Pergamon

Tetrahedron 54 (1998) 15445–15456

TETRAHEDRON

An AM1 MO Study of Bond Dissociation Energies in Substituted Benzene and Toluene Derivatives Relative to the Principle of Maximum Hardness

Gerritt P. Bean*

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

Received 26 February 1998; revised 9 September 1998; accepted 15 October 1998

Abstract. The heats of formation of a series of *m*- and *p*-substituted benzene and toluene derivatives, Ar-Y and $ArCH_2$-Y, and their phenyl or benzyl cations, anions, and radicals were calculated by the semiempirical AM1 MO method. Using this data and either the experimental values for the Y species or those obtained by the ab initio CBS-4 method, the heterolytic and homolytic bond dissociation energies (BDEs) were calculated along with the electron transfer energies for the ions. While the values of the homolytic BDEs were essentially independent of the ring substituents, a plot of the heterolytic BDEs versus the electron transfer energies gave a straight line of unit slope with an intercept at ΔH_{homo} thus confirming that $\Delta H_{het} = \Delta H_{ET} + \Delta H_{homo}$. Likewise, a plot of the appropriate HOMO or LUMO energies of the phenyl, benzyl, or Y ions versus ΔH_{het} gave a linear plot in agreement with the principle of maximum hardness. A positive charge adjacent to the bond being broken increases the ΔH_{homo} value while a negative charge decreases ΔH_{homo}.

Introduction.

Recently Parr and Arnett[1] have reported an investigation of the relationship between heterolytic and homolytic bond breaking in terms of the energy of electron transfer from the resulting ions to their radicals as measured by the reversible reduction potentials of the radicals. They noted that; 1) ΔH_{het} was related linearly to ΔG_{ET}, but 2) ΔH_{het} does not correlate with ΔH_{homo}, and 3) structural changes have a much smaller effect on ΔH_{homo} than on either ΔH_{het} or ΔG_{ET}. In this study they examined four systems; the reaction of the trityl ion with a variety of carbanions to form a C-C bond; the tropylium ion with nitranions to form C-N bonds; the trityl ion with phenoxide ions to form C- O bonds; and the perinaphthenium ion with thiophenoxide ions to form C-S bonds. For these cases, ΔH_{het} was equal to - ΔH_R, which had been measured calorimetrically for these reactions, while ΔH_{ET} was obtained from the reduction potentials of the ions involved. Because there is little change in entropy in the electron transfer process, $\Delta H_{ET} \approx \Delta G_{ET} = -23.06\ [\ E_{red}(R^+) - E_{red}(R\bullet)\ ]$. For each of these four systems, they found that the plots of ΔH_{het} versus ΔG_{ET} were linear with slopes of ~1 and $r^2 > 0.96$ (point 1 above). The intercepts of the plots were close to the values of ΔH_{homo}. Thus $\Delta H_{het} = \Delta H_{ET} + \Delta H_{homo}$. As indicated by point 2 above, there was no correlation between ΔH_{het} and ΔH_{homo}.

As Parr and Arnett pointed out, the energy of the electron transfer necessary to convert the ions into their radicals is determined by the HOMO-LUMO gap or, as Pearson would have expressed it, "the hardness".[2]

---

* bean@eefus.colorado.edu

0040-4020/98/$ - see front matter © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4020(98)00973-9

They used the following rationale to interpret these observations as a natural consequence of the "principle of maximum hardness".[3]

For the breaking of a C-Y bond, the relationship between ΔH for heterolytic and homolytic bond breaking and the energy of electron transfer, ΔH_{ET}, is given by the following thermocycle.[4]

$$\begin{array}{ll} \text{C-Y} \rightarrow \text{C}^+ + \text{Y}^- & \Delta H_{het} \\ \text{C}^+ + e^- \rightarrow \text{C}\bullet & \\ & -\Delta H_{ET} \\ \text{Y}^- \rightarrow \text{Y}\bullet + e^- & \\ \hline \text{C-Y} \rightarrow \text{C}\bullet + \text{Y}\bullet & \Delta H_{homo} \end{array}$$

Therefore,

$$\Delta H_{het} = \Delta H_{homo} + \Delta H_{ET} \qquad (1)$$

Because the values of ΔH_{homo} are generally found to be essentially constant, a plot of ΔH_{het} versus ΔH_{ET} would be expected to give a straight line of slope 1 and with the intercept equal to ΔH_{homo}. In addition, a plot of ΔH_{het} *versus* ΔH_{homo} should give a scattering of points. These are in agreement with Parr and Arnett's experimental observations.

Parr and Pearson's absolute hardness is [5]

$$\eta = (I - A) / 2 \qquad (2)$$

or in terms of the HOMO-LUMO gap, $\eta = (\varepsilon_{HOMO} - \varepsilon_{LUMO}) / 2$. For a heteronuclear C-Y bond

$$\eta = (I_{min} - A_{max}) / 2 \qquad (3)$$

where I_{min} is the smaller of the two ionization potentials and A_{max} is the maximum of the two electron affinities of C and Y. Thus for the heterolysis of the C-Y bond to C^+ and Y^-,

$$\Delta H_{ET} = I_Y - A_C = 2\,\eta \qquad (4)$$

and from equation 1,

$$\Delta H_{het} = 2\,\eta + \text{constant} \qquad (5)$$

In terms of the HOMO-LUMO gap,

$$\Delta H_{het} = (\text{HOMO}_Y - \text{LUMO}_C) + \text{constant} \qquad (6)$$

The larger the gap, the more difficult the heterolytic bond breaking becomes.

To examine the implications of these observations we have chosen to use the classic tool of physical organic chemistry, *i.e.*, the substituent effects of the derivatives of *m*- and *p*-substituted benzenes and toluenes. In this case we have used the semiempirical AM1 MO method[6] to investigate the heterolytic and homolytic bond breaking process for Ar-Y and $ArCH_2$-Y where Y is H, CH_3, HC≡C, CH_2=CH, NH_2, OH, F, or NO_2. Values of ΔH_{het}, for both the dissociation to C^+ and Y^- and to C^- and Y^+, and ΔH_{homo} for the radical dissociation were calculated from the heats of formation of the neutral molecules, their ions, and radicals. We also examined the relationship between ΔH_{het} and the HOMO and LUMO energies in terms of Parr and Pearson's hardness principle. In addition, we have considered the effect of charge on the bond breaking process and thus included Y = CH_2NH_2, $CH_2NH_3^+$, CH_2NH^-, CH_2OH, $CH_2OH_2^+$, and CH_2O^- for $ArCH_2$-Y. Recently ab initio calculations by Boyd *et al.* [7] have shown that in breaking the A-B bond in A-B-Z, the charge on Z has a dramatic effect on the bond dissociation energies (BDEs). For example, in CH_3CH_2Z where Z is successively changed from NH_3^+ to NH_2, to NH^-, the C-C BDEs decrease. Following the reasoning of Pauling, they have explained the change in bond strength as due to the change in electronegativity produced by the charges.[8]

Computational Methodology

The heats of formation of the neutral molecules, which we will symbolize as RY, and their anions, cations, and radicals (R^-, R^+, and $R^{\bullet}$) were calculated by the semiempirical AM1 MO method which directly provides heats of formation and has been shown to give reasonable values for neutral compounds, ions and radicals.[6] A representative set of *m*- and *p*-substituents on the aromatic ring and Y groups were chosen. The large number of compounds, ions, and radicals considered precluded the use of more sophisticated methods.[9] All of the calculations were made with the keyword PRECISE and full optimization of the geometry except keeping the ring planar.[10,11] The heats of formation of the neutral molecules are given in Table 1 while those of the benzyl and phenyl cations, anions, and radicals are given in Table 2. A plot of ΔH_f for either the substituted toluenes or phenyl compounds *versus* that of the benzyl or phenyl radicals gives straight lines of unit slope. A substituent on either the neutral compound or the radical produces the same change in their heats of formation. In contrast, plots of ΔH_f for the cations or anions do not correlate with each other or with the ΔH_f of either the neutral compounds or the radicals.[12] The AM1 heats of formation for the benzyl and phenyl radicals are 38.5 and 73.2 kcal/mol while their experimental values are 53.0 and 81.6, respectively.[13] Because the heats of formation of the benzyl and phenyl radicals parallel those of the $ArCH_2Y$ and ArY compounds (*i.e.*, unit slope), we have corrected the heats of formation of the benzyl and phenyl radicals by 14.5 (53.0 - 38.5) and 8.4 (81.6 - 73.2) kcal/mol, respectively.

The heats of formation of the Y species (Y^-, Y^+, or $Y^{\bullet}$) are either their experimental values or were calculated by the recently developed CBS-4 ab initio method which has been shown to give heats of formation within a few kcal/mol of the experimental values.[14] They and the AM1 heats of formation of the R^+, R^- and $R^{\bullet}$ species used in this study are given in Table 2.

Like the benzyl and phenyl ions, the heats of formation of the charged compounds, $ArCH_2$-Y, Y = CH_2NH^-, $CH_2NH_3^+$, CH_2O^- and $CH_2OH_2^+$, do not correlate with those of the neutral compounds. The heats of formation of those with a positive charge, Y = $CH_2NH_3^+$ and $CH_2OH_2^+$, do correlate with each other, as do those with negative charges, Y = CH_2NH^- and CH_2O^-; $r^2 < 0.999$ for either pair.

Table 1. AM1 Heats of Formation of the Substituted Benzenes and Toluenes Used in this Study (kcal/mol).

Heats of Formation for $ZC_6H_5CH_2Y$

Z	1 H	2 CH_3	3 NH_2	4 OH	5 F	6 NO_2	7 $CH_2NH_3^+$	8 CH_2NH_2	9 CH_2NH^-	10 $CH_2OH_2^+$	11 CH_2OH	12 CH_2O^-
H[a]	14.4	8.7	19.6	-30.5	-31.5	18.1	164.8	12.6	43.1	149.6	-38.1	-26.6
***p*-F**	-30.9	-36.7	-26.0	-76.4	-76.6	-28.2	121.6	-32.7	-5.2	106.6	-83.3	-74.8
***p*-CN**	45.5	39.8	50.8	0.43	0.4	49.4	199.3	43.9	66.7	185.7	-6.6	-2.0
***p*-Me**	6.8	1.1	11.8	-38.4	-39.8	8.8	156.6	5.0	35.6	141.2	-45.8	-34.1
***p*-OH**	-29.8	-35.6	-25.0	-75.5	-75.9	-27.9	120.5	-31.6	-1.7	105.2	-82.4	-71.4
***p*-CHO**	-16.8	-22.5	-11.5	-61.1	-62.0	-12.9	137.0	-18.4	5.4	122.2	-69.0	-63.3
***p*-NO_2**	17.3	11.5	22.5	-27.5	-27.3	24.0	175.8	15.7	37.1	161.4	-34.7	-35.1
***m*-F**	-30.9	-36.7	-25.3	-74.8	-76.3	-26.4	120.6	-32.7	-5.2	106.9	-83.3	-74.8
***m*-CN**	45.7	40.0	50.8	0.6	0.39	50.3	200.1	44.0	68.9	185.3	-6.6	-0.5
***m*-Me**	6.9	1.1	11.8	-38.8	-39.1	9.0	156.7	5.0	35.8	141.4	-45.7	-34.0
***m*-OH**	-29.8	-35.6	-24.6	-74.5	-75.5	-26.9	120.7	-31.6	-3.1	105.5	-82.2	-72.8
***m*-CHO**	-16.5	-22.3	-11.7	-61.9	-62.1	-13.6	134.2	-18.4	7.5	120.4	-68.9	-63.1
***m*-NO_2**	17.5	11.8	22.8	-27.4	-27.4	22.1	173.2	15.8	37.1	160.1	-34.5	-32.2

[a] Experimental ΔH_f of **1**, **2**, **3**, and **4** are 12.1, 7.1, 21.0, and -24.0 kcal/mol. Pedley, J. B., Naylor, R. D., Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed., Chapman and Hall, New York, 1986.

Heats of Formation for ZC_6H_5Y

Z	13 H	14 NH_2	15 OH	16 F	17 NO_2	18 $CH{\equiv}C$	19 $CH_2{=}CH$
H[b]	22.0	20.7	-22.2	-23.3	25.3	76.5[c]	38.7
***p*-F**	-23.3	-24.3	-67.3	-68.0	-19.1	31.3	-6.7
***p*-CN**	53.4	51.2	8.8	8.6	59.2	108.2	70.0
***p*-Me**	14.4	13.1	-29.8	-31.0	17.3	68.8	31.0
***p*-OH**	-22.2	-22.7	-65.7	-67.1	-19.6	32.1	-5.7
***p*-CHO**	-8.9	-11.7	-53.9	-54.1	-3.5	45.8	7.7
***p*-NO_2**	25.3	21.7	-19.6	-19.1	33.3	80.4	41.9
***m*-F**	-23.3	-24.8	-67.3	-67.9	-17.8	31.8	-6.4
***m*-CN**	53.4	52.2	9.9	9.3	59.2	108.3	70.2
***m*-Me**	14.4	13.2	-29.8	-30.9	17.6	69.0	31.2
***m*-OH**	-22.2	-23.9	-66.8	-67.5	-18.0	32.6	-5.4
***m*-CHO**	-8.9	-10.1	-52.5	-53.4	-4.3	45.8	7.8
***m*-NO_2**	25.3	24.3	-17.4	-17.8	33.1	80.6	42.1

[b] Experimental ΔH_f for **13 - 17**, and **19** are 19.7, 20.8, -23.0, -27.8, 16.1, and 35.3 kcal/mol. See reference above. [c] Experimental ΔH_f for **18** is 78.3 kcal/mol. Yaws, C. L. *Thermodynamic and Physical Property Data*, Gulf Publisher Co., Houston, 1992.

Table 2. Heats of Formation of the Ions and Radicals Used in This Study (kcal/mol).

CBS-4 or Experimental Heats of Formation of Y Species^{a}

	H	CH_3	CH_2CH_3	NH_2	OH	F	NO_2	HC≡C	CH_2=CH	CH_2NO_2	CH_2F
Cation	367.2^{b}	261.3^{b}	**227.7**	302^{b}	309^{b}	420.7^{b}	233^{b}	405.1^{b}	266^{b}	**305.1**	199^{b}
Anion	33.2^{b}	33.2^{b}	35.1^{b}	27.3^{b}	-32.8^{b}	-59.3^{b}	-45^{b}	66.8^{b}	56.2^{b}	27.3^{b}	**3.1**
Radical	52.1^{b}	35.0^{b}	28.9^{b}	45.1^{b}	9.4^{b}	19.0^{b}	7.9^{b}	135.1^{b}	71.6^{b}	**36.2**	**-8**^{b}

CBS-4 or Experimental Heats of Formation of Charged Y species

	$CH_2NH_3^+$	CH_2NH_2	CH_2NH^-	$CH_2OH_2^+$	CH_2OH	CH_2O^-
Cation	**581.5**	**184.3**	**23.5**	**569.6**	**175.0**	-26.0^{b}
Anion	**73.6**	**49.0**	**206.5**	**40.4**	**4.8**	**153.9**
Radical	**207.1**	**38.1**	**50.4**	**202.3**	**-2.5**	**-9.4**

AM1 Heats of Formation of $ZC_6H_5CH_2$ Species

Z	Cation	Anion	Radical^{c}
H	222.1	20.8	53.1 (38.5)
***p*-F**	177.7	-30.5	6.7 (-7.8)
***p*-CN**	262.3	33.8	84.1 (69.6)
***p*-Me**	209.8	12.2	45.0 (30.5)
***p*-OH**	169.9	-25.4	8.0 (-6.5)
***p*-CHO**	198.6	-28.8	22.0 (7.5)
***p*-NO_2**	244.1	-7.5	56.4 (41.9)
***m*-F**	184.0	-31.3	7.4 (-7.1)
***m*-CN**	262.0	41.2	84.1 (69.6)
***m*-Me**	213.3	13.5	45.3 (30.8)
***m*-OH**	181.2	-27.2	8.6 (-5.8)
***m*-CHO**	196.1	-17.8	22.3 (7.8)
***m*-NO_2**	240.5	5.8	56.9 (42.3)

AM1 Heats of Formation of ZC_6H_4 Species

Z	Cation	Anion	Radical^{c}
H	283.7	57.4	81.6 (73.2)
***p*-F**	246.3	5.8	36.3 (27.9)
***p*-CN**	325.6	74.8	113.3 (104.9)
***p*-Me**	274.3	49.5	73.9 (65.5)
***p*-OH**	241.5	11.1	37.4 (29.0)
***p*-CHO**	259.6	14.2	50.9 (42.5)
***p*-NO_2**	306.6	37.0	85.8 (77.4)
***m*-F**	246.1	4.5	36.1 (27.7)
***m*-CN**	326.0	75.9	113.5 (105.1)
***m*-Me**	273.6	49.5	73.7 (65.3)
***m*-OH**	241.5	8.6	37.2 (28.8)
***m*-CHO**	258.5	16.2	51.1 (42.7)
***m*-NO_2**	306.9	38.9	86.2 (77.8)

[a] CBS-4 values are in bold face. [b] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, H. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*. Suppl. 1. [c] Values in parentheses are the uncorrected heats of formation. See text

Results

Dissociation of Substituted Toluenes; C-H Bonds. The three processes considered for the substituted toluenes are their dissociation 1) to benzyl carbocations and hydride ions, ΔH_{het}^{+} (hydride ion affinities); 2) to benzyl anions and protons, ΔH_{het}^{-} (proton affinities); and 3) to benzyl and hydrogen radicals, the homolytic dissociation ΔH_{homo}. Table 3 lists the heats of dissociation, ΔH_{het}'s and ΔH_{homo}'s, electron transfer energies, ΔH_{ET}'s, and the HOMO and LUMO energies of the benzyl ions for the series of *m*- and *p*-substituted toluenes. The electron transfer energies were calculated for the processes, R^+ or R^- to $R^\bullet$ and H^+ or H^- to $H^\bullet$ by;

$$\Delta H_{ET}^{+} = [\Delta H_f\ R^\bullet) - \Delta H_f\ (R^+)] + [\Delta H_f\ (H^\bullet) - \Delta H_f\ (H^-)] \qquad (7a)$$

and

$$\Delta H_{ET}^{-} = [\Delta H_f\ (R^\bullet) - \Delta H_f\ (R^-)] + [\Delta H_f\ (H^\bullet) - \Delta H_f\ (H^+)] \qquad (7b)$$

These electron transfer energies are also listed in Table 3. As predicted by equation 1, plots of ΔH_{het}^{+} and ΔH_{het}^{-}, respectively *versus* the electron transfer energies, ΔH_{ET}^{+} and ΔH_{ET}^{-} give straight lines with unit slope, $r^2 > 0.998$. Slight variations in the ΔH_{het} values make the long extrapolation to the intercept less accurate. However, the average of the intercept values is close to the average of the ΔH_{homo} values. For the substituted toluenes, the intercepts are 83.0 and 99.7 kcal/mol, respectively. The average of these values, 91.4, is near the average of 90.6 kcal/mol for values of ΔH_{homo}. The experimental BDE for toluene is 89.9 ± 1.5 kcal/mol.[15]

Table 3. AM1 Heats of Dissociation and Electron Transfer and HOMO-LUMO's for Breaking C-H Bonds in Substituted Toluenes (kcal/mol).[a]

						HOMO[b]		LUMO[b]	
Substituent	ΔH_{het}^{+}	ΔH_{het}^{-}	ΔH_{homo}	ΔH_{ET}^{+}	ΔH_{ET}^{-}	**Cation**	**Anion**	**Cation**	**Anion**
H	241.0	373.6	90.7	-150.2	-282.8	-14.958	-1.650	-7.087	5.893
***p*-F**	241.9	367.7	89.7	-152.1	-278.0	-15.278	-1.861	-7.151	5.551
***p*-CN**	250.0	355.5	90.7	-159.3	-264.8	-15.206	-2.516	-7.442	4.931
***p*-Me**	236.3	372.6	90.3	-146.0	-282.3	-14.874	-1.715	-6.844	5.852
***p*-OH**	232.9	371.6	89.9	-143.0	-281.7	-14.730	-1.645	-6.689	5.600
***p*-CHO**	248.6	355.2	90.9	-157.7	-264.3	-14.907	-2.591	-7.364	4.642
***p*-NO_2**	260.1	342.5	91.3	-168.8	-251.2	-15.451	-3.177	-7.839	3.973
***m*-F**	248.1	366.8	90.5	-157.7	-276.4	-14.686	-1.974	-7.375	5.530
***m*-CN**	249.5	362.8	90.5	-159.0	-272.3	-14.952	-2.205	-7.388	4.486
***m*-Me**	239.7	373.8	90.6	-149.1	-283.2	-14.404	-1.675	-6.998	5.743
***m*-OH**	244.2	369.8	90.6	-153.7	-279.3	-14.144	-1.866	-7.186	5.804
***m*-CHO**	245.8	365.9	91.0	-154.9	-275.0	-14.695	-2.062	-7.236	4.090
***m*-NO_2**	256.2	355.5	91.4	-164.8	-264.1	-15.631	-2.578	-7.649	3.870

[a] The values for ΔH_{het}^{+}, and ΔH_{het}^{-} were taken from reference 10. [b] HOMO and LUMO energies are in e.v..

In the case of heterolysis we are keeping Y, either a proton or hydride ion, constant, therefore their HOMO and LUMO energies are also constants. Therefore, we only need to consider the variation in the HOMO and LUMO energies of the benzyl cations or anions. For the dissociation of the substituted toluenes into benzyl cations and hydride ions, the lower HOMO will be that of the hydride ion (a constant) while the higher LUMO will be that of the benzyl cation. Conversely, for dissociation into benzyl anions and protons, there is only the HOMO of the benzyl anion to consider. The values of ΔH_{het}^{+} *versus* the LUMO energies of the benzyl cation and

ΔH_{het}^- *versus* the HOMO energies of the benzyl anions are linearly correlated with $r^2 > 0.99$. As expected from equation 1, linear relationships are also found for electron transfer energies *versus* the appropriate HOMO or LUMO energies.[16],[17]

Dissociation of Substituted Ethylbenzenes; C-C Bonds. The changes in enthalpy for the heterolytic and homolytic breaking of the benzyl bond in the substituted ethylbenzenes were determined in the same manner as for the toluenes. As was found for the toluenes, there is an excellent linear correlation of ΔH_{het} with ΔH_{ET} of unit slope; $r^2 > 0.998$. The intercepts for the dissociation of the ethylbenzenes to the benzyl cations and methyl anions and to the benzyl anions and methyl cations are 71.2 and 85.1 kcal/mol, respectively. The average of the intercept values, 78.2 kcal/mol, is again close to the average of the ΔH_{homo} values, 79.3 kcal/mol. See Table 4.

Table 4. Correlation of ΔH_{homo} with that Calculated from the Intercept of ΔH_{het} and ΔH_{ET} for Bond Breaking in $ArCH_2$-Y Systems.

	Y	Ave. ΔH_{homo}	ΔH_{homo} from Intercept of ΔH_{het} and ΔH_{ET}[a]		
			From ΔH_{het}^+	From ΔH_{het}^-	Average
1	**H**	90.6 ± 0.5[b]	83.0 ± 0.3 (0.998)	99.7 ± 0.4 (0.999)	91.4
2	**CH_3**	79.2 ± 0.4	71.2 ± 0.3 (0.998)	85.1 ± 0.4 (0.999)	78.2
3	**NH_2**	78.5 ± 0.4	73.2 ± 0.3 (0.998)	84.2 ± 0.4 (0.999)	78.7
4	**OH**	92.9 ± 0.3	90.9 ± 0.6 (0.994)	97.5 ± 0.6 (0.997)	94.2
5	**F**	103.0 ± 0.4	105.3 ± 0.4 (0.997)	96.6 ± 0.4 (0.999)	101.0
6	**NO_2**	42.8 ± 1.1	57.8 ± 0.7 (0.989)	27.3 ± 0.8 (0.995)	42.6
7	**$CH_2NH_3^+$**	96.0 ± 2.4	107.0 ± 1.4 (0.942)	20.6 ± 1.1 (0.993)	-[c]
8	**CH_2NH_2**	81.2 ± 0.4	74.2 ± 0.3 (0.998)	83.7 ± 0.4 (0.998)	79.0
9	**CH_2NH^-**	66.7 ± 3.6	90.8 ± 1.5 (0.983)	42.0 ± 1.4 (0.959)	-[c]
10	**$CH_2OH_2^+$**	106.0 ± 2.7	110.4 ± 1.3 (0.938)	17.7 ± 1.1 (0.993)	-[c]
11	**CH_2OH**	90.6 ± 0.3	87.0 ± 0.3 (0.998)	92.2 ± 0.3 (0.999)	89.6
12	**CH_2O^-**	75.5 ± 3.4	96.9 ± 1.4 (0.984)	52.6 ± 1.2 (0.963)	-[c]

[a] r^2 values are in parentheses. [b] Experimental value of 89.9; reference 15. [c] Slope of line is not 1.00, see text.

Dissociation of Substituted Benzylamines, Benzyl Alcohols, Benzyl Fluorides, and α-Nitrotoluenes; C-N, C-O, C-F, and C-NO_2 Bonds. For breaking the benzyl bond to NH_2, OH and F in the substituted benzylamines, benzyl alcohols and benzyl fluorides the calculated homolytic BDEs increase with the electronegativity of the substituent; 78.5, 92.9, and 103.0 kcal/mol. The data are included in Table 4. However the CH_3 substituent has about the same BDE, 79.3 kcal/mol, as that produced by the more electronegative NH_2 group.[18] For substituted α-nitrotoluenes, ΔH_{homo} is only 42.8 kcal/mol due in part to the low heat of formation of the NO_2 radical produced in the bond breaking. This may also be due to systematic errors in ΔH_f's of the α-nitrotoluenes as calculated by the AM1 method. From the known ΔH_f's of nitromethane and nitrobenzene, the AM1 values are 8-9 kcal/mol too positive; thus the ΔH_{homo}'s for the α-nitrotoluenes are probably also too positive.

Dissociation of Substituted Ethylbenzene with Charged β-Substituents. To determine the effect of charged substituents on the energetics of the bond breaking processes, we examined the series; $ArCH_2$-CH_2Z, were Z was NH^-, NH_2, NH_3^+, O^-, OH, or OH_2^+. The data for these series are given in Table 4. Whereas a particular substituent has the same effect on the ΔH_f's of all the neutral compounds, this is not true for those compounds that carry a charge. Relative to the effect on the neutral compounds, electron-withdrawing substituents lower the heats of formation of those with a negative charge but raise the heats of formation for those with a positive charge. Therefore, electron-withdrawing substituents increase ΔH_{het} for the deprotonated phenethylamines and alcohols more than for the neutral molecules. Conversely they decrease ΔH_{het} for the protonated compounds.

(ΔH_{ET} values are unaffected by the charges.) Accordingly, the substituents cause some variation in the ΔH_{homo} values. More significant is that the plots of ΔH_{het} versus ΔH_{ET} are not of unit slope (~ 0.6 and ~ 1.4) and therefore the intercepts are far from the ΔH_{homo} value. The ΔH_{homo}'s increase, $R\text{-}CH_2Z^- < R\text{-}CH_2Z < R\text{-}CH_2Z^+$. Using the values for the unsubstituted compounds, the ΔH_{homo} increases by increments of about 18 kcal/mol, as the positive charge, and thus the electronegativity of Z, increases.[19] This is about the same incremental amount as found by Boyd, *et al.*, for $CH_3\text{-}CH_2Z$ where Z was NH^-, NH_2, NH_3^+, O^-, OH, and OH_2^+.[7b]

Dissociation of Phenyl-Y Bonds. The BDEs for breaking the bond between a substituted benzene ring and a H, CH_3, C_2H_5, $CH_2{=}CH$, $HC{\equiv}C$, NH_2, OH, F, or NO_2 group were determined from their heats of formation and the heats of formation of the substituted phenyl cations, anions, and radicals. Table 5. Their calculated heats of homolytic dissociation are 111.9, 102.8, 102.2, 114.7, 140.2, 106.2, 113.3, 123.0, and 63.0 kcal/mol, respectively; paralleling the results for breaking the benzyl bond.[20] The values for ΔH_{homo} for breaking the benzyl and phenyl bonds differ by ~ 25 kcal/mol regardless of the nature of Y.[21] The ΔH_{het}^+ values for the benzyl-Y and the phenyl-Y families differ by about 55 kcal/mol while ΔH_{het}^- values differ by about 30 kcal/mol (55 - 25). Values of ΔH_{homo} for the phenyl-CH_2Z bond breaking from the ΔH_f of the benzyl compounds where Z is NH_2, HO, F, and NO_2 are 103.4, 112.3, 105.0, and 100.1 kcal/mol; rather insensitive to the nature of Z due to the insulating effect of the CH_2 group. The data, along with experimental values, are also given in Table 5.[22] Except for the fluorobenzenes and nitrobenzenes there is a surprisingly good agreement with the experimental BDEs. For these series, the errors are due to systematic errors in the AM1 ΔH_f's for these compounds, which are 5-9 kcal/mol too positive. See Table 1.

Table 5. Correlation of ΔH_{homo} with that Calculated from the Intercept of ΔH_{het} and ΔH_{ET} for Bond Breaking in Ar -Y Systems.

				ΔH_{homo} from Intercept of ΔH_{het} and ΔH_{ET}		
	Y	**Ave. ΔH_{homo}**	**Exp. ΔH_{homo}[a]**	**From ΔH_{het}^+**	**From ΔH_{het}^-**	**Average**
1	**Me**	102.8 ± 0.6	104.2 ± 0.6	85.5 ± 0.3 (0.999)	116.6 ± 0.2 (0.999)	101.1
2	**CH_3CH_2**	102.2 ± 0.6	103.0 ± 0.8	85.6 ± 0.3 (0.999)	113.3 ± 0.2 (0.999)	99.5
3	**CH_2NH_2**	103.4 ± 0.6	-	89.5 ± 0.4 (0.997)	109.8 ± 0.4 (0.998)	99.7
4	**CH_2OH**	112.3 ± 0.7	101.0 ± 0.7	101.0 ± 0.7 (0.992)	119.2 ± 0.6 (0.994)	110.1
5	**CH_2F**	105.0 ± 0.3	-	103.9 ± 0.4 (0.997)	106.2 ± 0.4 (0.998)	105.1
6	**CH_2NO_2**	100.1 ± 1.0	-	113.0 ± 0.8 (0.983)	84.8 ± 0.9 (0.991)	98.9
13	**H**	111.9 ± 0.4	113.5 ± 0.6	97.9 ± 0.3 (0.998)	127.3 ± 0.3 (0.999)	112.6
14	**NH_2**	106.2 ± 0.7	105.5 ± 0.7	91.0 ± 0.6 (0.994)	126.5 ± 0.5 (0.997)	108.8
15	**OH**	113.3 ± 0.6	113.6 ± 0.6	105.8 ± 0.6 (0.993)	129.0 ± 0.5 (0.996)	117.2
16	**F**	123.0 ± 0.7	127.9 ± 0.7	125.1 ± 0.3 (0.998)	120.2 ± 0.3 (0.998)	122.7
17	**NO_2**	63.0 ± 1.3	73.0 ± 0.6	81.5 ± 1.1 (0.970)	42.9 ± 1.1 (0.987)	62.2
18	**$HC{\equiv}C$**	140.2 ± 0.4	-	136.5 ± 0.3 (0.998)	141.5 ± 0.3 (0.999)	139.1
19	**$CH_2{=}CH$**	114.7 ± 0.5	117.5 ± 1.1	102.4 ± 0.3 (0.998)	123.4 ± 0.3 (0.999)	112.9

[a] See reference 22.

Relationship between Hardness, HOMO-LUMO Gap, and Bond Dissociation Energies

As found by Parr and Arnett, the heats of reaction for the homolytic bond breaking are essentially insensitive to the substituents; *i.e.*, their electronic effect. On the other hand, the heats of heterolytic bond breaking vary according to the substituents as do the electron transfer energies. The relative heats of heterolytic bond breaking depend upon the HOMO-LUMO gap of the products; their "hardness" or the difficulty in transferring electrons. Plots of ΔH_{het}^+, or ΔH_{ET}^+, *versus* the LUMO energies of the resulting cations give a series of straight lines with the same slope. This is also true for ΔH_{het}^{-} or ΔH_{ET}^{-} and the HOMO energies of the resulting anions. Thus the substituents have the same relative effect on the HOMO-LUMO gap as on either the heterolytic bond breaking energies or the electron transfer energies. Substituents that increase the HOMO-LUMO gap, the hardness, increase the heterolytic BDEs and the electron transfer energies by the same amount. Plots of either ΔH_{het} or ΔH_{ET} of any series *versus* another series, *e.g.*, the toluenes *versus* the anilines, are linear with unit slope. (This is also seen in the heats of formation of the neutral compounds.) We have reported earlier that a plot of the hydride or proton affinities of substituted benzyl ions obtained from AM1 MO calculations *versus* the σ^{+} or σ^{-} values gave surprisingly good correlations; $r^2 > 0.88$.[10] Because the electron transfer energies and the HOMO and LUMO energies of the benzyl anions and cations correlate with their proton and hydride affinities it is not unexpected that there are similar correlations with the σ^{-} and σ^{+} values of the substituents ($r^2 > 0.92$ and 0.86, respectively). The LUMO energies of the Y^{+} species give a good linear relationship with the corresponding ΔH_{het}^{-} values as do the HOMO energies of the Y^{-}species versus ΔH_{het}^{+} for breaking either the benzyl- or phenyl-Y bond; $r^2 > 0.98$.[23] Thus, the magnitude of the HOMO-LUMO gap is proportional to the heterolytic BDEs. Arnett has suggested that "ionization potentials, electron affinities or redox potentials are just appropriate to use as are σ values".[1b,24] It can be seen that this can also be extended to include the HOMO-LUMO gap, or hardness.

As expected from equation 1, the homolytic BDEs are essentially insensitive to the ring substituents for the $ArCH_2$-Y and Ar-Y compounds. This is because the electronic effects of the substituents on the heats of formation of the neutral molecules, RY, and their radicals, $R^{\bullet}$, parallel each other. Because

$$\Delta H_{homo} = [\Delta H_f\,(R^{\bullet}) + \Delta H_f\,(Y^{\bullet})] - \Delta H_f\,(RY) \qquad (8a)$$

or rearranging as

$$\Delta H_{homo} = [\Delta H_f\,(R^{\bullet}) - \Delta H_f\,(RY)] + \Delta H_f\,(Y^{\bullet}) \qquad (8b)$$

the parallel changes in the ΔH_f of $R^{\bullet}$ and RY will cancel each other; and ΔH_{homo} will only depend upon the nature of Y.[25]

In breaking the bond to the phenyl or the benzyl group, the more electronegative the Y atom or group, the greater will be the heat of homolytic bond breaking. A more electronegative Y group decreases ΔH_{het}^{+} while increasing ΔH_{het}^{-}. The effect is opposite for the electron transfer energies, ΔH_{ET}^{+} and ΔH_{ET}^{-}.

Summary and Conclusions

The ΔH_{homo} and ΔH_{het} values for breaking the benzyl and phenyl bonds in a series of *m*- and *p*-substituted toluenes and benzenes, $ArCH_2$-Y and Ar-Y, were calculated from the heats of formation of the compounds and the resulting anions, cations, and radicals. Although the values for ΔH_{homo} remain essentially constant, regardless of the substituents, there is a linear relationship between the ΔH_{het} values and the electron transfer energies, ΔH_{ET}, for breaking either a benzyl or a phenyl bond. This substantiates Parr and Arnett's conclusion; $\Delta H_{het} = \Delta H_{homo} + \Delta H_{ET}$. Moreover, there is a linear dependence of ΔH_{het}^{+} with the LUMO energies of the benzyl or phenyl cations and with ΔH_{het}^{-} and the HOMO energies of the corresponding anions. In addition, the LUMO energies of the Y^+ species give a good linear relationship with the corresponding ΔH_{het}^- values, as do the HOMO energies of the Y^- species *versus* ΔH_{het}^+. The relationship between the HOMO-LUMO energy gap with ΔH_{het} and ΔH_{ET} for the bond breaking confirms that it is the hardness of the products, or the difficulty in transferring electrons, that is responsible for the heterolytic BDEs.

The ΔH_{homo} values remain constant regardless of the nature of the substituents because the parallel changes in the heats of formation of the compounds and their resulting radicals cancel each other. The homolytic BDEs increase with the electronegativity of the Y fragment.

The electronic effect of the substituents have the same relative effect on the HOMO-LUMO gap as on either the heterolytic bond breaking energies or the electron transfer energies. Because the electron transfer energies and the HOMO and LUMO energies of the benzyl anions and cations correlate with their proton and hydride affinities they also correlate with the σ^- and σ^+ values of the substituents ($r^2 > 0.92$ and 0.86, respectively). Thus, the magnitude of the HOMO-LUMO gap is proportional to the heterolytic BDEs.

In the case of breaking either the bond to the phenyl group or the benzyl bond, the more electronegative the Y atom or group, the greater the heat of homolytic bond breaking. A positive charge adjacent to the bond that is being broken increases the homolytic BDE while a negative charge decreases this BDE. Positive charges decrease ΔH_{het}^+ while increasing ΔH_{het}^- . The charges have a similar effect on the electron transfer energies, ΔH_{ET}^+ and ΔH_{ET}^-.

Acknowledgments. I am indebted to Drs. G. B. Ellison, C. H. DePuy, E. M. Arnett, and G. A. Petersson for their helpful comments. I also wish to thank the Department of Chemistry and Biochemistry, University of Colorado at Boulder, for the generous use of their computer facilities.

References and Notes

[1] (a) Chattaraj, P. K.; Cedillo, A.; Parr, R. G.; Arnett, E. M. *J. Org. Chem.*, **1995**, *60*, 4707.(b) Arnett, E. M.; Ludwig, R. T., *J. Am. Chem. Soc.* 1995, 117, 6627.

[2] Pearson, R. G., *J. Am. Chem. Soc.* **1963**, *85*, 3533; *ibid.*, **1986,** *108*, 6109.

[3] (a) Pearson, R. G., *Acc. Chem. Res.* **1993**, *26*, 250. (b) Parr, R. G.; Zhou, Z., *ibid.* **1993**, *26*, 256.

[4] (a) Brauman, J. I. "Frontiers of Free Radical Chemistry", W. A. Pryor, Ed., Academic Press, New York, 1980. (b) Bordwell, F. G.; Bausch, M. J., *J. Am. Chem. Soc.* **1986**, *108*, 1979. (c) Wayner, D. D. M.; Parker, V. D., *Acc. Chem. Res.* **1993**, *26*, 287.

[5] Parr, R. G; Pearson, R. G., *J. Am. Chem. Soc.* **1983**, *105*, 7512.

[6] Dewar, M. J. S.; Zoebisch, E. G; Healy, E. F. Stewart, J. J. P., *J. Am. Chem. Soc.* 1985, 107, 3092.

[7] (a) Boyd, R. J.; Glover, J. N. M.; Pincock, J. A; *J. Am. Chem. Soc.* **1989**, *111*, 5152, (b) Boyd, S. L.; Boyd, R. J.; Bessonette, P. W.; Kerdraon, D. L.; Aucoin, N., T., *ibid.* **1995**, *117*, 8816.

[8] Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed.; Cornell Univ. Press; Ithaca, NY, 1960.

[9] As was explained by Hehre, *et al.*, "Hartree-Fock theory with any basis set gives poor results for direct calculation of energy of homolytic dissociation process..", and electron correlation is necessary. Hehre, W. J.; Radom, L.; Schleyer, P. v.R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley; New York, 1986, p 273.

[10] The AM1 heats of formation of the substituted toluenes and the benzyl cations and anions along with their HOMO-LUMO energies were available from a previous study of their proton and hydride ion affinities; Bean, G. P. *J. Org. Chem.*, **1993**, *58*, 7336. For the *m*-HO and CHO compounds, the conformer with the lower energy was used.

[11] Stewart, J. J. P. QCPE no. 455, MOPAC, revision 6.

[12] Plots of ΔH_f for the anions or cations of the benzyl ions *versus* those of the phenyl ions separate the *meta* and *para* substituted families. As expected, NO_2, CN, and CHO groups at the *para* position of the benzyl anions have a much greater effect on the ΔH_f than they have in the phenyl ions.

[13] Berkowitz, J.; Ellison, G. B.; Gutmann, D., *J. Phys. Chem.* **1994**, *98*, 2744.

[14] (a) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B., *J. Am. Chem. Soc.* **1995**, *117*, 11299. (b) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., *J. Chem. Phys.* **1996**,*104*, 2598. (c) Gaussian 94, Revision C.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, J. A. K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh PA, 1995. (d) The heats of formation were corrected to 298 K.

[15] Ellison, G. B.; Davico, G. E.; Bierbaum, V. M.; DePuy, C. H. *Int. J. Mass Spectrom. Ion Processes* **1996**, *156*, 109.

[16] Vlasov and coworkers have recently reported a linear correlation between the gas phase pK_a 's of a series of alcohols and the HOMO energies, as calculated by the AM1 MO method, of their conjugate bases. Vlasov, V. M.; Koppel, I. A.; Burk, P.; Koppel, I., *J. Phys. Org. Chem.* **1995**, *8*, 364.

[17] We find similar relationships between the HOMO and LUMO energies of the phenoxy ions and the ΔH_{hst} values for the breaking of the O-H bond in substituted phenols although there is a greater variation (±4 kcal/mol) in the ΔH_{homo} values than found for the toluenes. It has been suggested that electron-withdrawing groups at the *para* position of the phenols increase the BDE by delocalizing the lone pair on the oxygen atom in the neutral phenol. Conversely, electron-donating groups stabilize the phenoxy radicals by increasing the spin delocalization and thus decreasing the BDE. See Brinck, T.; Haeberlein, M.; Jonsson, M. *J. Am. Chem. Soc.* **1997**, *119*, 4239; and references therein.

[18] The BDEs calculated by the CBS-Q method for the CH_3-Y compounds where Y is H, CH_3, NH_2, OH, F, and NO_2 are 103.6, 88.9, 83.7, 90.7, 108.4 and 57.7 kcal/mol, respectively; reference 14a. The ordering compares well to that observed here; 90.6, 79.2, 78.5, 92.9, 103.0, and 42.8 kcal/mol.

[19] Liu and Bordwell have estimated the gas phase BDEs for the H-B^+ bonds in the conjugate acids of several amines from their proton affinities and adiabatic ionization potentials. These are higher than the corresponding bonds in the neutral amines. Liu, W-Z.; Bordwell, F. G., *J. Org. Chem.* **1996**, *61*, 4778.

[20] The experimental BDE for benzene is 113.5 ± 0.5 kcal/mol. Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R., *J. Am. Chem. Soc.* **1995**, *117*, 2590.

[21] This difference results from the difference in the heats of formation of the benzyl and phenyl radicals, 81.6 and 53.0, Table 2.

[22] The experimental BDEs in Table 5 were calculated from the experimental heats of formation of Ar-Y, and the Ar and Y radicals. Data were provided by Dr. G. B. Ellison. Based on these values, the average error in our BDEs, using the adjusted ΔH_f's for the radicals, is 3.2 ± 3.6 kcal/mol.

[23] The LUMO and HOMO energies of the Y species were also obtained from AM1 MO calculations. They parallel the HOMO and LUMO energies from the CBS-4 calculations (3-21G* level).

[24] Wayner, *et al.*, have demonstrated that the oxidation and reduction potentials of substituted benzyl cations and anions give linear correlations with σ^+ and σ^-. Sims, B. A.; Milne, P. H.; Griller, D.; Wayner, D. D. M., *J. Am. Chem. Soc.* 1990, *112*, 6635.

[25] (a) Based on density functional MO calculations for *p*-substituted toluenes and their benzyl radicals, Wu *et al.*, have recently noted that whereas electron withdrawing substituents stabilize both the toluenes and benzyl radicals, electron donating groups destabilize the toluenes but stabilizes the radicals. Therefore [ΔH_f (R$^\bullet$) - ΔH_f (RY)] does not remain quite constant; however this effect is less than 2 kcal/mol. With the exception of the closely related ethylbenzenes, plots of ΔH_{homo} values for the substituted ArCH$_2$-Y and Ar-Y compounds *versus* the ΔH_{homo} values for the toluenes are random but within a range of less than 2 kcal/mol. Wu., Y-D.; Wong, C-L.; Chan, K. W. K.; Ji, G-Z.; Jiang, X-K., *J. Org. Chem.* 1996, *61*, 746. (b) Also see reference 4c and Suryan, M. M.; Stein, E. E., *J. Phys. Chem.* 1991, *83*, 777.