees), H^{298}, via the experimental atomization energies of the elements. For all allyl fluorides, the calculation was performed on the trans isomer to avoid any possibility of steric or hydrogen-bonding effects between the substituent Y and the CH_2F group and to mimic the similar absence of such effects in para-substituted benzyl fluorides. The designations we use for the different conformers shown in Table 1 are exemplified in Chart 1.

The results of Table 1 indicate that the particular conformation of the compounds examined affects the energy, sometimes substantially. Examples from Table 1 are the four entries for conformers of HOCH$=$$CHCH_2F$, where there is a difference of 2.2 kcal mol^{-1} between the most stable conformer and the

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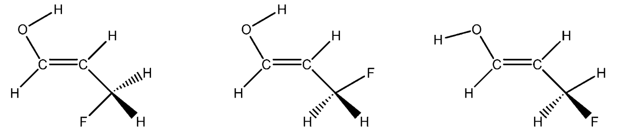
TABLE 1. Calculated (G3) Enthalpies of Formation at 298 K for Species Examined in This Work

compound[a]	$\Delta_f H°$,[b] kcal mol^{-1}	H^{298},[c] hartree	conformer remarks[d]
(*E*)-$(CH_3)_2NCH=CHCH_2F$	−38.63	−350.823228	F gauche, out of plane
(*E*)-$(CH_3)_2NCH=CHCH_2F$	−36.72	−350.820204	F endo planar; N−CH_3 gauche
(*E*)-$(CH_3)_2NCH=CHCH_3$	7.19	−251.619922	one N−CH_3 nearly in plane
(*E*)-$H_2NCH=CHCH_2F$	−37.74	−272.298741	F exo planar; one N−H nearly planar
(*E*)-$H_2NCH=CHCH_2F$	−35.75	−272.295567	F endo planar; N−H gauche
(*E*)-$H_2NCH=CHCH_3$	7.04	−173.095627	N−H nearly in plane
(*E*)-$HOCH=CHCH_2F$	−80.43	−292.166432	O−H endo planar; F gauche
(*E*)-$HOCH=CHCH_2F$	−79.38	−292.164760	O−H exo planar; F gauche
(*E*)-$HOCH=CHCH_2F$	−78.54	−292.163408	O−H endo planar; F endo planar
(*E*)-$HOCH=CHCH_2F$	−78.19	−292.162861	O−H exo planar; F endo planar
(*E*)-$HOCH=CHCH_3$	−35.76	−192.964945	O−H endo planar
(*E*)-$HOCH=CHCH_3$	−34.77	−192.963358	O−H exo planar
(*E*)-$CH_3OCH=CHCH_2F$	−76.93	−331.422404	O−CH_3 endo planar; F endo planar
(*E*)-$CH_3OCH=CHCH_2F$	−74.79	−331.418988	O−CH_3 exo planar; F gauche
(*E*)-$CH_3OCH=CHCH_2F$	−73.45	−331.416847	O−CH_3 exo planar; F endo planar
(*E*)-$CH_3OCH=CHCH_3$	−31.96	−232.220406	O−CH_3 endo planar
(*E*)-$CH_3OCH=CHCH_3$	−30.07	−232.217400	O−CH_3 exo planar
(*E*)-$CH_3CH=CHCH_2F$	−46.42	−256.250442	F exo planar
(*E*)-$CH_3CH=CHCH_2F$	−45.92	−256.249623	F endo planar
(*E*)-$CH_3CH=CHCH_3$	−2.61	−157.050305	
(*E*)-$CH_2=CHCH=CHCH_2F$	−24.36	−294.313476	F gauche; C=C−C=C is s-*trans*
(*E*)-$CH_2=CHCH=CHCH_2F$	−24.17	−294.313159	F endo planar; C=C−C=C is s-*trans*
(*E*)-$CH_2=CHCH=CHCH_3$	18.87	−195.114289	C=C−C=C is s-*trans*
$CH_2=CHCH_2F$	−38.38	−216.976095	F endo planar
$CH_2=CHCH_2F$	−38.35	−216.976038	F exo planar
$CH_2=CHCH_3$	4.42	−117.777081	
(*E*)-$ClCH=CHCH_2F$	−44.77	−676.439385	F gauche
(*E*)-$ClCH=CHCH_2F$	−44.62	−676.439139	F endo planar
(*E*)-$ClCH=CHCH_3$	−2.27	−577.241312	
(*E*)-$CF_3CH=CHCH_2F$	−202.29	−553.889773	one F and allylic F both endo planar
(*E*)-$CF_3CH=CHCH_3$	−159.94	−454.691967	one F endo planar
(*E*)-$NCCH=CHCH_2F$	−6.21	−309.183384	F endo planar
(*E*)-$NCCH=CHCH_2F$	−5.07	−309.181552	F gauche
(*E*)-$NCCH=CHCH_3$	35.76	−209.986177	
(*E*)-$HCOCH=CHCH_2F$	−66.78	−330.242902	F endo planar; C=C−C=O is s-*trans*
(*E*)-$HCOCH=CHCH_2F$	−66.18	−330.241945	F gauche; C=C−C=O is s-*trans*
(*E*)-$HCOCH=CHCH_2F$	−64.06	−330.238545	F gauche; C=C−C=O is s-*cis*
(*E*)-$HCOCH=CHCH_3$	−24.88	−231.045806	C=C−C=O is s-*trans*
(*E*)-$HCOCH=CHCH_3$	−22.74	−231.042386	C=C−C=O is s-*cis*
(*E*)-$O_2NCH=CHCH_3F$	−42.64	−421.389885	F endo planar; two N−O planar
(*E*)-$O_2NCH=CHCH_2F$	−41.35	−421.387835	F gauche; two N−O planar
(*E*)-$O_2NCH=CHCH_3$	−1.07	−322.193342	
$H\cdot$	52.10[e]	−0.498642	
$F\cdot$	18.90	−99.681844	
(*E*)-$(CH_3)\ _2NCH=CHCH_2\cdot$	39.63	−250.986549	one N−CH_3 nearly planar
(*E*)-$H_2NCH=CHCH_2\cdot$	40.37	−172.462302	one N−H nearly planar
(*E*)-$HOCH=CHCH_2\cdot$	−1.53	−192.328727	O−H endo planar
(*E*)-$HOCH=CHCH_2\cdot$	−1.27	−192.328310	O−H exo planar
(*E*)-$CH_3OCH=CHCH_2\cdot$	2.20	−231.584323	O−CH_3 exo planar
(*E*)-$CH_3OCH=CHCH_2\cdot$	2.82	−231.583330	O−CH_3 endo planar; O−CH_3 gauche
(*E*)-$CH_3CH=CHCH_2\cdot$	32.06	−156.413408	
(*E*)-$H_2C=CH-CH=CHCH_2\cdot$	48.23	−194.485819	all trans
$CH_2=CHCH_2\cdot$	39.54	−117.139938	
(*E*)-$ClCH=CHCH_2\cdot$	32.02	−576.605028	
(*E*)-$CF_3CH=CHCH_2\cdot$	−123.86	−454.052944	one F endo planar
(*E*)-$NCCH=CHCH_2$	68.81	−209.351830	
(*E*)-$HCOCH=CHCH_2\cdot$	8.50	−230.410949	C=C−C=O is s-*trans*
(*E*)-$HCOCH=CHCH_2\cdot$	9.28	−230.409692	C=C−C=O is s-*cis*
(*E*)-$O_2NCH=CHCH_2\cdot$	33.82	−321.556083	two N−O planar
$CH_2=CHN(CH_3)_2$	13.14	−212.348890	N−CH_3 gauche
$CH_2=CHNH_2$	14.18	−133.824161	one N−H nearly planar
$CH_2=CHOH$	−29.73	−153.693791	O−H endo planar
$CH_2=CHOH$	−28.63	−153.692045	O−H exo planar
$CH_2=CHOCH_3$	−26.02	−192.949438	O−CH_3 endo
$CH_2=CHOCH_3$	−24.38	−192.946810	O−CH_3 exo
$CH_2=CHCH=CH_2$	26.66	−155.840333	planar, s-*trans*
$H_2C=CH_2$	12.33	−78.503419	
$CH_2=CHCl$	5.32	−537.967728	
$CH_2=CHCF_3$	−151.30	−415.416611	one F endo planar
$CH_2=CHCN$	44.81	−170.710226	planar
$CH_2=CHCHO$	−15.91	−191.769974	planar, C=C−C=O is s-trans
$CH_2=CHCHO$	−13.77	−191.766567	planar, C=C−C=O is s-cis
$CH_2=CHNO_2$	7.90	−282.917506	two N−O planar

[a] The first entry for each species is the most stable conformer. [b] Obtained invoking experimental enthalpies of formation of atoms in the G3 calculation. [c] Energy released in the formation of the molecule from isolated nuclei and electrons. One atomic unit (au) or hartree = 627.51 kcal mol^{-1}. [d] For a description of the designations, see Chart 1. [e] Experimental value.

CHART 1



F endo, in alkene plane
H-O endo, in alkene plane

F exo, in alkene plane
H-O endo, in alkene plane

F gauche, out of alkene plane
H-O exo, in alkene plane

TABLE 2. BDE[*trans*-YCH═CHCH$_2$−F], Molecule Stabilization Energies, Radical Stabilization Energies, and σ^+ Substituent Constants[a]

Y−	BDE	MSE[b]	RSE[b]	σ^+
$(CH_3)_2N-$	97.16	+2.69	+2.37	−1.70
H_2N-	97.01	+2.57	+2.40	−1.30
HO−	97.80	+1.55	+0.58	−0.92
CH_3O-	98.04	+1.87	+0.67	−0.78
H_3C-	97.38	+0.70	+0.15	−0.31
$CH_2{=}CH-$	91.50	+0.11	+5.44	−0.16
H−	96.83	0.00	0.00	0.00
Cl−	95.70	−0.59	+0.54	+0.11
F_3C-	97.25	−0.75	−1.18	+0.61
NC−	93.94	−1.13	+1.76	+0.66
HCO−	94.19	−1.20	+1.43	+0.73
O_2N-	95.36	−1.55	+0.07	+0.79

[a] Energy values in kcal mol^{-1}. Values obtained by calculating enthalpies of reactions in hartrees, then multiplying by 627.51 kcal mol^{-1} per hartree. [b] Positive values denote stabilization. MSE = closed shell parent molecules, RSE = radicals.

least stable of the listed energy minima, the two listed conformers of $H_2NCH{=}CHCH_2F$ differing by 2.0 kcal mol^{-1}, etc. We made extensive searches of various conformers to locate the global minimum for each species, which is the first entry among conformers of the same compound in Table 1. In no case were there imaginary frequencies in the structures described. Some, but not all, local minima are also shown in Table 1. This type of conformational effect has been also reported previously for *m*-methylphenol where BDE[O−H] depended on whether the H−O bond was directed toward the methyl or away, H−O being coplanar with the ring in both cases.[24]

BDE[C−F] values in kcal mol^{-1} were obtained for reaction 2 as H^{298}[YCH═CHCH$_2^\bullet$] + H^{298}[F$^\bullet$] − H^{298}[YCH═CHCH$_2$F] from Table 1, the result multiplied by 627.51 kcal mol^{-1} per hartree to yield a purely theoretical value.

$$YCH{=}CHCH_2{-}F \rightarrow YCH{=}CHCH_2^{\bullet} + F^{\bullet} \qquad (2)$$

This approach avoids invoking experimental enthalpies of formation of atoms in the calculation of BDE. The most stable conformers of the allyl fluorides and allyl radicals were used in the calculation. The results are shown in Table 2. The order of the entries in Table 2 is that of decreasing electron-donating ability of the substituent from dimethyamino to nitro, as quantified by their substituent constants (whether σ^+ or Hammett σ_p). The very low BDE for the vinyl substituent reflects the large stabilization of the radical by the resonance $CH_2{=}CHCH{=}CHCH_2^\bullet \leftrightarrow {}^\bullet CH_2CH{=}CHCH{=}CH_2$, 5 ± 1 kcal mol^{-1} greater than the resonance stabilization of the allyl radical.[25] Reliability of the method is supported by the computed BDE[$CH_2{=}CHCH_2{-}F$] = 96.8 kcal mol^{-1}, in line with reported experimental values of 96.9, 97.4 ± 2, and 96.8 ± 2 kcal mol^{-1}.[26] The corresponding experimental BDE for benzyl fluoride is 98.7 ± 1 kcal mol^{-1},[27] about 2 kcal mol^{-1} stronger for benzyl bonds as compared to allyl bonds. Therefore, spin contamination resulting from the use of the unrestricted wave function in the calculation of radical energies do not seem to affect the resulting BDE and any such effects would be very similar for all substituted allyl radicals. Also, evaluated experimental enthalpies of formation are available[27] for 14 of the entries in Table 1 and the average absolute deviation between the two sets is 0.95 kcal mol^{-1}.

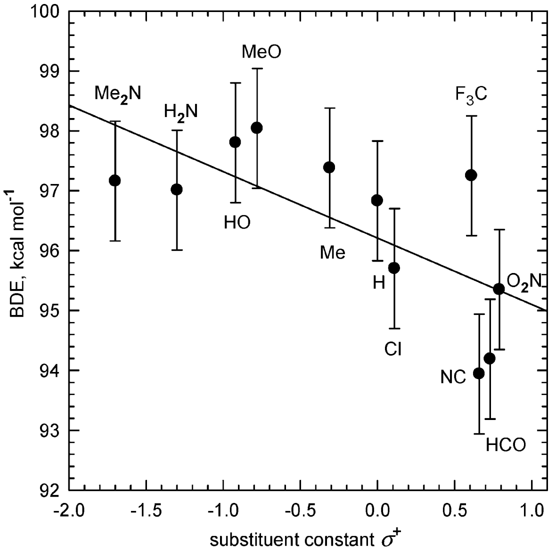


FIGURE 1. Plot of YCH═CHCH$_2$−F bond dissociation energies vs σ^+ substituent constants. BDE = 96.2 − 1.11σ^+. Correlation coefficient = −0.69. Error bars indicate estimated uncertainty as ±1 kcal mol^{-1}.

A plot of BDE vs Hammett σ_p, excluding the special case of the vinyl substituent, yields a linear regression line of BDE = 96.5 − 1.80σ_p, with a correlation coefficient of $r = -0.69$. A plot of BDE vs σ^+ yields BDE = 96.2 − 1.11σ^+, also with $r = -0.69$, and is shown in Figure 1. The correlation is quite poor. BDEs of 8 of the 11 Y's may even be considered to be the same, within the estimated uncertainty of ± 1 kcal mol^{-1} of G3 results for these relatively small molecules. The greatest variation in BDE[C−F] is a 4.1 kcal mol^{-1} decrease from *trans*-$CH_3OCH{=}CHCH_2{-}F$ to *trans*-$NCCH{=}CHCH_2{-}F$. The reason for the lack of a better correlation with substituent constants is that BDEs are affected not only by the stabilization enthalpy of the closed shell parent molecules involved (molecule stabilization enthalpy, MSE) but also by the radical stabilization enthalpy (RSE) of the radicals formed by the C−F bond cleavage. The effects of substituents on MSE and RSE are different, and the C−F dipole argument applies only to the MSE component.[17]

We obtained MSE values of $YCH{=}CHCH_2F$, relative to that of $CH_2{=}CHCH_2{-}F$, from the enthalpies of the isodesmic reaction 3. In formulating an isodesmic reaction the choice of the reference reaction will determine the results to be obtained.

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[25] Rogers, D. W.; Matsunaga, N.; Zavitsas, A. A. *J. Org. Chem.* **2006**, *71*, 2214−2219.

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$$\mathrm{YCH{=}CHCH_2F + CH_2{=}CHCH_3 \rightarrow YCH{=}CHCH_3 + CH_2{=}CHCH_2F} \quad (3)$$

The half-reactions of reaction 3 are (a) Y−CH═CHCH$_2$−F → Y−CH═CHCH$_2$−H and (b) H−CH═CHCH$_2$−H → H−CH═CHCH$_2$−F. Half-reaction (a) is related to the effect of Y on the allylic C−F and C−H bonds as transmitted through −CH═CHCH$_2$−. Half-reaction (b) is related to the effect of H on C−F and C−H bonds as transmitted through −CH═CHCH$_2$− and is the reference reaction used in this work. The difference between (a) and (b) is the enthalpy of reaction 3, i.e., the difference between perturbation by Y and perturbation by H. The standard of comparison is Y = H, the substituent constant of H being assigned the value of zero in all σ scales. Positive MSE values, as defined here, denote greater stability of the parent molecule (relative to CH$_2$═CHCH$_2$F) and contribute to an increase in BDE[YCH═CHCH$_2$−F]. Negative values have the reverse effect. We used enthalpies of formation from Table 1 to calculate the MSE values listed in Table 2.

Similarly, RSE values of YCH═CHCH$_2^\bullet$, relative to that of CH$_2$═CHCH$_2^\bullet$, are calculated from the enthalpies of reaction 4 and are also shown in Table 2.

$$\mathrm{CH_2{=}CHCH_3 + YCH{=}CHCH_2^{\bullet} \rightarrow CH_2{=}CHCH_2^{\bullet} + YCH{=}CHCH_3} \quad (4)$$

Positive values indicate greater stability of YCH═CHCH$_2^\bullet$ relative to the unsubstituted reference CH$_2$═CHCH$_2^\bullet$ and contribute to a decrease in BDE. Therefore, ΔBDE = BDE[YCH═CHCH$_2$−F] − BDE[CH$_2$═CHCH$_2$−F] = MSE − RSE.

The electron-donating or -withdrawing ability of Y should stabilize or destabilize the dipole C→F ↔ C$^{\delta+}$−F$^{\delta-}$ of the YCH═CHCH$_2$F molecule. MSE values should be correlated with the substituent constant of Y and we obtain an excellent correlation vs σ^+, as shown in Figure 2. Linear regression yields MSE = −0.02 − 1.78σ^+, with $r = -0.985$. The intercept of −0.02 is appropriately near zero. The vinyl substituent now behaves normally and its point is located near the linear regression line, because there is no radical conjugation involved. The MSE effect is significant, amounting to a decrease of 4.2 kcal mol^{-1} in going from the dimethylamino to the nitro substituent.

RSE values show no correlation with substituent constants. All substituents, except CF$_3$, stabilize the allyl radicals to various extents. The uniqueness of CF$_3$ in this respect has also been noted previously.[10c] RSE values are generally small, averaging 1.1 ± 0.7 kcal mol^{-1} for 10 entries in Table 2 (excluding vinyl with its extended resonance stabilization of the odd electron). Because RSE effects are small in substituted allyl radicals and generally in the direction causing a decrease in BDE, MSE effects can become the dominant factor with some C−F bonds, even though they are not the exclusive factor. Substituents such NC, HCO, and O$_2$N containing multiple bonds might be suspected of providing greater resonance stabilization, as does Y = CH$_2$═CH and as suggested by one reviewer of the manuscript, but they do not have RSE values particularly larger than those of some of the other substituents and RSE for the nitro group is essentially zero. The fact that RSE effects are small with substituted allyl fluorides must not be generalized as applicable to other quasibenzylic systems (phenols, anilines, etc.).

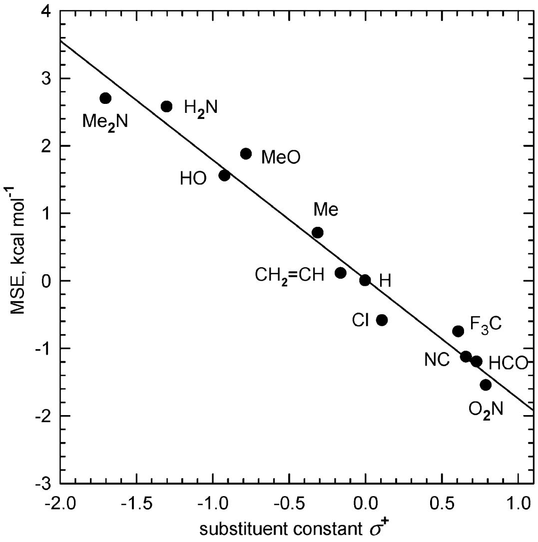

FIGURE 2. Plot of YCH═CHCH$_2$F molecule stabilization energies calculated by reaction 3 vs σ^+ substituent constants. MSE = −0.02 − 1.77σ^+. Correlation coefficient = −0.985.

Examination of the MSE and RSE effects (Table 2) clarifies the lack of good correlation of BDE with σ^+. The effects of MSE and RSE roughly cancel each other out in the domain of electron donors, $\sigma^+ < 0$, but are generally additive for $\sigma^+ > 0$ (with the exception of CF$_3$).

Our results contrast with those previously published for benzyl fluorides,[19b] where the maximum variation in BDE was only 1.7 kcal mol^{-1} by the AM1 calculation and 1.8 by the DFT approach, whereas we find variations as large as 4.1 kcal mol^{-1} in the allyl fluorides by G3 (Table 2). MSE values correlate best with σ^+, as reported for benzyl fluorides, but we obtain a considerably steeper slope of $\rho^+ = -1.77$ for allyl fluorides vs the reported $\rho^+ = -0.90$ by AM1 for benzyl fluorides. These differences may be due partially to the known greater reliability of G3 calculations over AM1. Also, the reported results with benzyl fluorides do not specify conformations of substituents such as HO− or CH$_3$O− having their H−O and O−CH$_3$ bonds directed toward or away from the fluorine, which was reported as coplanar with the ring. There is the possibility that the smaller effects reported by the AM1 method for benzyl fluorides indicate that a benzene ring does not transmit remote substituent effects as efficiently as a double bond. To investigate this, we calculated MSE values for YCH═CHCH$_2$F by the AM1 method. The result is MSE = −1.09 − 0.95σ^+, $r = -0.86$. The slope by AM1 is only 53% of that of Figure 2 by G3.

A difference between our BDE results for allyl fluorides and those reported[19b] for benzyl fluorides is that we do not find the unsubstituted allyl fluoride to have the strongest C−F bond (Table 2), whereas such was reported to be the case with unsubstituted benzyl fluoride from the lower level calculations. The G3 results support the suggestion that the direction of G−X bond dipoles in YC$_6$H$_4$G−X affect MSE and are significant factors contributing to BDE[G−X].

The effect of MSE on BDE has been reported[13] to change with a change in the direction of the dipole, as originally suggested.[17] From DFT calculations for a series of p-YC$_6$H$_4$-SiH$_2$−X, plots of BDE[Si→F] vs σ^+ had a negative slope ($\rho^+ = -2.34$, $r = -0.95$), of BDE[Si→Cl] a smaller negative slope ($\rho^+ = -1.70$, $r = -0.97$) and of BDE[Si←Li] a large positive slope vs σ^- ($\rho^- = +9.12$, $r = -0.93$), where the energy units were kJ mol^{-1}. The small electronegativity difference between Si and H, 0.3 in Pauling's scale of the elements, resulted in small substituent effects, with a maximum difference of only 0.8 kcal mol^{-1} and a great deal of scatter for BDE[$\mathrm{Si}{\rightarrow}\mathrm{H}$] ($\rho^+ = 0.09$, $r = 0.24$), as might be expected because MSE effects are small and RSE effects are also small and scattered. Experimental determination of BDE[$\mathrm{YC_6H_4S{-}NO}$] for meta- and para-substituted nitrosothiols[12] also showed a small decrease of 2.6 kcal mol^{-1} in going from *p*-MeO to *p*-NO_2, consistent with the direction of the $\mathrm{S}{\leftarrow}\mathrm{NO}$ dipole.

The evidence cited above supports the proposal that the direction and magnitude of the dipole of the bond to be cleaved contributes to BDE via MSE.[17] However, a series of DFT calculations of BDE[*p*-$\mathrm{YC_6H_4O{-}CH_3}$] and BDE[*p*-$\mathrm{YC_6H_4O{-}H}$] gave essentially the same Y-induced BDE changes for anisoles as for phenols,[10c] despite the difference in Pauling's electronegativities of O−H and O−C, 1.3 and 1.0 units, respectively.[10c] On this basis, the conclusion was that proposals of the importance of the direction and magnitude of the dipole of the bond being cleaved should be discarded. However, experimental measurements do not support these DFT results. Two examples follow: ΔBDE = BDE[*p*-$\mathrm{NO_2C_6H_4O{-}H}$] − BDE[$\mathrm{C_6H_5O{-}H}$] has been reported as +6.0,[8b] +2.2,[8c] and +4.8[8d] kcal mol^{-1} in phenols, and ΔBDE = BDE[*p*-$\mathrm{NO_2C_6H_4O{-}CH_3}$] − BDE[$\mathrm{C_6H_5O{-}CH_3}$] is only +1.1[8c] and +1.2[10a] in anisoles. With the *p*-CH_3O substituent ΔBDE has been reported as −5.9,[8a] −5.6,[8b] −5.3,[8c] −5.3,[8d] and −5.5[8e] in phenols, but ΔBDE for anisoles is only −3.9[10a] and −3.1 from thermolysis measurements (corrected to 298 K) accompanying the DFT results.[10c] Thus, the experimental ΔBDE values are larger for phenols than for anisoles, as would be expected from the larger electronegativity difference in O−H compared to O−C. Also, the effect of the substituents on BDE is in the direction required by the bond dipole proposals,[17] as we also find with the allyl fluorides.

If the principle of vinylogy holds, values obtained for *trans*-$\mathrm{YCH{=}CHCH_2F}$ parent molecule stabilization energies should correlate with physical molecular properties of their aromatic vinylogues, specifically at the benzylic position. We provide examples below demonstrating that this is indeed the case.

Chemical shifts of ^{13}C NMR have been reported for several α,α,α-trifluorotoluenes, *p*-$\mathrm{YC_6H_4{}^{13}CF_3}$.[28a] Figure 3 shows a plot of MSE values of $\mathrm{YCH{=}CHCH_2F}$ from Table 2 vs the reported differences in ^{13}C chemical shifts of the benzylic carbon, for Ys common to the two sets of data. There is a good correlation between the two quantities and a linear regression yields: MSE = 0.78 + 1.95(Δppm), $r = 0.95$.

A similar plot of MSE vs differences in ^{13}C chemical shifts of benzonitriles,[28a] *p*-$\mathrm{YC_6H_4{}^{13}CN}$, also produced a good correlation, shown in Figure 4: MSE = 0.60 + 1.15(Δppm), $r = 0.97$. The $\mathrm{C}{\rightarrow}\mathrm{F}$ and $\mathrm{C}{\rightarrow}\mathrm{N}$ dipoles are in the same direction and the slopes of Figures 3 and 4 are positive.

A plot of MSE vs changes in the benzyl ^{13}C NMR chemical shift[29a] of toluenes, *p*-$\mathrm{YC_6H_4{}^{13}CH_3}$, yields MSE = −0.34 − 2.37(Δppm), $r = -0.96$, Figure 5. The $\mathrm{C}{\leftarrow}\mathrm{H}$ dipole is in a direction opposite to that of $\mathrm{C}{\rightarrow}\mathrm{F}$ and $\mathrm{C}{\rightarrow}\mathrm{N}$. As a result, the slope reverses and is negative. Similar slope reversals have been reported for ^{13}C NMR chemical shifts of the α carbon of toluenes and benzyl halides, their dipoles being in opposite directions.[28]

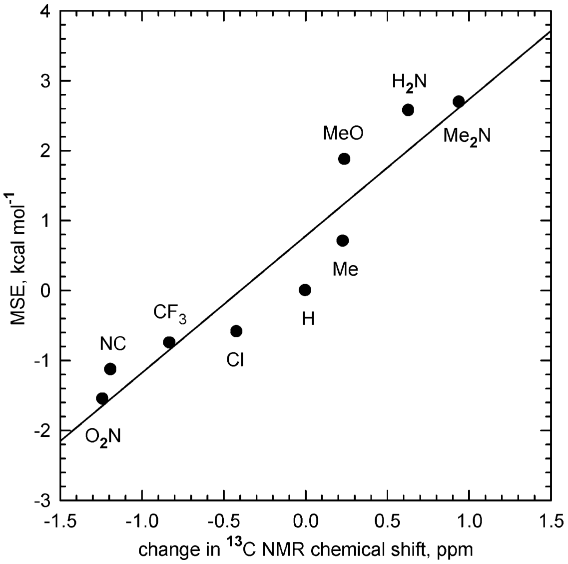

FIGURE 3. Plot of MSE[$\mathrm{YCH{=}CHCH_2F}$] by reaction 3 vs change in ^{13}C NMR chemical shift of *p*-$\mathrm{YC_6H_4{}^{13}CF_3}$. MSE = 0.78 + 1.95($\Delta$ppm). Correlation coefficient = 0.95.

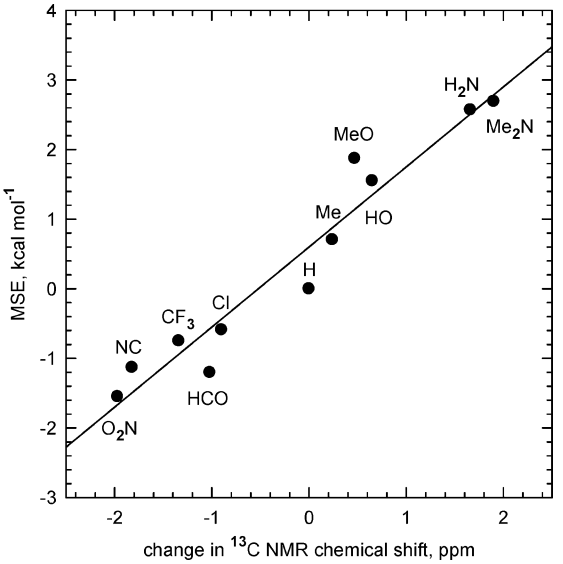

FIGURE 4. Plot of MSE[$\mathrm{YCH{=}CHCH_2F}$] by reaction 3 vs change in ^{13}C NMR chemical shift of *p*-$\mathrm{YC_6H_4{}^{13}CN}$. MSE = 0.60 + 1.15($\Delta$ppm). Correlation coefficient = 0.97.

There is also a correlation of MSE with the ^{1}H NMR chemical shifts[29a] of the benzyl hydrogens of para-substituted toluenes, *p*-$\mathrm{YC_6H_4C{}^1H_3}$. MSE[$\mathrm{YCH{=}CHCH_2F}$] = 40.53 − 17.27(ppm), $r = -0.91$, Figure 6. The shielding of the benzylic ^{1}H increases (smaller ppm) with increasing electron-donating ability of Y, as might be expected.

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(28) (a) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J. *Aust. J. Chem.* **1977**, *30*, 351−355. (b) Craik, D. J.; Brownlee, R. T. C. *Prog. Phys. Org. Chem.* **1983**, *14*, 1−73. (c) Blackwell, L. F.; Buckley, P. D.; Jolley, K. W. *Aust. J. Chem.* **1976**, *29*, 2423−2429.

(29) (a) Saito, T.; Hayamizu, K.; Yanagisawa, M.; Yamamoto, O. National Institute of Advanced Industrial Science and Technology, AIST, Japan, date of access 11/04/2006. SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/. The ^{13}C NMR spectrum of *p*-$\mathrm{ClC_6H_4{}^{13}CH_3}$ was obtained in our laboratory, 400 Mz in acetone-d_6. The ^{1}H NMR chemical shift 2.40 ppm for the benzyl H of *p*-$\mathrm{CF_3C_6H_4CH_3}$ is from DeCosta, D.; Pincock, J. *J. Org. Chem.* **2002**, *67*, 9484−9487. (b) Kinugasa, S.; Tanabe, K.; Tamura, T. also AIST, liquid phase infrared spectra, 2200 cm^{-1} region.

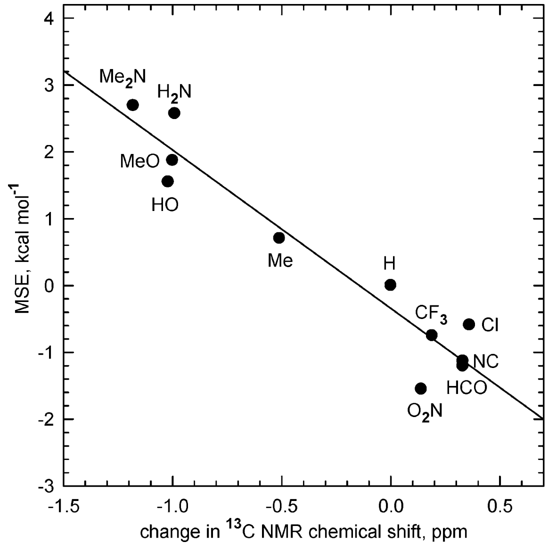

FIGURE 5. Plot of MSE[YCH=CHCH$_2$F] by reaction 3 vs change in ^{13}C NMR chemical shift of p-YC$_6$H$_4$^{13}CH$_3$. MSE $= -0.34 - 2.37(\Delta\text{ppm})$. Correlation coefficient $= -0.96$.

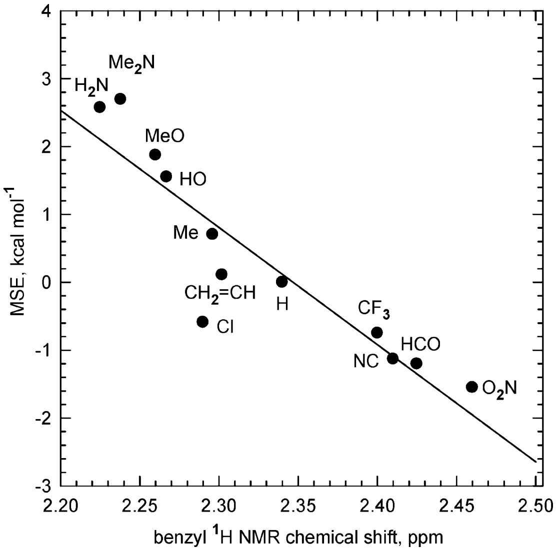

FIGURE 6. Plot of MSE[YCH=CHCH$_2$F] by reaction 3 vs ^{1}H NMR chemical shift of p-YC$_6$H$_4$C^{1}H$_3$. MSE $= -40.53 - 17.27$(ppm). Correlation coefficient $= -0.91$.

MSE values of YCH=CHCH$_2$F also correlate with C−N infrared stretching frequencies[29b] of benzonitriles, p-YC$_6$H$_4$C≡N: MSE $= 389.4 - 0.175\nu$, $r = -0.95$, Figure 7. In the benzonitriles, the C−N frequency ν increases as the electron-withdrawing ability of Y increases. This reflects an increase in the ionic character of the C−N bond, increasing the $^{\delta+}$C−N$^{\delta-}$ dipole and frequency, in the same way that X substituents in acyl compounds, RCO−X, affect carbonyl stretching frequencies. In Figures 1−7, we estimate that the accuracy of MSE values obtained by G3 is of the order of ±1 kcal mol^{-1} for these relatively small molecules.

The correlations between properties of YCH=CHCH$_2$F molecules with properties of their various benzylic counterparts confirms that vinylogy is operative in this work and that the current findings with *trans*-YCH=CHCH$_2$−F reflect benzylic effects. While it is literally true that the direction and magnitude of the dipole being broken is not controlling BDE[C−F] in allyl and, by analogy, benzyl fluorides,[19b,22a] this fact should not obscure the importance of the direction and magnitude of the dipole on the MSE component, which brings about the overall BDE result.

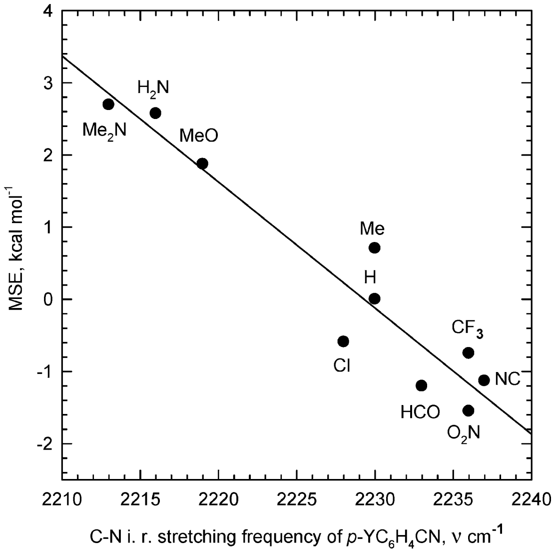

FIGURE 7. Plot of MSE[YCH=CHCH$_2$F] by reaction 3 vs C−N infrared stretching frequency of p-YC$_6$H$_4$CN. MSE $= 389.4 - 0.175\nu$. Correlation coefficient $= -0.95$.

The correlations of Figures 2−7 demonstrate the validity of isodesmic reaction 3 as a measure of molecular properties. The form of isodesmic reaction 3 has been used previously to evaluate MSE in anisoles[10a] and in benzyl halides,[19b] where the relevant reactions are, respectively, YC$_6$H$_4$OCH$_3$ + C$_6$H$_5$OH → YC$_6$H$_4$OH + C$_6$H$_5$OCH$_3$ and YC$_6$H$_4$CH$_2$X + C$_6$H$_5$CH$_3$ → YC$_6$H$_4$CH$_3$ + C$_6$H$_5$CH$_2$X. However, the form of isodesmic reaction 3 is not the only one that has been used to evaluate MSE. The alternative that has been used is of the form of reaction 3′.

$$\text{YCH=CHCH}_2\text{F} + \text{CH}_2\text{=CH}_2 \rightarrow \text{YCH=CH}_2 + \text{CH}_2\text{=CHCH}_2\text{F} \quad (3')$$

For example, with anisoles,[10c] the reaction used is YC$_6$H$_4$OCH$_3$ + C$_6$H$_6$ → C$_6$H$_5$OCH$_3$ + C$_6$H$_5$Y.

With anilines,[9e] the form of reaction 3′ used is YC$_6$H$_4$NH$_2$ + C$_6$H$_6$ → C$_6$H$_5$NH$_2$ + C$_6$H$_5$Y, written in the direction in which we define the sign of MSE. Form 3′ was used also with thiophenols and thiophenyl ethers,[11c] with toluenes and anisoles,[30] with a large variety YC$_6$H$_4$G−X bonds,[4bb] with various aromatic silanes[13] YC$_6$H$_4$SiH$_2$−X, and toluenes, anilines, and phenols.[22a] Reactions 3 and 3′ yield different MSE values, and the question must be answered as to which definition of MSE is preferable. Different MSE results were reported from AM1 calculations based on Pauling's electronegativity equation and on those obtained by using equivalents of reaction 3′,[17d] where isodesmic reaction 3′ was not recommended "since it may lead to incorrect predictions". Nevertheless, reactions equivalent to those of 3′ have continued to be used. Rather than depend on semiempirical or other theoretical calculations, we demonstrate below that reaction 3′ is definitively invalid, its results failing

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(30) (a) Wu, Y. D.; Wong, C.-L.; Chan, K. W. K.; Ji, G.-Z.; Jiang, X.-K. *J. Org. Chem.* **1996**, *61*, 746−750. (b) Wu, Y.-D.; Lai, D. K. W. *J. Org. Chem.* **1996**, *61*, 7904−7910.

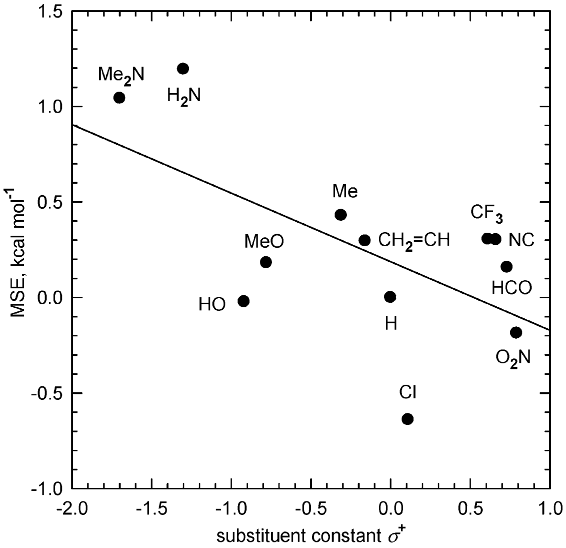

FIGURE 8. Plot of MSE[YCH=CHCH$_2$F] by reaction 3′ vs σ^+ substituent constants. MSE $= 0.19 - 0.37\sigma^+$. Correlation coefficient $= -0.61$.

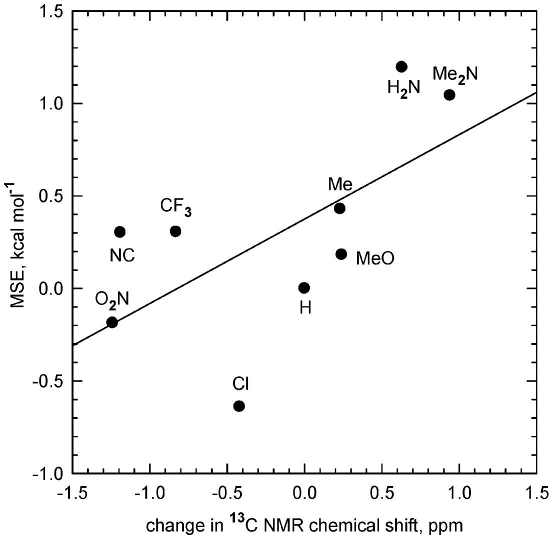

FIGURE 9. Plot of MSE[YCH=CHCH$_2$F] by reaction 3′ vs change in ^{13}C NMR chemical shift of p-YC$_6$H$_4$^{13}CF$_3$. MSE $= 0.376 + 0.456(\Delta\text{ppm})$. Correlation coefficient $= 0.63$.

to correlate with substituent constants or experimental data of physical properties, such as those shown in Figures 2–7. Calculating MSE[YCH=CHCH$_2$F] according to 3′ leads to a poor correlation with σ^+. A linear regression yields MSE $= 0.19 - 0.36\sigma^+$, $r = -0.61$, in Figure 8, which shows a great deal of scatter compared to Figure 2.

MSE values of the allyl fluorides calculated according to 3′ are plotted against ^{13}C NMR chemical shifts of the benzyl carbon p-YC$_6$H$_4$^{13}CF$_3$ in Figure 9. Linear regression yields MSE $= 0.376 + 0.456(\Delta\text{ppm})$, $r = 0.63$, showing poor correlation with the NMR data as compared to Figure 3. Similarly, plots of MSE values calculated by reaction 3′ vs the physical properties of Figures 4–7 show much poorer correlation coefficients, ranging from 0.45 to 0.69. Some of the same authors who defined MSE in the form of reaction 3 for benzyl halides and obtained good correlations with $\sigma^{+,19b}$ subsequently defined MSE in the form of 3′ for anilines, thiophenols, phenols, and toluenes.[9e,11c,22a] Seemingly similar and equally valid isodesmic reactions, such as 3 and 3′, can be deceiving, yielding quite different results. Problems of this kind have been known and have been discussed.[31]

The half reactions of reaction 3′ are (a) Y–CH=CHCH$_2$–F → H–CH=CHCH$_2$–F and (b) H–CH=CH–H → Y–CH=CH–H. Half reaction (a) reflects the difference in the allylic BDE[C(sp^3)–F], under the perturbing influence of Y through –CH=CHCH$_2$– relative to Y = H. Half reaction (b) reflects the difference in BDE[C(sp^2)–H], under the perturbing influence of Y through –CH=CH–, and is the reference reaction chosen in formulating reaction 3′. Half reaction (b) can be viewed as measuring the influence of Y on stabilizing or destabilizing the double bond of ethylene, e.g., affecting its enthalpy of hydrogenation. Half reactions (a) and (b) are not related and do not measure the effect of interest here. In the examples cited (ref 4bb, 9e, 10c, 11c, 22a, and 30), the equivalent to reaction 3′ used is p-YC$_6$H$_4$G–H + C$_6$H$_6$ → C$_6$H$_5$G–H + YC$_6$H$_5$ (G = CH$_2$, O, S, NH). The half reactions are (a) p-Y–C$_6$H$_4$G–H → H–C$_6$H$_4$G–H and (b) H–C$_6$H$_4$–H → Y–C$_6$H$_4$–H. Half reaction (a) reflects the difference in benzylic BDE[G–H], under the perturbing influence of Y through –C$_6$H$_4$G–, relative to Y = H. Half reaction (b) reflects the difference in the stability of the aromatic ring under the perturbing influence of Y. The two half reactions are not related. The "spacers" between Y–(spacer)–H and H–(spacer)–H are not the same. In half reaction (a) the spacer is –C$_6$H$_4$G–, and in half reaction (b) it is –C$_6$H$_4$–.

The effect of using reaction 3′, instead of 3, to calculate MSE is demonstrated by examining the very detailed and meticulously presented results of calculations of Pratt et al.[9e] pertaining to a large variety of anilines. Values from their Supporting Information allow the calculation of MSE effects in the quasibenzylic bonds of p-YC$_6$H$_4$NH–CH$_3$ and of p-YC$_6$H$_4$NH–F. Calculating according to the form of reaction 3′, as Pratt does (H–C$_6$H$_4$-NH–X + Y–C$_6$H$_4$–H → Y–C$_6$H$_4$NH–X + H–C$_6$H$_4$–H), yields MSE $= -1.35 - 2.71\sigma^+$ for the N–C bonds and MSE $= -0.65 - 0.69\sigma^+$ for the N–F bonds, as shown in Figure 10a. These results force the conclusion that both the *direction* and *magnitude* of the dipole of the bond being broken do not affect MSE. If they did, (a) the slopes would be in *opposite* directions because of the opposite directions of the dipoles of N←C and of N→F and (b) MSE[N–F] would be *more sensitive* to remote Y-substituent effects (greater absolute value of the slope) because of the greater electronegativity difference of N–F vs N–C, respectively about 1.0 and 0.5 Pauling units for the elements. Neither (a) nor (b) are so. However, calculating MSE according to the form of reaction 3, Y–C$_6$H$_4$NH–X + H–C$_6$H$_4$NH–H → Y–C$_6$H$_4$NH–H + H–C$_6$H$_4$NH–X, we obtain MSE $= 0.40 + 0.37\sigma^+$ for the N–C bonds and MSE $= -0.78 - 1.57\sigma^+$ for N–F as shown in Figure 10b. Now, (a) the slopes are in opposite directions, each consistent with the direction of the dipole, and (b) MSE[N–F] values are 4.2 times more sensitive to Y-substituent effects than those of MSE[N–C]. This ratio of the absolute values of the slopes is almost exactly what is expected from the electronegativity differences because their effects on bond energies are proportional to the square of such differences, $1.0^2/0.5^2 = 4.0$ according to Pauling's electronegativity equation.[26] Use of the form of the isodesmic reaction 3 supports the proposals[11a,17] that *the direction and magnitude of the dipole of the bonds being broken*

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(31) For recent leading references, see: (a) Fishtik, I.; Datta, R. *J. Phys. Chem. A* **2004**, *107*, 10471–10476. (b) Rogers, D. W.; Zavitsas, A. A.; Matsunaga, N. *J. Phys. Chem. A* **2005**, *109*, 9169–9173.

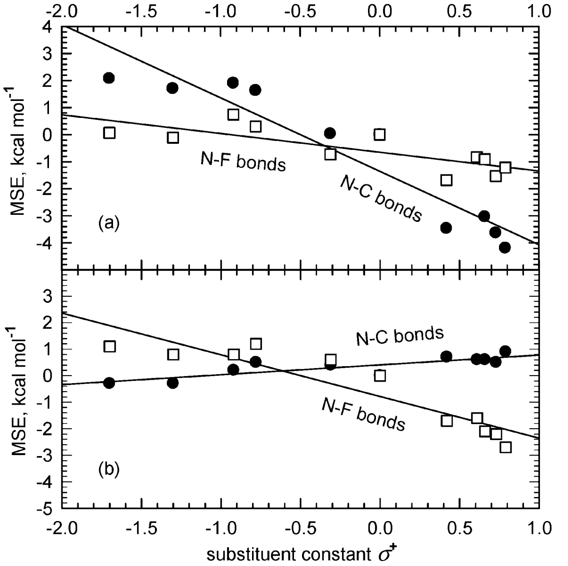

FIGURE 10. Plot of p-$YC_6H_4NH-CH_3$ and of p-YC_6H_4NH-F molecule stabilization energies vs σ^+ substituent constants. Panel (a) calculated by a form of reaction 3′ (see text) and panel (b) by reaction 3. Filled circles are p-$YC_6H_4NHCH_3$; open squares are p-YC_6H_4NHF.

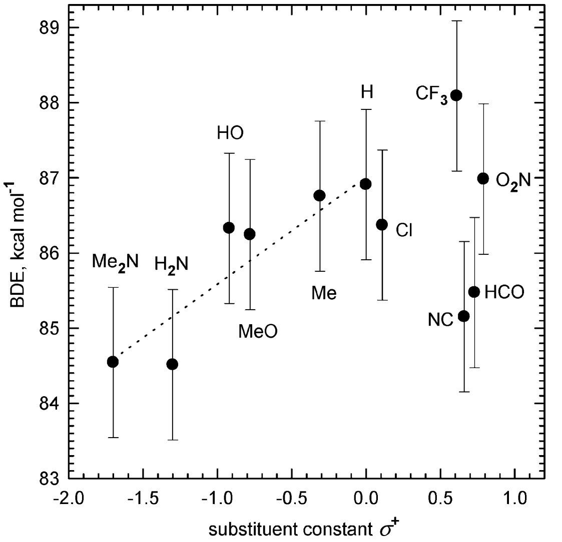

FIGURE 11. Plot of $YCH=CHCH_2-H$ bond dissociation energies vs σ^+ substituent constants. Error bars indicate estimated uncertainty as ± 1 kcal mol^{-1}.

affect MSE. The deceptive isodesmic reaction 3′ leads to wrong conclusions about the causes of substituent effects.

RSE values have also been calculated by the form of the isodesmic reaction 4′, and the results are different from those obtained from reaction 4, as is required from $\Delta BDE = MSE - RSE$.

$$YCH=CHCH_2^{\bullet} + CH_2=CH_2 \rightarrow CH_2=CHCH_2^{\bullet} + YCH=CH_2 \quad (4')$$

RSE values obtained by isodesmic reactions equivalent to those of 4′ are invalid in view of the above problems of MSE obtained from reactions of the form of 3′ and the requirement that $\Delta BDE = MSE - RSE$.

BDE[$YCH=CHCH_2-H$] values are obtained unequivocally from the enthalpy of reaction 5. The results are shown in Figure 11,[32] plotted vs σ^+.

$$YCH=CHCH_2-H \rightarrow YCH=CHCH_2^{\bullet} + H^{\bullet} \qquad (5)$$

$Y = CH_2=CH-$ is not included because of its effect of stabilization by extended conjugation of the odd electron. The BDE values and trends are similar to some reported from other calculations for toluenes[22a] and for $YC_6H_4SiH_2-H$.[13] Consistent with these results, we have reported that substituent effects on BDE of benzyl C−H are relatively small, as measured experimentally by reversible bromination studies of some substituted toluenes.[7b]

There is significant scatter in Figure 11 because MSE effects would be small due to the small C−H electronegativity difference and RSE effects are scattered (Table 2), but generally stabilizing the radical except for Y = CF_3. MSE for $YCH=CHCH_3$ cannot be obtained by reaction 3, because this is the reference compound in half reaction 3(a) and an identity expression is obtained.[33] The C←H dipole is $^{\delta-}C-H^{\delta+}$, and electron-donating substituents should destabilize the molecule by further increasing electron density on carbon and, thus, decreasing BDE[C−H]. Accordingly, MSE and RSE effects would be in the same direction for electron donors and in opposite directions for electron-withdrawing groups, again with the exception of CF_3. Figure 11 shows a fairly monotonic increase for electron-donating substituents from Me_2N to H (negative σ^+ domain, electron donors) and rather scattered values for the electron-withdrawing groups from H to O_2N (positive σ^+), where RSE effects would overwhelm the small MSE effects.[34] The greatest ΔBDE is between Y = $(CH_3)_2N$ and CF_3, the latter being 3.6 kcal mol^{-1} stronger.

With quasibenzylic compounds such as ArNH−H and ArO−H, the resonance stabilization enthalpy of the radicals formed on loss of the quasibenzylic hydrogen has been found to play a much greater role in affecting BDE than RSE effects do for $ArCH_2-H$ bonds and $ArSiH_2-H$ bonds. Our general understanding of substituent effects on bond dissociation energies has been enhanced greatly by the proposal that, in quasi-benzylic radicals $ArG^{\bullet}$, the shorter the bond length between Ar and G$\cdot$ the greater the interaction of the unpaired electron orbital with the ring.[22] The bond length in phenol is r_e[C−O] = 1.364 Å, in aniline r_e[C−N] = 1.431 Å, and in toluene r_e[C−C] = 1.524 Å. Thus, in phenols RSE effects make the major contribution to ΔBDE, in anilines RSE and MSE effects make about equal contributions, and in toluenes RSE effects are small. Phenols show the largest BDE changes, anilines somewhat smaller, and toluenes even smaller.[22]

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[32] The BDE values plotted in Figure 11 are (Y, BDE in kcal mol^{-1}): $(CH_3)_2N$, 84.54; H_2N, 84.51; HO, 86.38; CH_3O, 86.24; CH_3, 86.76; H, 86.91; Cl, 86.37, CF_3, 88.09; NC, 85.15; HCO, 85.47; O_2N, 86.98.

[33] A different reference reaction must be devised, something that we have been unable to do satisfactorily. However, Nau's approach[17d] of using Pauling's electronegativity equation would be applicable to species of types $YCH=CHCH_2X$ and of $YCH=CHCH_3$. The problem is that full G3 calculations on the needed symmetrical $YCH=CHCH_2CH_2CH=CHY$, or the vinylogues $YC_6H_4CH_2CH_2C_6H_4Y$, are currently too demanding.

[34] Good linearity with electron-donating groups and scatter with electron-withdrawing groups was also reported in plots of calculated by DFT (B3LYP functional) $\sigma^{\bullet}_{\alpha}$ vs σ^+ for para-substituted benzyl radicals, where $\sigma^{\bullet}_{\alpha}$ measures the substituent's ability to delocalize the odd electron: Singh, N. K.; Popelier, P. L. A.; O'Malley, P. J. *Chem. Phys. Lett.* **2006**, *426*, 219−221.

Method of Calculations

The calculations reported in Table 1 were carried out using the G3 model chemistry programmed in GAUSSIAN03. Input files were created using PCMODEL and their geometries were optimized in the MM3 force field, after which they were uploaded to the National Center for Supercomputing Applications host computer. Details of the options used, of the search for conformers, full references, and Cartesian coordinates of the compounds studied are given in the Supporting Information.

Conclusions

The effects of Y substituents on molecule stabilization energies of *trans*-YCH═CHCH$_2$F, as vinylogues of *p*-YC$_6$H$_4$-CH$_2$F, have been shown to be significant, decreasing by 4.2 kcal mol^{-1} from Y = (CH$_3$)$_2$N to O$_2$N, and correlate well with σ^+ substituent constants. Radical stabilization energies do not correlate with σ^+. BDE[C−F] is affected by both MSE and RSE and does not correlate well with substituent constants, but decreases by 4.1 kcal mol^{-1} between from Y = CH$_3$O to NC. We report results supporting proposals that the direction and magnitude of dipole of the allylic or benzylic bond cleaved are significant factors affecting stabilization of the parent molecule, contrary to previous conclusions.

BDE[YCH═CHCH$_2$−H] values are less sensitive to Y substituents because of the smaller dipole of C−H compared to C−F. Calculated BDE[C−H] does not change monotonically with electron donating or withdrawing abilities of the remote substituent. With Y = electron donating, MSE and RSE effects are in the same direction and BDE decreases as the electron-donating ability of Y increases. With Y = electron withdrawing, calculated BDE values are scattered because MSE and RSE effects are in opposite directions, except for CF$_3$, and are roughly of equal magnitude.

Acknowledgment. We acknowledge grants of computer time to D.W.R. from the National Science Foundation and the National Center for Supercomputing Applications.

Supporting Information Available: Details of the method of calculation and energies and geometries of the molecules studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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