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Remote Substituent Effects on Homolytic Bond Dissociation Energies

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In the study we tried to answer two questions. First, does X-Z homolytic bond dissociation energy (BDE) of Y-C_6H_4-X-Z obey the Hammett relationship? Second, if it does what factors determine the magnitude and sign of the slope (ρ^+) of Hammett regression against substituent $\sigma_p{}^+$ constants? We collected a large number of X-Z BDEs for over one-thousand Y-C_6H_4-X-Z systems using the RMP2/6-311++G**// UB3LYP/6-31G* method. We found that remote substituent effects on X-Z BDEs are determined by both the ground effect (i.e. stabilization/destabilization of X-Z by the substituents) and the radical effect (i.e. stabilization/destabilization of $X^•$ by the substituents). The ground or radical effect is determined by the electron demand of X-Z or $X^•$ in the same way as the deprotonation enthalpy of HOOC-C_6H_4-X-Z or HOOC-C_6H_4-$X^•$ is affected by X-Z or $X^•$. As a result, ρ^+(BDE) for X-Z bond homolysis can be quantitatively predicted by using the change in deprotonation enthalpy from HOOC-C_6H_4-X-Z to HOOC-C_6H_4-$X^•$.

1. Introduction

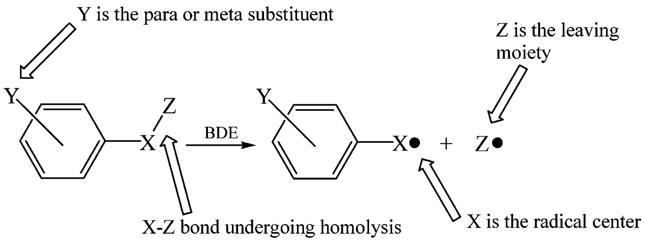
The Hammett relationship provides that the effect of a substituent on the property of an aromatic molecule is proportional to the effect of the same substituent on the acidity of benzoic acid.[1] It is an elegant model in chemistry. Using the Hammett relationship one can predict compound properties and understand reaction mechanisms efficiently.[2]

Nonetheless, application of the Hammett relationship to radicals has not been very successful. Two questions remain to be answered.[3−20] First, does the homolytic X-Z bond dissociation energy (BDE) of compound Y-C_6H_4-X-Z (Scheme 1) obey eq 1?

$$\mathrm{BDE}(\text{Y-C}_6\text{H}_4\text{-X-Z}) - \mathrm{BDE}(\text{C}_6\text{H}_5\text{-X-Z}) = \rho\sigma_Y \quad (1)$$

Second, if eq 1 is true, what factors determine the sign and magnitude of ρ?

SCHEME 1



Considerable effort has been devoted to the above two questions, but the answer remains unclear. In 1991, Wayner found that the para-substituent effect on C-Br BDEs of benzyl bromides is very different from the para-substituent effect on C-H BDEs of toluenes.[9a] However,

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(1) Hammett, L. P. *Chem. Rev.* **1935**, *17*, 225.

(2) (a) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd Ed.; Plenum Press: New York, 1990. (b) March, J. *Advanced Organic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1992.

(3) (a) Hansch, C.; Gao, H. *Chem. Rev.* **1997**, *97*, 2995. (b) Adams, W.; Harrer, H. M.; Kita, F.; Nau, W. M. *Adv. Photochem.* **1998**, *34*, 205. (c) Cherkasov, A. R.; Jonsson, M.; Galkin, V. I.; Cherkasov, R. A. *Usp. Khim.* **2001**, *70*, 3.

(4) (a) Mahoney, L. R.; DaRooge, M. A. *J. Am. Chem. Soc.* **1970**, *92*, 890. (b) Mahoney, L. R.; DaRooge, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 4722.

(5) Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390.

(6) (a) Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090. (b) Laarhoven, L. J. J.; Born, J. G. P.; Arends, I. W. C.; Mulder, P. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2307.

(7) (a) Suryan, M. M.; Kafafi, S. S.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 4594. (b) Suryan, M. M.; Stein, S. E. *J. Phys. Chem.* **1989**, *93*, 7362.

(8) (a) Lind, J.; Shen, X.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479. (b) Jonsson, M.; Lind, J.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1994**, *116*, 1423. (c) Jonsson, M.; Lind, J.; Merényi, G.; Eriksen, T. E. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2149. (d) Jonsson, M.; Lind, J.; Merényi, G.; Eriksen, T. E. *J. Chem. Soc., Perkin Trans. 2* **1995**, 61.

(9) (a) Clark, K. B.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1991**, *113*, 9363. (b) Wayner, D. D. M.; Sim, B. A.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 4853. (c) Wayner, D. D. M.; Lusztyk, E.; Ingold, K. U.; Mulder, P. *J. Org. Chem.* **1996**, *61*, 6430. (d) MacFaul, P. A.; Wayner, D. D. M.; Ingold, K. U. *J. Org. Chem.* **1997**, *62*, 3413.

(10) (a) Bordwell, F. G.; Cheng, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1736. (b) Zhang, X.-M.; Bordwell, F. G.; Bares, J. E.; Cheng, J.-P.; Petrie, B. C. *J. Org. Chem.* **1993**, *58*, 3051. (c) Bordwell, F. G.; Zhang, X.-M.; Satish, A. V.; Cheng, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 6605. (d) Bordwell, F. G.; Zhao, Y. Y.; Cheng, J. P. *J. Phys. Org. Chem.* **1998**, *11*, 10.

(11) (a) Lucarini, M.; Pedulli, G. F.; Cipollone, M. *J. Org. Chem.* **1994**, *59*, 5063. (b) Lucarini, M.; Pedrielli, G. F.; Pedulli, S.; Carbiddu, C.; Fattuoni, G. *J. Org. Chem.* **1996**, *61*, 9259. (c) Brigati, G.; Lucarini, M.; Mugnaini, V.; Pedulli, G. F. *J. Org. Chem.* **2002**, *67*, 4828.

(12) Fox, T.; Kollman, P. *J. Phys. Chem.* **1996**, *100*, 2950.

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

(14) (a) Wright, J. S.; Carpenter, D. J.; McKay, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1997**, *119*, 4245. (b) DiLabio, G. A.; Pratt, D. A.; LoFaro, A. D.; Wright, J. S. *J. Phys. Chem. A* **1999**, *103*, 1653.

(15) Brinck, T.; Haeberlein, M.; Jonsson, M. *J. Am. Chem. Soc.* **1997**, *119*, 4239.

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TABLE 1. ΔBDEs (kcal/mol) of X-H Bonds Calculated for 4-Y-C_6H_4-X-H

			X = NH		X = O				X = S	
Y	X = BH	X = CH_2	calcd	exptl[a]	calcd	exptl[a]	X = SiH_2	X = PH	calcd	exptl[b]
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_3	0.0	−0.3	−1.1	−1.0	−1.7	−1.6	0.0	−0.1	−0.7	−0.8
NH_2	0.0	−1.0	−4.2	−3.1	−6.5	−12.6	−0.1	−0.4	−2.0	−9.3
OH	0.1	−0.5	−2.7	-	−4.2	−8.2	−0.1	−0.1	−1.9	
F	0.2	0.1	−0.8	−0.9	−1.6		0.1	0.2	−0.8	
CN	0.2	0.1	2.0	2.8	1.8	4.6	0.0	−0.1	1.1	
NO_2	0.1	0.4	2.8	4.4	1.9	5.2	0.2	0.1	2.0	2.3

[a] Average value from refs 8 and 10. The values converted to 0 K, using the theoretical thermal corrections. [b] Value from ref 10.

Pratt found later that the para-substituent effect on C-Z BDEs of $PhCH_2$-Z (Z = H, F, Cl, Br) is roughly equal for each Z.[17a] Pratt also proposed that the effect of the remote substituent (Y) on X-Z BDEs of Y-C_6H_4-X-Z should be independent of Z.[17b] However, our recent studies showed that this proposal is not correct.[20]

Trying to get full answers for the above questions, we recently conducted systematic studies on the homolysis of Si-Z, P-Z, and N-Z bonds.[20] We originally thought each system should have its own pattern of substituent effects. However, we gradually learned that they actually have the same mechanism. Therefore, we decided that it is time to put all the systems together and perform a comprehensive study about the remote substituent effects on BDEs.

In the present study, we obtained X-Z BDEs of compounds 4-Y-C_6H_4-X-Z (Y = H, CH_3, F, OH, NH_2, CN, NO_2; X = BU, CHU, NU, O, SiHU, PU, S; U = H, CH_3, F, Li, NH_2, CN; Z = H, F, CH_3, Li).

Based on these data, we established a model that can be used to explain and to predict remote substituent effects on BDEs.

2. Method

The calculations were done with Gaussian 98.[21] The geometry of a neutral molecule or radical was optimized with the UB3LYP/6-31G* method. Each final structure was checked by UB3LYP/6-31G* frequency calculation to be a real minimum without any imaginary frequency. Radom et al. showed that UB3LYP/6-31G* optimization is adequate for benzenoid systems with approximately 10 heavy atoms.[22]

Single-point calculations were performed at the RMP2/6-311++G** level. The results were corrected by the zero-point energies calculated at the UB3LYP/6-31G* level scaled by 0.9806.[22] Therefore, the obtained BDEs correspond to the enthalpy changes of the reaction 4-Y-C_6H_4-X-Z → 4-Y-C_6H_4-$X^\bullet$ + $Z^\bullet$ in the gas phase at 0 K. Radom et al. showed that RMP2 is quite reliable in calculating relative BDE (i.e. ΔBDE), defined in eq 2.[22] Radom et al. also showed that temperature corrections are not necessary for the study of substituent effects on BDEs because they should show substantial cancellation.[22]

$$\Delta BDE_{X,Y,Z} = BDE(Y\text{-}C_6H_4\text{-}X\text{-}Z) - BDE\ (C_6H_5\text{-}X\text{-}Z) \quad (2)$$

We examined the remote substituent effect on BDEs by conducting Hammett regression between $\Delta BDE_{X,Y,Z}$ and substituent σ_p^+ constants[23] within this paradigm:

$$\Delta BDE_{X,Y(para),Z} = \rho^+ \sigma_p^+ \quad (3)$$

3. Observations

3.1. Y-C_6H_4-X-H Systems. X-H ΔBDEs of para-substituted Ph-BH-H, Ph-CH_2-H, Ph-NH-H, Ph-O-H, Ph-SiH_2-H, Ph-PH-H, and Ph-S-H are shown in Table 1. According to Table 1, theoretical ΔBDEs agree with experimental ΔBDEs for Ph-NH-H. However, for Ph-O-H or Ph-S-H the theoretical ΔBDEs are often smaller than the experimental values. As demonstrated before, this disagreement may be caused by the solvent effects in the experiment.[24] (Also see Appendix.) Therefore, we believe that the theoretical results are reliable.

According to Table 1 (also see Figure 1), the substituent effects on BDEs of Ph-BH-H, Ph-CH_2-H, Ph-SiH_2-H, and Ph-PH-H are small. In comparison, the substituent effects on BDEs of Ph-NH-H, Ph-O-H, and Ph-S-H are significant. For X-H ΔBDEs of Y-C_6H_4-X-H, ρ^+ (the unit

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(16) (a) Nau, W. M. *J. Org. Chem.* **1996**, *61*, 8312. (b) Nau, W. M. *J. Phys. Org. Chem.* **1997**, *10*, 445.

(17) (a) Pratt, D. A.; Wright, J. S.; Ingold, K. U. *J. Am. Chem. Soc.* **1999**, *121*, 4877. (b) Pratt; D. A.; de Heer, M. I.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 5518. (c) Pratt, D. A.; DiLabio, G. A.; Valgimigli, L.; Pedulli, G. F.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 11085.

(18) (a) Zhao, Y. Y.; Huan, Z. W.; Cheng, J.-P. *Acta Chim. Sin.* **1994**, *52*, 980. (b) Liu, B.; Huan, Z. W.; Cheng, J.-P. *Acta Chim. Sin.* **1997**, *55*, 123. (c) Cheng, J.-P.; Liu, B.; Lu, Y.; Mi, J. L.; Huan, Z. W. *Chem. J. Chin. Univ.* **1997**, *18*, 1080. (d) Cheng, J.-P.; Liu, B.; Zhao, Y.; Wen, Z.; Sun, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9987. (e) Wen, Z.; Li, Z.; Shang, Z.; Cheng, J.-P. *J. Org. Chem.* **2001**, *66*, 1466.

(19) Luo, Y.-R. *Int. J. Chem. Kinet.* **2002**, *34*, 453.

(20) (a) Fu, Y.; Lin, B.-L.; Song, K.-S.; Liu, L.; Guo, Q.-X. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1223. (b) Cheng, Y.-H.; Liu, L.; Song, K.-S.; Guo, Q.-X. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1406. (c) Cheng, Y.-H.; Fang, Y.; Zhao, X.; Liu, L.; Guo, Q.-X. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1715. (d) Cheng, Y.-H.; Zhao, X.; Song, K.-S.; Liu, L.; Guo, Q.-X. *J. Org. Chem.* **2002**, *67*, 6638. (e) Song, K.-S.; Liu, L.; Guo, Q.-X. *J. Org. Chem.* **2003**, *68*, 262.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(22) (a) Parkinson, C. J.; Mayer, P. M.; Radom, L. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2305. (b) Henry, D. J.; Parkinson, C. J.; Mayer, P. M.; Radom, L. *J. Phys. Chem. A* **2001**, *105*, 6750. (c) Also see our recent study on the choice of theoretical methods in the calculation of BDEs: Song, K.-S.; Cheng, Y.-H.; Fu, Y.; Liu, L.; Guo, Q.-X. *J. Phys. Chem. A* **2002**, *106*, 6651.

(23) (a) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979. (b) Hansch, C.; Leo, A. R.; Taft, W. *Chem. Rev.* **1991**, *91*, 165.

(24) Laarhoven, L. J. J.; Mulder, P.; Wayner, D. D. M. *Acc. Chem. Res.* **1999**, *32*, 342.

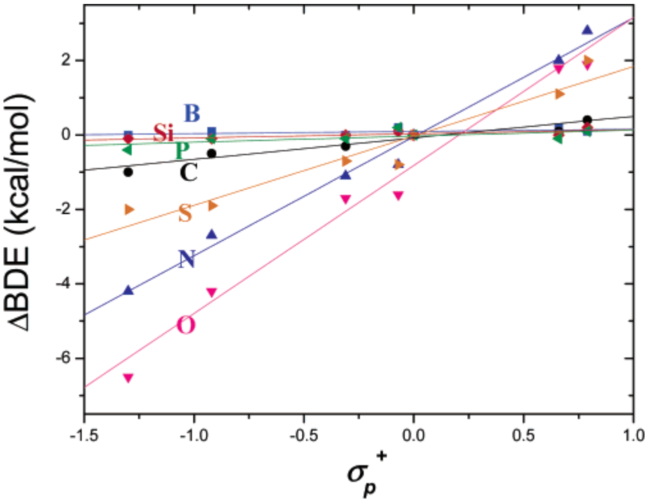

FIGURE 1. Hammett regression for the remote substituent on X-H BDEs of 4-Y-C_6H_4-X-H (X = BH, CH_2, NH, O, SiH_2, PH, and S).

TABLE 2. ρ^+ Values (kcal/mol) of Hammett Regression between ΔBDEs vs Substituent σ_p^+ Constants for X-Z Homolysis of 4-Y-C_6H_4-X-Z[a]

Z	X = BH	X = CH_2	X = NH	X = O	X = SiH_2	X = PH	X = S
H	0.0	0.6	3.2	4.0	0.1	0.2	1.9
CH_3	0.4	0.6	3.4	4.2	0.1	0.3	1.9
F	0.2	−0.2	1.7	1.2	−0.6	−0.8	1.5
Li	1.9	3.2	5.3	6.7	1.9	1.7	2.7

[a] The σ_p^+ constants are as follows: H (0.00), CH_3 (−0.31), NH_2 (−1.30), OH (−0.92), F (−0.07), CN (0.66), and NO_2 (0.79).

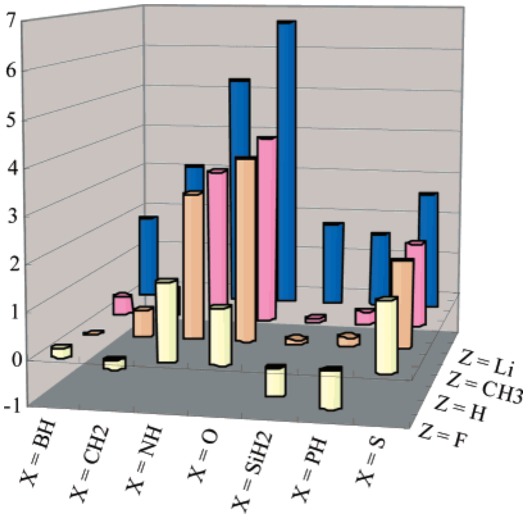

FIGURE 2. ρ^+ values of Hammett regression between ΔBDEs vs substituent σ_p^+ constants for X-Z homolysis of 4-Y-C_6H_4-X-Z (X = BH, CH_2, NH, O, SiH_2, PH, and S; Z = F, H, Me, and Li).

TABLE 3. ρ^+ Values (kcal/mol) of Hammett Regression between ΔBDEs vs the Substituent σ_p^+ Constants for X-Z Homolysis of 4-Y-C_6H_4-X-Z[a]

Z	X = BCH_3	X = $CHCH_3$	X = NCH_3	X = $SiHCH_3$	X = PCH_3
H	0.1	0.0	2.7	0.0	0.0
CH_3	0.5	0.4	2.6	0.1	0.1
F	0.2	−0.2	0.9	−0.3	−0.5
Li	2.1	3.4	4.7	1.6	2.2
Z	**X = BF**	**X = CHF**	**X = NF**	**X = SiHF**	**X = PF**
H	0.2	0.4	1.6	−0.2	−0.7
CH_3	0.5	−0.1	1.6	0.3	0.0
F	0.1	−0.7	0.9	−0.5	−1.3
Li	1.8	1.7	8.0	2.0	2.2
Z	**X = BLi**	**X = CHLi**	**X = NLi**	**X = SiHLi**	**X = PLi**
H	−2.9	−0.1	3.4	0.1	0.2
CH_3	−1.8	0.9	3.6	0.0	0.8
F	−2.5	−0.8	−6.8	−0.3	0.5
Li	2.5	2.8	5.1	1.3	1.7
Z	**X = BNH_2**	**X = $CHNH_2$**	**X = NNH_2**	**X = $SiHNH_2$**	**X = PNH_2**
H	−0.9	−1.3	0.9	−0.3	0.0
CH_3	−0.8	−1.3	0.8	−0.1	0.3
F	−0.9	−1.8	−0.6	−0.6	−0.5
Li	2.0	1.8	3.5	1.5	2.1
Z	**X = BCN**	**X = CHCN**	**X = NCN**	**X = SiHCN**	**X = PCN**
H	0.1	0.9	4.0	0.1	0.4
CH_3	0.6	1.1	4.2	0.4	0.5
F	0.5	−0.4	1.7	−0.4	−0.5
Li	1.9	3.1	5.7	2.0	1.8

[a] The σ_p^+ constants are as follows: H (0.00), CH_3 (−0.31), NH_2 (−1.30), OH (−0.92), F (−0.07), CN (0.66), and NO_2 (0.79).

for all ρ^+ in this paper is kcal/mol) increases in the order X = BH (0.0) < SiH_2 (0.1) < PH (0.2) < CH_2 (0.6) < S (1.9) < NH (3.2) < O (4.0).

3.2. Y-C_6H_4-X-Z Systems. Similarly we calculated ΔBDEs associated with X-CH_3, X-Li, and X-F homolysis, where X = BH, CH_2, NH, O, SiH_2, PH, or S. Detailed results can be found in the Supporting Information. The results of Hammett regression are shown in Table 2.

According to Table 2 (also see Figure 2), the substituent effects on X-H and X-Me BDEs are almost identical. The substituent effect on X-F BDE, however, has a significantly lower ρ^+ than X-H. Case in point, ρ^+ for O-F BDE (1.2) is much smaller than ρ^+ for O-H BDE (4.0). CH_2-F, SiH_2-F, and PH-F BDEs even have negative ρ^+. In comparison, the substituent effect on X-Li BDE has dramatically higher ρ^+ than X-H. For example, ρ^+ for CH_2-Li BDE (3.2) is much higher than ρ^+ for CH_2-H BDE (0.6).

3.3. Effects of α-Substitution at X. For boranes, toluenes, anilines, silanes, and phosphines, we can change the α-substitution at X from H to another substituent (e.g. from 4-Y-C_6H_4-BH-Z to 4-Y-C_6H_4-BF-Z). The ρ^+ values after α-substitution exchange are shown in Table 3.

From Table 3 it can be seen that ρ^+ values remain almost unchanged when X = BH, CH_2, NH, SiH_2, and PH are changed to X = BCH_3, $CHCH_3$, NCH_3, $SiHCH_3$, and PCH_3. Therefore, replacement of α-H by α-CH_3 has little impact on the remote substituent effects on X-Z BDEs. A change from X = BH, CH_2, NH, SiH_2, and PH to X = BF, CHF, NF, SiHF, and PF does not significantly change the remote substituent effect on X-Z BDEs, either. However, a change from X = BH, CH_2, NH, SiH_2, and PH to X = BLi, CHLi, NLi, SiHLi, and PLi causes an irregular change of ρ^+.

A more interesting α-substituent effect is observed for NH_2 and CN α-substitution (Figure 3). For NH_2, a change from X = BH, CH_2, NH, SiH_2, and PH to X = BNH_2, $CHNH_2$, NNH_2, $SiHNH_2$, and PNH_2 is found to significantly lower ρ^+. For example, ρ^+ for C-H BDEs of 4-Y-

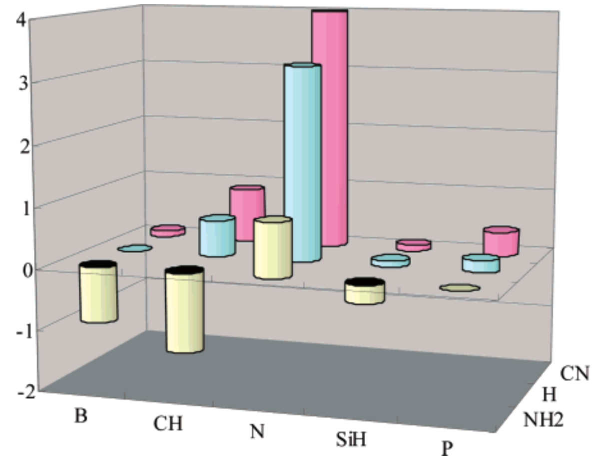

FIGURE 3. ρ^+ values of for X-H homolysis of 4-Y-C_6H_4-X-H. The front row is for X = BNH_2, $CHNH_2$, NNH_2, $SiHNH_2$, and PNH_2. The middle row is for X = BH, CH_2, NH, SiH_2, and PH. The back row is for X = BCN, CHCN, NCN, SiHCN, and PCN.

C_6H_4-CH_2-H is 0.6, whereas ρ^+ for C-H BDEs of 4-Y-C_6H_4-$CH(NH_2)$-H is −1.3. Also, ρ^+ for N-H BDEs of 4-Y-C_6H_4-NH-H is 3.2, whereas ρ^+ for N-H BDEs of 4-Y-C_6H_4-$N(NH_2)$-H is 0.9.

In comparison, a change from X = BH, CH_2, NH, SiH_2, and PH to X = BCN, CHCN, NCN, SiHCN, and PCN is found to result in a slight increase of ρ^+ for most cases. For example, ρ^+ for C-H BDEs of 4-Y-C_6H_4-CH_2-H is 0.6, whereas ρ^+ for C-H BDEs of 4-Y-C_6H_4-CH(CN)-H is 0.9. Also, ρ^+ for N-H BDEs of 4-Y-C_6H_4-NH-H is 3.2, whereas ρ^+ for N-H BDEs of 4-Y-C_6H_4-N(CN)-H is 4.0.

4. A Theoretical Model for the Remote Substituent Effects on BDEs

4.1. GE and RE. According to Section 3, most BDEs exhibit a good Hammett relationship. Both X and Z in Y-C_6H_4-X-Z affect ρ^+ values of the correlation. In addition, α-substitution at X exerts some influence on the remote substituent effects. At this point, we wish to establish a model to explain all the observations.

For this purpose, we separate the remote substituent effects on BDEs into the ground effect (GE) and radical effect (RE) (eqs 4 and 5).

$$\text{Y-}C_6H_4\text{-X-Z} + C_6H_6 \rightarrow \text{Y-}C_6H_5 + C_6H_5\text{-X-Z} \quad (4)$$

$$\text{Y-}C_6H_4\text{-X}^\bullet + C_6H_6 \rightarrow \text{Y-}C_6H_5 + C_6H_5\text{-X}^\bullet \quad (5)$$

According to eq 4, GE reflects the energetic effect of separating remote substituent (Y) from the intact X-Z moiety. According to eq 5, RE reflects the energetic effect of separating remote substituent (Y) from the radical center ($X^\bullet$).

We calculated GE and RE for each type of bond dissociation using the RMP2/6-311++G** method. We also conducted Hammett regression for every GE and RE against substituent σ_p^+ constants (Supporting Information). The results indicate that most GE and RE show a good Hammett relationship.

It should be noted that if GE or RE has a positive ρ^+, separating an electron-withdrawing group from X-Z or $X^\bullet$ is an energetically unfavorable process whereas separating an electron-donating group from X-Z or $X^\bullet$ is energetically favorable. On the other hand, if GE or RE has a negative ρ^+, separating an electron-withdrawing group from X-Z or $X^\bullet$ is energetically favorable whereas separating an electron-donating group from X-Z or $X^\bullet$ is energetically unfavorable.

It should also be noted that the subtraction of eq 5 from eq 4 gives eq 6.

$$\text{Y-}C_6H_4\text{-X-Z} + C_6H_5\text{-X}^\bullet \rightarrow \text{Y-}C_6H_4\text{-X}^\bullet + C_6H_5\text{-X-Z} \quad (6)$$

As a result, subtraction of ρ^+(RE) of Y-C_6H_4-$X^\bullet$ from ρ^+(GE) of Y-C_6H_4-X-Z gives ρ^+ for X-Z BDE of Y-C_6H_4-X-Z.

$$\rho^+(\text{BDE}) = \rho^+(\text{GE}) - \rho^+(\text{RE}) \quad (7)$$

4.2. Use of GE and RE To Explain BDE. Here we show an example of how to use GE and RE to explain the substituent effects on BDEs.

For the compounds 4-Y-C_6H_4-O-Z, ρ^+(GE) values of O-H, O-CH_3, O-F, and O-Li are +0.9, +1.1, -1.9, and +3.6. ρ^+(RE) of $O^\bullet$ is −3.1. Because ρ^+(GE) for O-H is positive, it is easier to separate O-H from electron-donating groups than from electron-withdrawing groups, due to the fact that O-H is an electron donor. On the other hand, because ρ^+(RE) for $O^\bullet$ is negative, it is easier to separate O-H from electron-withdrawing groups than from electron-donating groups, due to the fact that $O^\bullet$ is an electron acceptor. O-CH_3 has a higher ρ^+(GE) than O-H, because O-CH_3 is a better donor than O-H. O-Li has the highest ρ^+(GE) because O-Li is the best donor. O-F has a negative ρ^+(GE) so that O-F is an acceptor.

ρ^+(BDE)'s for O-H, O-CH_3, O-F, and O-Li are +4.0, +4.2, +1.2, and +6.7. These values are equivalent to the difference between ρ^+(GE) and ρ^+(RE). Therefore, O-Z BDEs show good Hammett relationships because $O^\bullet$ has a large negative ρ^+(RE). Different O-Z BDEs show dissimilar ρ^+ because of the different GE.

4.3. A Predictive Model for GE and RE. According to 4.2 ρ^+(GE) and ρ^+(RE) depend on the electron demand of the X-Z or $X^\bullet$ moiety. According to Hammett theory, the electron demand of a substituent can be quantitatively described by the electronic constants (e.g. σ_p) of the substituent. As a result, we hypothesize that ρ^+(GE) and ρ^+(RE) should have quantitative dependence on the σ_p constants of the X-Z or $X^\bullet$ moiety.

We found that there is a good correlation between ρ^+(GE) or ρ^+(RE) for X-Z or $X^\bullet$ and substituent σ_p constants of X-Z or $X^\bullet$ (Figure 4). Therefore, ρ^+(GE) or ρ^+(RE) are dictated by the electron demand of the X-Z or $X^\bullet$ moiety in the same way as the acidity of HOOC-C_6H_4-X-Z or HOOC-C_6H_4-$X^\bullet$ is affected by X-Z or $X^\bullet$.

Because σ_p constants are not available for many X-Z or $X^\bullet$ moieties, we sought to use the gas-phase deprotonation enthalpy (ΔH_{dep}) of HOOC-C_6H_4-X-Z or HOOC-C_6H_4-$X^\bullet$ directly to predict ρ^+(GE) and ρ^+(RE). Therefore, we calculated the relative gas-phase deprotonation enthalpy ($\Delta\Delta H_{\text{dep}}$) of HOOC-$C_6H_4$-X-Z or HOOC-$C_6H_4$-$X^\bullet$

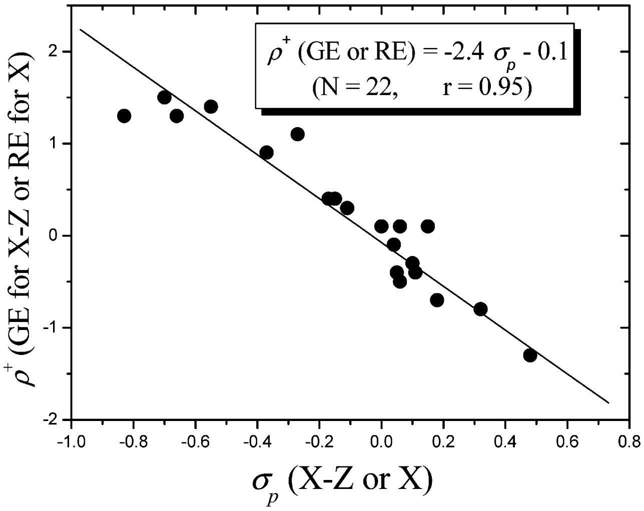

FIGURE 4. Correlation between ρ^+(GE) or ρ^+(RE) for X-Z or X$^\bullet$ and substituent σ_p constants for X-Z or X$^\bullet$. GE is the enthalpy changes for the reaction Y-C_6H_4-X-Z + C_6H_6 → Y-C_6H_5 + C_6H_5-X-Z. RE is the enthalpy changes for the reaction Y-C_6H_4-X$^\bullet$ + C_6H_6 → Y-C_6H_5 + C_6H_5-X$^\bullet$.

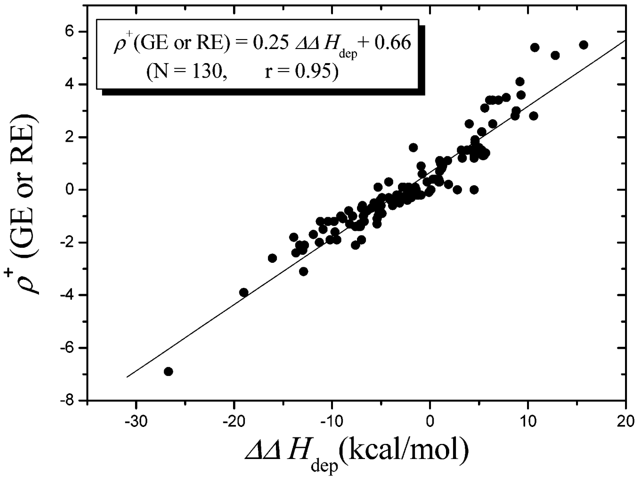

FIGURE 5. Correlation between ρ^+(GE) or ρ^+(RE) for X-Z or X$^\bullet$ and relative gas-phase deprotonation enthalpy ($\Delta\Delta H_{dep}$) for HOOC-C_6H_4-X-Z or HOOC-C_6H_4-X$^\bullet$.

(relative to benzoic acid) as the enthalpy changes of the following reactions (Supporting Information).

$$\text{HOOC-}C_6H_4\text{-X-Z} + {}^-\text{OOC-}C_6H_5 \rightarrow {}^-\text{OOC-}C_6H_4\text{-X-Z} + \text{HOOC-}C_6H_5 \quad (8)$$

$$\text{HOOC-}C_6H_4\text{-X}^\bullet + {}^-\text{OOC-}C_6H_5 \rightarrow {}^-\text{OOC-}C_6H_4\text{-X}^\bullet + \text{HOOC-}C_6H_5 \quad (9)$$

Correlation between ρ^+(GE) or ρ^+(RE) for X-Z or X$^\bullet$ and $\Delta\Delta H_{dep}$ for HOOC-C_6H_4-X-Z or HOOC-C_6H_4-X$^\bullet$ (Figure 5 and eq 11) is very good for 130 X-Z and X$^\bullet$ moieties. It indicates again that ρ^+(GE) or ρ^+(RE) are dictated by the electron demand of X-Z or X$^\bullet$ moiety in the same way as the acidity of HOOC-C_6H_4-X-Z or HOOC-C_6H_4-X$^\bullet$ is affected by X-Z or X$^\bullet$.

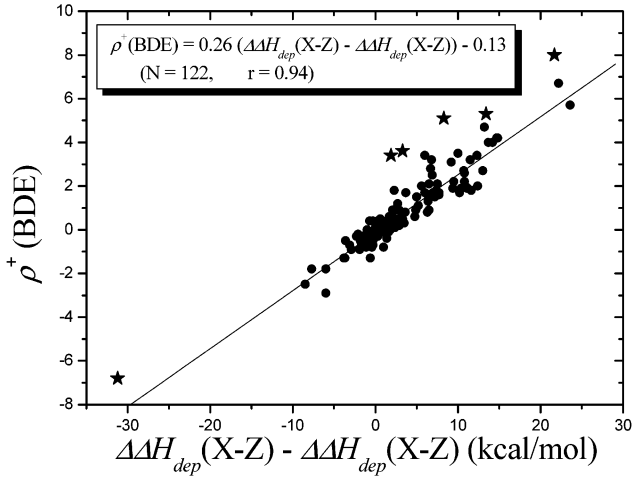

FIGURE 6. Correlation between ρ^+(BDE) for the X-Z bond and the change of $\Delta\Delta H_{dep}$ from HOOC-C_6H_4-X-Z to HOOC-C_6H_4-X$^\bullet$. The stars show significant deviation from the general trend. They are all for the Li compound.

$$\rho^+(\text{GE for X-Z or RE for X}^\bullet) = 0.25\Delta\Delta H_{dep}(\text{X-Z or X}^\bullet) + 0.66 \quad (10)$$

It should be noted that in order to know $\Delta\Delta H_{dep}$ we need to consider only one chemical reaction. However, to know ρ^+(GE) or ρ^+(RE) we need to consider a series of reactions with different substituents. Therefore, by correlating ρ^+(GE) or ρ^+(RE) with the electron demand of X-Z or X$^\bullet$ we provide a simple way to predict ρ^+(GE) and ρ^+(RE).

4.4. A Predictive Model for Remote Substituent Effects on BDEs. According to eq 7, if we can explain and predict ρ^+(GE) or ρ^+(RE), we should be able to explain and predict ρ^+(BDE). Indeed, correlation between ρ^+(BDE) for the X-Z bond and the change of $\Delta\Delta H_{dep}$ from HOOC-C_6H_4-X-Z to HOOC-C_6H_4-X$^\bullet$ is very good for our sample of 122 chemical bonds (Figure 6).

$$\rho^+(\text{BDE for X-Z}) = 0.26[\Delta\Delta H_{dep}(\text{X-Z}) - \Delta\Delta H_{dep}(\text{X}^\bullet)] - 0.13 \quad (11)$$

The slope of eq 11 (0.26) is almost the same as that of eq 10 (0.25), showing the reliability of the transformation in eq 7. Also, the positive slope for eq 11 means that an increase of acidity from HOOC-C_6H_4-X-Z to HOOC-C_6H_4-X$^\bullet$ causes a positive ρ^+(BDE) for X-Z homolysis, whereas a decrease of acidity from HOOC-C_6H_4-X-Z to HOOC-C_6H_4-X$^\bullet$ causes a negative ρ^+(BDE) for X-Z homolysis.

5. Summary

In the paper we presented a large number of theoretical data about the remote substituent effects on the BDEs of various chemical bonds. Hammett analyses were performed on all the BDEs, and a large number of ρ^+ values were obtained. It was found that ρ^+(BDE) for X-Z bond homolysis of Y-C_6H_4-X-Z can be quantitatively

TABLE 4. ΔBDEs of 4-HO-C_6H_4-OH, 4-NH_2-C_6H_4-OH, and 4-NH_2-C_6H_4-SH with UQCISD(T)/6-31+G* and CBS-4M Methods in a Vacuum (kcal/mol)

	RMP2/6-311++G**			UQCISD(T)/ 6-31+G(d)	CBS-4M	
compd	vacuum	acetonitrile	DMSO	vacuum	vacuum	exptl
C_6H_5-O(S)H	0.0	0.0	0.0	0.0	0.0	0.0
4-NH_2-C_6H_4-OH	−6.5	−10.4	−10.5	−6.4	−7.7	−12.3
4-HO-C_6H_4-OH	−4.2	−6.2	−6.3	−4.0	−3.4	−7.9
4-NH_2-C_6H_4-SH	−2.0	−5.2	−5.4	−2.2	−3.1	−9.2

predicted by using the change in acidity from HOOC-C_6H_4-X-Z to HOOC-C_6H_4-X•.

6. Appendix

We calculated ΔBDEs of 4-HO-C_6H_4-OH, 4-NH_2-C_6H_4-OH, and 4-NH_2-C_6H_4-SH using UQCISD(T)/6-31+G* and CBS-4M methods in a vacuum (see the Table 4) The results agree with RMP2/6-311++G** values in a vacuum. Therefore, the theoretical results at the RMP2 level are reliable. On the other hand, when we used the polarized continuum model (PCM) and RMP2/6-311++G** method to calculate ΔBDEs in acetonitrile and DMSO, we found that ΔBDEs in solution are significantly larger than those in a vacuum. This may explain why the experimental values are higher than theoretical ones.

It should be mentioned that BDEs are defined as enthalpy changes in the gas phase. Although Bordwell et al. has developed a solution-phase method for BDE measurements, this solution-phase approach often yielded inaccurate "experimental" BDEs because of the incomplete cancellation of the solvation effect.

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Supporting Information Available: Detailed relative bond dissociation energies and deprotonation enthalpies. This material is available free of charge via the Internet at http://pubs.acs.org.

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