

The Nonpolar Resonance Effects and the Non-Hammett Behaviors

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In the study we tried to unify the observed non-Hammett behaviors in various fields by proposing the nonpolar resonance effect. This effect was shown to be important not only for carbon radicals but also for some closed-shell systems. Therefore, the odd electron or spin is not the essential cause of the effect. The real origin of the non-Hammett effect should be the $\text{HOMO}_{\text{reaction-center}}\text{-LUMO}_{\text{acceptor}}$ and $\text{LUMO}_{\text{reaction-center}}\text{-HOMO}_{\text{donor}}$ interactions. This means that the nonpolar resonance effect is a universal effect. However, we found that the nonpolar resonance effect could not be well exhibited in many systems because of the serious competition from the polar Hammett effect. Finally, we showed that our proposal of the nonpolar resonance effect was valuable from a practical point of view, because using it we could perform much better correlation studies on some “tough” problems such as radical and multiple bond stabilities, UV and IR spectra, and molecular structures.

1. INTRODUCTION

The Hammett relationship occupies a central position in theoretical organic chemistry.¹ It was developed on the basis of the finding that a plot of $\log K_a$ for benzoic acid ionization against $\log k$ for ester hydrolysis over many substituents is fairly linear, which indicates that the substituents may exert a similar effect in quite different reactions.² Quantitatively, if we define $\log K_X/K_H = \sigma_X$, where σ_X is the substituent constant, we have

$$\log k_X/k_H = \rho \log K_X/K_H = \rho \sigma_X \quad (1)^3$$

A central concept to the Hammett relationship is the electronic demand, which remained fundamentally important in all of its later modified versions (i.e. introduction of the σ_X^+ and σ_X^- constants to accommodate the enhanced resonance). According to the concept, the substituent is either a donor or acceptor. Thus it either supplies or removes electrons from the reaction center, shifting the properties of a chemical system in opposite directions.⁵

However, sometimes both the donors and acceptors were found to shift the property of a system in the same direction, which then is called the non-Hammett behavior. Of course experimental errors may cause a non-Hammett behavior, which does not merit discussion. However, for many well-defined data like the UV frequencies of aromatic compounds,⁶ it remains necessary to get a clear understanding of the non-Hammett behavior.

Another notorious example for the non-Hammett behavior is the substituent effect on the radical stability. This problem was noticed 50 years ago⁷ and first discussed in depth by Streitwieser and Perrin.⁸ In 1966,⁹ Walter proposed that there should be two classes of radicals: class *O* (for opposite) for those exhibiting Hammett effects and class *S* (for same) for those displaying non-Hammett behaviors. Usually, the het-

eroatomic radicals (i.e. N, O, and S radicals) belong to class *O*. Since the carbon-centered radicals are believed to be stabilized by both the electron-donating and withdrawing substituents, they belong to class *S*.

Unlike the UV case where chemists gave up the correlation analysis, in radical chemistry a special scale of substituent constants (σ^\bullet) was purposely proposed to correlate the carbon radical stability.¹⁰ It is unclear whether the proposal of a special scale of constants for a fairly limited field is important. Nevertheless, so far quite a few scales of σ^\bullet constants have been developed, among which the Arnold's σ_A , Fisher's σ_F , Jackson's σ_J , Creary's σ_C , Jiang's σ_{IJ} , and Adam-Nau's ΔD scales are the most famous^{11,12} (Table 1).

In the present study we would like to do a systematic work on the non-Hammett behaviors. We wish to find a general mechanism for them. We also wish to find a good way to do correlation studies on them. The major questions interest us include the following: 1. Where can we see the non-Hammett behaviors? 2. Are the non-Hammett behaviors shown in different places independent of each other? 3. If not, do they have the same mechanism? 4. Can we define a scale of universal substituent constants to do correlation studies for the non-Hammett behaviors?

2. METHODS

All the calculations were done with GAUSSIAN 98.¹³ The molecules were fully optimized with B3LYP/6-31g(d) (or B3LYP/6-31+g(d)) method without any constraint. Each optimized structure was checked by the frequency calculation at B3LYP/6-31g(d) level to be a real minimum on the potential surface without any imaginary frequency. Total energies were then calculated at B3LYP/6-311++g(2d,2p) level and corrected with the B3LYP/6-31g(d) zero point energies scaled by 0.9806.¹⁴ It should be mentioned that all the substituents in this study are at the *para* position.

3. RESULTS AND DISCUSSION

3.1. The Stabilities of Benzyl Radicals Show Non-Hammett Behaviors. The isodesmic reactions (eq 2) can

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Table 1. Different Scales of *Para*-Substituent Constants^a

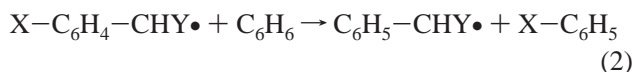
substituent	σ_p^a	σ_p^{+a}	σ_p^{-a}	F ^b	R ^b	σ_I^c	σ_R^{0c}	σ_R (BA) ^c	σ_F^d	σ_R^d	σ_{JJ}^d	σ_A^d	σ_F^d	σ_J^d	σ_C^d	ΔD^d
CH ₃	-0.17	-0.31	-0.17	-0.01	-0.41	-0.05	-0.10	-0.11	0.00	-0.08	0.15	0.015	-0.02	0.23	0.11	0.02
Cl	0.23	0.11	0.19	0.72	-0.24	0.47	-0.21	-0.23	0.45	-0.17	0.22	0.011	0.08	0.18	0.12	0.09
CN	0.66	0.66	1.00	0.90	0.71	0.52	0.14	0.13	0.60	0.10	0.42	0.040	0.34	0.63	0.46	0.54
COCH ₃	0.50		0.84	0.50	0.90	0.28	0.19	0.16	0.26	0.17	0.54	0.060	0.53	0.58		
COOH	0.45	0.42	0.77	0.44	0.66						0.38					
F	0.06	-0.07	-0.03	0.74	-0.60	0.51	-0.34	-0.45	0.44	-0.25	-0.02	-0.011	-0.25	-0.03	-0.08	-0.17
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.000	0.00	0.00	0.00	0.00
NO ₂	0.78	0.79	1.27	1.00	1.00	0.64	0.19	0.15	0.65	0.18	0.36		0.27	0.76	0.36	0.90
CONH ₂	0.36		0.61								0.38					
SCH ₃	0.00	-0.60	0.06	0.68	-1.30	0.19	-0.17	-0.32	0.25	-0.27	0.62			0.55	0.43	0.29 ^e
CF ₃	0.54	0.61	0.65	0.64	0.76	0.41	0.13	0.08	0.44	0.07	-0.01	-0.009		0.09	0.08	0.11
N(CH ₃) ₂	-0.83	-1.70	-0.12	0.69	-3.81	0.05	-0.52	-0.83	0.10	-0.64	1.00				0.90	0.32
COOMe	0.45	0.49	0.75			0.31	0.15	0.14	0.24	0.16	0.33	0.043		0.54	0.35	0.52
SiMe ₃	-0.07	0.02		-0.10	0.16				-0.02	0.02	0.31					

^a Values from Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. ^b Values from (a) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 4328. (b) Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492. ^c Values from ref 22. ^d Values from ref 11 and 12. Note that some of the original values in ref 12a were revised by the authors (Dust, J. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6531.). ^e Value for SET.

Table 2. Substituent Effects on the Energy Changes of the Isodesmic Reaction X-C₆H₄-CHY• + C₆H₆ → C₆H₅-CHY• + X-C₆H₅ Calculated Using B3LYP/6-311++G(2d,2p)//B3LYP/6-31+G(d) Method (kJ/mol)

substituent	Y = H	Y = F	Y = Cl	Y = Li
CH ₃	1.1	1.1	1.6	-1.2
Cl	1.2	0.2	0.3	5.4
CN	5.0	4.1	2.8	18.8
COCH ₃	6.1	6.0	4.8	16.5
COOH	5.2	5.5	4.1	15.3
F	-0.9	-2.1	-1.7	1.2
H	0.0	0.0	0.0	0.0
NO ₂	6.1	5.6	3.7	25.2
CONH ₂	3.7	3.4	2.5	12.4
SCH ₃	4.2	3.5	4.4	2.5
CF ₃	1.1	0.5	-0.3	11.4
N(CH ₃) ₂	5.6	5.0	7.4	-3.7
COOMe	4.3	4.7	3.6	12.3
SiMe ₃	2.0	2.1	2.2	2.5

be used to evaluate the substituent effect on the stability of a benzyl radical. The results are listed in Table 2.



According to Table 2, except for F all the substituents, either donors or acceptors, stabilize CH₂• because the separation of the substituent from CH₂• is energy-uphill. Thereby, the Hammett relationship cannot be used here, which is also reflected by the low correlation coefficients (0.24, -0.02, and 0.61) for the σ_p , σ_p^+ , or σ_p^- constants (Table 3). In comparison, when the σ^\bullet constants are used the correlation is significantly better. The small error bars (<15%) for the predicted regression slopes also indicate that the correlations are real.

Nevertheless, the σ_{JJ} and σ_F constants do not show good correlations. This can be attributed to the residue Hammett effects in the system.¹⁵ To separate the Hammett and non-Hammett effects we use both the Hammett and radical substituent effects in a double variable linear regression equation, i.e.

$$\text{substituent effect} = a_0 + a_1 \times \sigma_{\text{Hammett}} + a_2 \times \sigma^\bullet \quad (3)$$

Table 3. Regression of the Energy Changes of the Reaction X-C₆H₄-CH₂• + C₆H₆ → C₆H₅-CH₂• + X-C₆H₅ against Different Scales of Substituent σ Constants^a

σ	a_0	Δa_0	a_1	Δa_1	r^b
σ_p	2.9	0.7	1.4	1.6	0.24
σ_p^+	2.9	0.7	0.0	1.1	-0.02
σ_p^-	1.9	0.8	3.1	1.2	0.61
σ_{JJ}	0.9	0.6	6.8	1.5	0.79
σ_A	0.5	0.4	92.7	11.5	0.96
σ_F	2.7	1.4	0.1	0.2	0.12
σ_J	-0.3	0.3	8.8	0.7	0.98
σ_C	0.7	0.6	7.6	1.5	0.87
ΔD	0.8	0.5	7.1	1.2	0.92

^a The regression equations are $\Delta H = a_0(\pm \Delta a_0) + a_1(\pm \Delta a_1) \times \sigma$. Δa_i is the possible error of the regression given by the software for a_i . ^b r is the correlation coefficient as usually defined.

For the σ_{JJ} constants we have

$$\Delta H(\text{CH}_2\bullet) = -0.3 (\pm 0.3) + 10.1 (\pm 0.8) \times \sigma_{JJ} + 2.6 (\pm 0.4) \times \sigma_p^+ \quad (r = 0.97)^{16} \quad (4)$$

According to eq 4 the inclusion of σ_p^+ greatly improves the correlation. Thereby, either the benzyl radical or σ_{JJ} is "contaminated" by some Hammett effects. The relative importance of the σ_{JJ} and σ_p^+ constants in the regression can also be evaluated by the t -value of each variable.¹⁷ In eq 4, the t -value for σ_{JJ} is 12.0, which is larger than that for σ_p^+ , 7.2. Therefore, σ_{JJ} contributes more to the total substituent effects than σ_p^+ .

For σ_F we have

$$\Delta H(\text{CH}_2\bullet) = 1.0 (\pm 0.5) + 7.3 (\pm 4.2) \times \sigma_F + 2.9 (\pm 2.1) \times \sigma_p^+ \quad (r = 0.95) \quad (5)$$

As the t -value for σ_F in eq 5 is 1.7 which is only slightly larger than that for σ_p^+ , 1.4, the contamination by the Hammett effects is stronger here.

Nevertheless, the contamination is not always serious. In the following equation

$$\Delta H(\text{CH}_2\bullet) = -0.2 (\pm 0.2) + 8.0 (\pm 0.4) \times \sigma_J + 0.5 (\pm 0.2) \times \sigma_p^+ \quad (r = 0.99) \quad (6)$$

the t -value for σ_J is 20.2 dwarfing that for σ_p^+ , 1.9.

Table 4. Regression of the Energy Changes of the Reaction $X-C_6H_4-CHY\bullet + C_6H_6 \rightarrow C_6H_5-CHY\bullet + X-C_6H_5$ against Different Scales of Substituent Constants^a

Y	a_0	Δa_0	a_1	Δa_1	r^b
		$\sigma = \sigma_p^+$			
H	2.9	0.7	0.0	1.1	-0.02
F	2.5	0.8	0.0	1.1	0.01
Cl	2.4	0.7	-1.6	1.0	-0.44
Li	7.1	1.6	10.4	2.5	0.80
Li ($\sigma = \sigma_p^-$)	0.7	0.5	18.4	0.8	0.99
		$\sigma = \sigma_I$			
H	-0.3	0.3	8.8	0.7	0.98
F	-0.8	0.5	9.1	1.0	0.95
Cl	-0.6	0.5	7.2	1.1	0.92
Li	0.9	3.2	23.6	7.2	0.76

^a The regression equations are $\Delta H = a_0(\pm\Delta a_0) + a_1(\pm\Delta a_1) \times \sigma$. Δa_i is the possible error of the regression given by the software for a_i .
^b r is the correlation coefficient as usually defined.

3.2. To Show the Non-Hammett Behaviors the Radicals Must Be Fairly Nonpolar.

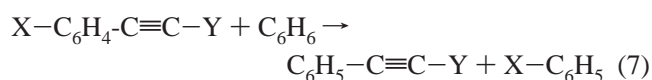
The non-Hammett behavior of benzyl radicals presumably is caused by the fact that a radical has a singly occupied orbital (SOMO) which can interact both with the low-lying LUMO of acceptors or with the high-lying HOMO of the donor. As a result, both the donor and acceptor can stabilize a radical.¹⁸

If the above SOMO interaction mechanism were correct, one would expect to see the non-Hammett behaviors for all the radicals. However, many radicals such as $X-C_6H_4-O\bullet$ and $X-C_6H_4-NH\bullet$ show good to excellent Hammett relationships.¹⁹ From section 3.1, one may realize that this is caused by the "contamination" from the polar effect.

We did not calculate the oxygen and nitrogen radicals, because the highly polar C-O and C-N bonds should obviously bring considerable polar Hammett effects. Nevertheless, we would like to know if the carbon radicals always show the non-Hammett effects. Thus, we put different α substituents on the benzyl radicals.

As seen from Table 2, the α substituent exerts significant influence on the direction and magnitude of substituent effects. Correlation analyses (Table 4) indicate that $X-C_6H_4-CHF\bullet$ and $X-C_6H_4-CHCl\bullet$ also show significant non-Hammett behaviors. Nevertheless, $X-C_6H_4-CHLi\bullet$ shows strong Hammett effects (e.g. $r = 0.99$ for σ_p^-). Therefore, $X-C_6H_4-CHLi\bullet$ should be classified as the *O*-type, despite the fact that they are carbon radicals. Presumably, the highly polar C-Li bond causes the Hammett effect. In comparison, for $X-C_6H_4-CH_2\bullet$ the $X-C_6H_4$ and $CH_2\bullet$ moieties are connected through a fairly nonpolar $C(sp^2)-C(sp^2)$ bond. Thus, the radical non-Hammett effect is principally a nonpolar effect. The Walter's classification of *O*- and *S*-type radicals on the basis of whether the radicals are heteroatomic or carbon ones is not valid.²⁰

3.3. Closed-Shell Systems Can Also Show the Non-Hammett Behaviors. Substituted phenylacetylenes are closed-shell systems. The *para* substituent effects on the stabilities of $C\equiv C$ triple bonds can be evaluated on the basis of the enthalpy changes of the isodesmic reactions (eq 7) at 0 K as listed in Table 5.

**Table 5.** Substituent Effects on the Energy Changes of the Isodesmic Reaction $X-C_6H_4-C\equiv C-Y + C_6H_6 \rightarrow C_6H_5-C\equiv C-Y + X-C_6H_5$ Calculated Using B3LYP/6-311++G(2d,2p)//B3LYP/6-31+G(d) Method (kJ/mol)

substituent	Y = NO ₂	Y = BH ₂	Y = H	Y = CH ₃	Y = NH ₂	Y = Li
CH ₃	4.0	3.1	1.3	0.6	-0.1	-0.8
Cl	-3.2	-1.1	-1.1	0.3	0.5	2.9
CN	-11.0	-6.0	-2.1	1.2	5.2	9.8
COCH ₃	-4.9	-2.5	-0.2	2.0	5.1	7.8
COOH	-6.4	-3.4	-0.8	1.6	5.2	7.4
F	-1.9	-0.5	-1.2	-0.7	-1.1	1.0
H	0.0	0.0	0.0	0.0	0.0	0.0
NO ₂	-12.9	-6.8	-2.3	2.0	7.7	12.7
CONH ₂	-4.3	-2.1	-0.5	1.8	3.4	5.5
SCH ₃	7.1	6.3	2.4	2.3	0.8	-
CF ₃	-8.1	-4.1	-1.3	0.2	4.2	7.6
N(CH ₃) ₂	19.3	14.9	5.4	2.9	0.5	-2.4
COOMe	-4.5	-2.3	-0.3	1.6	4.4	6.0
SiMe ₃	3.1	2.5	1.1	1.4	2.2	1.5

Table 6. Regression of the Energy Changes of the Reaction $X-C_6H_4-C\equiv C-Y + C_6H_6 \rightarrow C_6H_5-C\equiv C-Y + X-C_6H_5$ against the Substituent Constants^a

Y	a_0	Δa_0	a_1	Δa_1	r^b
		$\sigma = \sigma_p^+$			
NO ₂	-0.8	0.6	-12.6	0.9	-0.98
BH ₂	0.5	0.3	-8.6	0.5	-0.98
H	0.2	0.2	-3.0	0.3	-0.94
CH ₃	1.1	0.3	-0.6	0.4	-0.36
		$\sigma = \sigma_p^-$			
CH ₃	1.3	0.3	-0.3	0.7	-0.12
		$\sigma = \sigma_p^-$			
CH ₃	0.9	0.4	0.6	0.6	0.29
NH ₂	0.2	0.2	5.6	0.4	0.98
Li	0.3	0.4	9.4	0.6	0.98
		$\sigma = \sigma_I$			
NO ₂	-0.8	3.2	-7.9	7.1	-0.36
BH ₂	0.0	2.1	-4.1	4.6	-0.30
H	-0.3	0.8	-0.4	1.8	-0.10
CH ₃	-0.2	0.2	3.2	0.5	0.93
NH ₂	-0.1	1.0	7.9	2.3	0.77
Li	1.0	1.5	12.7	3.5	0.80
		$\sigma = \sigma_A$			
CH ₃	0.0	0.1	32.8	3.8	0.96

^a The regression equations are $\Delta H = a_0(\pm\Delta a_0) + a_1(\pm\Delta a_1) \times \sigma$. Δa_i is the possible error of the regression given by the software for a_i .
^b r is the correlation coefficient as usually defined.

The regression results are shown in Table 6.

According to Table 6, the pattern of the substituent effects on the $C\equiv C$ stability is strongly affected by the group to which the $C\equiv C$ is attached. Usually, a good correlation with either the σ_p^+ or σ_p^- constants can be obtained ($r > 0.95$), indicating strong Hammett effects. However, for a particular case, i.e., $X-C_6H_4-C\equiv C-CH_3$, Hammett regression with any of the σ_p , σ_p^+ , and σ_p^- constants fails. Instead, using σ_I a good correlation ($r = 0.93$) can be obtained for that case. Using Arnold's σ_A constants, the correlation coefficient is as high as 0.96.

Therefore, $X-C_6H_4-C\equiv C-CH_3$ shows a non-Hammett behavior similar to the benzyl radicals. In fact, comparing Tables 2 and 6 one can see that both the benzyl radicals and $C\equiv C$ are stabilized by both the donor and acceptor substituents. The only substituent that destabilizes the $C\equiv C$ bond is F, which is also the only one that destabilizes the benzyl radical.

Table 7. Substituent Effects on the Energy Changes of the Isodesmic Reaction $X-C_6H_4-(CH=CH)_n-CH=CH_2 + C_6H_6 \rightarrow C_6H_5-(CH=CH)_n-CH=CH_2 + X-C_6H_5$ Calculated Using B3LYP/6-311++G(2d,2p)/B3LYP/6-31g(d) Method (kJ/mol)

substituent	$n = 1$	$n = 2$	$n = 3$
CH ₃	0.77	1.02	1.04
Cl	0.08	0.34	0.43
CN	1.42	2.29	2.84
COCH ₃	2.00	2.80	3.32
COOH	1.88	2.84	3.30
F	-0.62	-0.80	-0.83
H	0.00	0.00	0.00
NO ₂	1.81	2.38	4.23
CONH ₂	1.29	1.89	2.18
SCH ₃	1.36	1.86	2.10
CF ₃	0.38	0.98	1.29
N(CH ₃) ₂	3.14	4.18	4.61
COOMe	1.45	2.04	2.51
SiMe ₃	0.94	1.33	2.12

The above results indicate that the benzyl radical and $X-C_6H_4-C\equiv C-CH_3$ may have the same mechanism of substituent effects. For $C\equiv C$ in $X-C_6H_4-C\equiv C-CH_3$ the stabilization by the substituents cannot be attributed to any polar effect, as otherwise the Hammett relationship would be seen. The only mechanism that can operate is the nonpolar resonance effect. That is, the stabilization of $C\equiv C$ by an acceptor should come from the interaction between the $C\equiv C$ HOMO and the low-lying LUMO of the substituent. The $C\equiv C$ LUMO does not strongly interact with the acceptor's HOMO because the energy level of the latter is too low. On the other hand, the stabilization of $C\equiv C$ by a donor should come from the interaction between the $C\equiv C$ LUMO and the donor's high-lying HOMO. The interaction between the $C\equiv C$ HOMO and the LUMO of the donor is weak because the latter's energy is too high.

It should be noted that the above HOMO–LUMO interactions are also the cause of the benzyl radical stability, as long as one notices that the SOMO of a radical is the lowest un-(fully)-occupied orbital as well as the highest the occupied orbital. Therefore, the non-Hammett behaviors of the carbon radicals and $C\equiv C$ share the same mechanism, i.e., nonpolar resonance effect. From section 3.2, we know that although the SOMO–HOMO (or LUMO) interactions are involved in all the radicals, to show the non-Hammett behavior the radical has to be highly nonpolar. Similar requirement is also seen for $C\equiv C$, as only $X-C_6H_4-C\equiv C-CH_3$ shows the non-Hammett behavior. Presumably, the CH₃ group modifies the electronegativity of $C\equiv C$, so that $X-C_6H_4$ and $C\equiv C$ are connected through a fairly nonpolar $C(sp)-C(sp^2)$ bond. In comparison, acceptors including NO₂, BH₂, and H make $C\equiv C-Y$ more electronegative than $X-C_6H_4$ in the order NO₂ > BH₂ > H. Thus, they show good Hammett effects with decreasing regression slopes from -12.6 to -8.6 to -3.0. On the other hand, donors including NH₂ and Li make $C\equiv C-Y$ less electronegative than $X-C_6H_4$. They also show good Hammett effects but with positive regression slopes, +5.6 and +9.4.

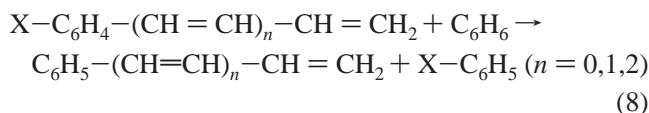
3.4. More Closed-Shell Examples for the Nonpolar Resonance Effect. In Table 7 are summarized the enthalpy changes of the isodesmic reactions (eq 8) at 0 K, which reflect the *para* substituent effects on the stability of the double bonds. It should be mentioned that all the olefins in eq 8 are trans in conformation.

Table 8. Regression of the Energy Changes of the Reaction $X-C_6H_4-CH=CH-(CH=CH)_n-CH=CH_2 + C_6H_6 \rightarrow C_6H_5-(CH=CH)_n-CH=CH_2 + X-C_6H_5$ against the Substituent Constants^a

n	a_0	Δa_0	a_1	Δa_1	r^b
$\sigma = \sigma_p$					
0	1.2	0.3	-0.3	0.7	-0.13
1	1.7	0.4	-0.2	0.9	-0.06
2	2.0	0.5	0.0	1.0	0.00
$\sigma = \sigma_J$					
0	-0.1	0.2	2.9	0.4	0.94
1	0.0	0.2	3.8	0.5	0.93
2	-0.1	0.3	5.2	0.6	0.95

^a The regression equations are $\Delta H = a_0(\pm \Delta a_0) + a_1(\pm \Delta a_1) \times \sigma$. Δa_i is the possible error of the regression given by the software for a_i .

^b r is the correlation coefficient as usually defined.



The regression results are summarized in Table 8. According to Table 8, the $C=C$ stability does not have any dependence on σ_p , indicated by the low correlation coefficients (-0.13, -0.06, and 0.00). The same conclusion can also be drawn from the analyses of the slopes of the regressions, which are -0.3, -0.2, and 0.0, respectively, compared to their error bars, 0.7, 0.9, and 1.0. In fact, from Table 7 it can be seen that except for F, all the other substituents, regardless of being a donor or acceptor, stabilize the double bonds to varying extents. Therefore, the stability of the double bonds also shows the non-Hammett behavior.

On the other hand, the $C=C$ stability shows significant dependence on σ_J , indicated by the high correlation coefficient (0.94, 0.93, 0.95). The same conclusion can also be drawn from the fact that the slopes of the regressions (2.9, 3.8, 5.2) are much larger than the error bars (0.4, 0.5, 0.6). Clearly, the $X-C_6H_4$ and $(CH=CH)_n-CH=CH_2$ moieties are connected to each other through a fairly nonpolar $C(sp^2)-C(sp^2)$ bond. As a result, the $C=C$ double bond stability is another closed-shell example for the nonpolar resonance effects.

3.5. Nonpolar Resonance Effect Is Independent from Any Other Substituent Effect. The above results justify the proposal of the nonpolar resonance effect to unify many observed non-Hammett behaviors. They show that this effect is not limited to radicals only but applicable to closed-shell systems as well. At this point, it is necessary to know whether the nonpolar resonance effect is really independent from the other substituent effects ever proposed for closed-shell systems, because we do not need to propose any substituent effect that can be described as a linear combination of the others.

Thus we perform linear regression of Jiang's σ_{JJ} constants against the σ_p , σ_p^+ , and σ_p^- constants. The low correlation coefficients (-0.24, -0.55, and -0.10)²¹ clearly show that σ_{JJ} is independent from the other three. It should be mentioned that the reason that we choose σ_{JJ} to do the analyses lies in the fact that this scale covers more substituents. We will also show in this section that selection of any σ scale should be the statistically the same.

Table 9. Regression of σ_{JJ} Constants against the Combination of F, R, σ_I , σ_R^0 , $\sigma_R(\text{BA})$, σ_R^+ , and σ_R^- Constants Using Eq 9^a

a_0	Δa_0	T_0	a_1	Δa_1	t_1	X_1	a_2	Δa_2	t_2	X_2	r
0.19	0.13	1.50	0.22	0.21	1.04	F	-0.13	0.06	-2.24	R	0.64
0.35	0.18	1.93	-0.14	0.48	-0.30	σ_I	-0.34	0.46	-0.74	σ_R^0	0.32
0.31	0.18	1.69	-0.08	0.45	-0.18	σ_I	-0.40	0.33	-1.22	$\sigma_R(\text{BA})$	0.44
0.17	0.23	0.74	0.17	0.54	0.31	σ_I	-0.23	0.19	-1.18	σ_R^+	0.44
0.42	0.18	2.34	-0.30	0.49	-0.62	σ_I	0.09	0.33	0.26	σ_R^-	0.22

^a The regression equations are $Y = a_0(\pm\Delta a_0) + a_1(\pm\Delta a_1) \times X_1 + a_2(\pm\Delta a_2) \times X_2$. Δa_i is the possible error for a_i . t_i is the t -value for a_i . r is the correlation coefficient.

Table 10. Regression of Different Scales of $\Sigma\bullet$ Constants against σ_{JJ} and σ_p^+ Constants^a

$\sigma\bullet$	a_0	Δa_0	t_0	a_1	Δa_1	t_1	a_2	Δa_2	t_2	r
σ_A	-0.006	0.004	-1.35	0.120	0.020	5.84	-0.001	0.010	-0.14	0.96
σ_F	-0.117	0.064	-1.84	0.870	0.390	2.23	0.118	0.163	0.72	0.94
σ_I	0.006	0.048	0.11	1.188	0.148	8.02	0.262	0.069	3.80	0.96
σ_C	-0.026	0.034	-0.75	0.974	0.089	10.95	0.068	0.038	1.79	0.98
ΔD	-0.084	0.068	-1.23	1.157	0.181	6.36	0.443	0.076	5.80	0.94

^a The regression equations are $Y = a_0(\pm\Delta a_0) + a_1(\pm\Delta a_1) \times \sigma_{JJ} + a_2(\pm\Delta a_2) \times \sigma_p^+$.

Table 11. Bond Lengths and Vibration Frequencies of X-C₆H₄-CH=CH₂ Calculated Using B3LYP/6-31g(d) Method

substituent	C-C (Å)	C=C (Å)	C=C freq (cm ⁻¹)
CH ₃	1.47113	1.33926	1713.6
Cl	1.47123	1.33883	1714.6
CN	1.47062	1.33918	1712.5
COCH ₃	1.47071	1.33928	1712.1
COOH	1.47089	1.33921	1712.5
F	1.47151	1.33892	1714.7
H	1.47223	1.33900	1713.7
NO ₂	1.47060	1.33910	1712.5
CONH ₂	1.47116	1.33911	1713.0
SCH ₃	1.46939	1.33963	1711.1
CF ₃	1.47184	1.33874	1714.8
N(CH ₃) ₂	1.46735	1.34059	1709.8
COOMe	1.47093	1.33919	1711.7
SiMe ₃	1.47147	1.33917	1713.3

The σ_{JJ} constants cannot be described by a separation of Hammett effect into resonance (or mesomeric) effect and inductive/field effect (eq 9)²² either.

$$\log(k_X/k_H) = \rho_I\sigma_I + \rho_R\sigma_R \quad (9)$$

As shown in Table 9, none of the Taft's four types of resonance effects (σ_R^- , σ_R^+ , σ_R^0 , and $\sigma_R(\text{BA})$) can be used to explain the σ_{JJ} constants.

Finally, it must be noted that all $\sigma\bullet$ constants are not independent from each other. In fact, when we use σ_{JJ} and σ_p^+ to do a double variable linear regression on the other $\sigma\bullet$ constants (Table 10), we find that the correlations are always good ($r > 0.94$). Therefore, as long as we use one scale of $\sigma\bullet$ constants to account for the nonpolar resonance effect and one scale of Hammett-type constants to account for the polar effect, the final analysis results should be equally good. The only difference between the different scales of $\sigma\bullet$ substituent constants is the varying extent of "contamination" from the polar Hammett effect.

3.6. Application of the Nonpolar Substituent Effects to Other Problems. Jiang et al. recently showed that the nonpolar resonance effect can be used to account for the UV spectra of aromatic compounds such as styrenes, phenylacetylenes, acetophenones, and methylsulfonylstyrenes.²³ This finding is valuable, because correlation studies of UV using Hammett equations had been a frustrating

Table 12. Regression of the Bond Lengths and Vibration Frequencies of X-C₆H₄-CH=CH₂ against the Substituent σ_p and σ_{JJ} Constants^a

	a_0	Δa_0	a_1	Δa_1	r^b
$\sigma = \sigma_p$					
C-C	1.47047	0.00032	0.00150	0.00070	0.52
C=C	1.33939	0.00010	-0.00074	0.00022	-0.69
C=C freq	1712.6	0.4	1.07	0.93	0.31
$\sigma = \sigma_{JJ}$					
C-C	1.47213	0.00021	-0.00400	0.00048	-0.92
C=C	1.33875	0.00009	0.00144	0.00022	0.88
C=C freq	1714.4	0.2	-4.77	0.59	-0.92

^a The regression equations are $\Delta H = a_0(\pm\Delta a_0) + a_1(\pm\Delta a_1) \times \sigma$. Δa_i is the possible error of the regression given by the software for a_i .

^b r is the correlation coefficient as usually defined.

problem for a long time. In fact, Brownlee and Topsom once commented that "previously claimed simple relationships between UV frequency and substituent electronic properties are mostly unfounded".⁶

Bond lengths represent another problem for Hammett relationship. Herein, we calculate the C-C and C=C bond lengths associated with CH=CH₂ in *para*-X-C₆H₄-CH=CH₂ (Table 11). According to the correlation analyses (Table 12) the correlation of the bond length with σ_p is poor. In comparison, correlation of the bond length with σ_{JJ} is much better showing the involvement of nonpolar resonance effects. The dual-parameter equations are

$$\begin{aligned} \text{bond length (C-C)} &= 1.47188 (\pm 0.00022) + \\ &0.00063 (\pm 0.00030, t = 2.1) \times \sigma_p - \\ &0.00366 (\pm 0.00046, t = -8.0) \times \sigma_{JJ} \quad (r = 0.95) \quad (10) \end{aligned}$$

$$\begin{aligned} \text{bond length (C=C)} &= 1.33893 (\pm 0.00006) - \\ &0.00046 (\pm 0.00008, t = -5.5) \times \sigma_p + \\ &0.00119 (\pm 0.00013, t = 9.3) \times \sigma_{JJ} \quad (r = 0.97) \quad (11) \end{aligned}$$

Clearly, these two equations show that the nonpolar resonance effect plays a more important role than the polar Hammett effect in the correlation as indicated by the t -values.

Vibration frequencies are experimentally assessable quantities. Correlation studies on them were also not very

successful before. Herein, we calculate the C=C vibration frequencies of $X-C_6H_4-CH=CH_2$ (Table 11). Through correlation analyses, we find that the vibration frequencies have little dependence on σ_p ($r = 0.31$). In comparison, the correlation with σ_{JJ} is much more successful ($r = 0.92$), which means that the nonpolar resonance effect is also significant in this system. The dual-parameter equation is

$$\begin{aligned} \text{vibration (C=C)} &= 1714.5 (\pm 0.3) - \\ &0.1 (\pm 0.4, t = -0.2) \times \sigma_p - \\ &4.8 (\pm 0.6, t = -7.3) \times \sigma_{JJ} \quad (r = 0.92) \quad (12) \end{aligned}$$

It shows clearly through the t -values that the nonpolar resonance effect is the dominant factor for the substituent effects on the vibration frequencies.

4. CONCLUSION

On the basis of ab initio calculations we have found the following:

1. The stabilities of benzyl radicals show significant non-Hammett behaviors. They correlate well with all scales of radical substituent constants (σ^\bullet), if the polar Hammett effects are appropriately separated. However, putting a highly polar α substituent to the benzyl radicals considerably diminishes the non-Hammett effects. The carbon radicals are not always of the S -type in contrast to Walter's theory.

2. The non-Hammett behavior can also be observed for some closed-shell systems. Therefore, the essential cause of the effect is not the spin, but the HOMO_{reaction-center}-LUMO_{acceptor} and LUMO_{reaction-center}-HOMO_{donor} interactions. We call these HOMO-LUMO interactions as the nonpolar resonance effect, which clearly is a universal effect. However, this effect cannot always be well displayed because of the serious competition from the polar Hammett effect.

3. The nonpolar resonance effect is orthogonal to the previously documented substituent effects. Proposal of this effect enables us to give a unified explanation for the many observed non-Hammett behaviors in different fields. In addition, all the σ^\bullet scale substituent constants can be used to describe this effect, because in the binary vector space of Hammett effect and nonpolar resonance effect they are linearly correlated with each other.

4. Proposal of the nonpolar resonance effect is also valuable from a practical point of view, because using this relationship we can perform better correlation studies on some "tough" problems such as radical and multiple bond stabilities, UV and IR spectra, and molecular structures. It remains interesting to see if the nonpolar resonance effect can be useful for other studies on the qualitative structure-activity relationships (QSAR).

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