

Establishment and Successful Application of the σ_{JJ}^{\bullet} Scale of Spin-Delocalization Substituent Constants

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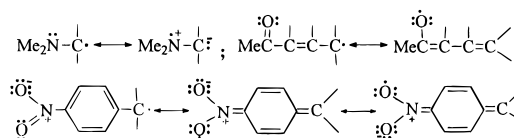
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Structure–property relationships in nonradical chemistry have been discussed and understood mainly in terms of steric and polar (including resonance polar) effects.¹ An ocean of literature reports successful application of Hammett-type polar substituent constants σ^x , e.g., σ_p , σ_m , σ^+ , etc.² Radical chemistry, however, is complicated by a third major effect, namely, spin-delocalization.³ Spin delocalization is a resonance effect involving the unpaired electron or spin. It can reduce the spin density of a carbon radical by delocalizing the spin into the substituent Y, as illustrated by Scheme 1, with Y = $-\text{NMe}_2$, $-\text{COMe}$, or $-\text{NO}_2$. Since knowledge of the relative abilities of various substituents (Y) to delocalize the spin on a carbon radical is of great interest and importance to organic, physical, polymer, and bioorganic chemists, quite a few radical chemists have dedicated their efforts to setting up a useful sigma-dot (σ^{\bullet}) scale of spin-delocalization substituent constants, i.e., a scale that will give us the relative abilities of the Y substituents to delocalize the spin,^{4,5} even though many radical reactions had been correlated by the σ^+ scale of polar substituent constants.⁶ A true σ^{\bullet} scale should, however, be independent of steric and polar effects (σ^x) and applicable to all kinds of carbon radicals in which spin delocalization can occur, as exemplified by the resonance structures in Scheme 1.

Among the various approaches to the setting up of a σ^{\bullet} scale, those of Arnold ($\sigma_{\alpha}^{\bullet}$),^{5b} Creary (σ_c^{\bullet}),^{5c} Jackson (σ_j^{\bullet}),^{5d} Fisher,^{5e} and Viehe^{5f} are of particular interest. However, most of the previously reported approaches are not completely free from one or more of the following difficulties:⁷ (1) residual polar effects were not completely separated, (2) an insufficient number of well-distributed substituents were used, (3) the defining reaction may be complex, (4) the F atom was judged to be a “radical destabilizing substituent”, whereas recent experimental results have shown that the F atom of the FCH_2^{\bullet} radical is a weakly stabilizing substituent, and (5) the reliability and rigor of some of the kinetic methods used were not meticulously confirmed. Therefore, since 1980, we have worked on a project of setting up a new σ^{\bullet} scale (later

Scheme 1



designated as σ_{JJ}^{\bullet})^{5a,7,8} which is free from these difficulties, and we have demonstrated its trustworthiness by its successful applications to kinetic data derived from a rigorous methodology developed for the present study (vide infra).^{9–17}

The main objective of our work has been, however, to try to answer the following intriguing and puzzling question: If the spin-delocalization effect is an ever-present effect in radical reactions, then why does it fail to show up in the structure–reactivity correlation analyses in many reactions? In other words, it would seem that in the absence of measurable steric effects, the dual-parameter eq 1 for a reaction series with Y's as substituents should always yield better correlation results than the single-parameter eq 2 could. Many reactions, especially H-atom abstraction reactions have, however, been successfully correlated by eq 2 with $\sigma^x = \sigma^+$.⁶ The present Account

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Xi-Kui Jiang was the subject of an earlier biological note in *Acc. Chem. Res.* (**1988**, *21*, 362). He was elected to the Chinese Academy of Sciences in 1991 and is an Executive-Committee Member of the Chemistry Division of the Academy.

Table 1. Recommended σ_{JJ}^* and σ_{mb} Values for Substituents Y

Y	σ_{JJ}^*	σ_{mb}	Y	σ_{JJ}^*	σ_{mb}	Y	σ_{JJ}^*	σ_{mb}
H	0	0	SO ₂ Me	0.41 ± 0.04	0.64	<i>t</i> -Bu	0.26 ± 0.04	-0.22
NMe ₂	1.00 ± 0.11	-0.96	COOH	0.38 ± 0.05	0.31	OMe	0.23 ± 0.03	-0.77
CF ₂ =CF	0.86 ± 0.02	0.40	CONH ₂	0.38 ± 0.03	0.10	Br	0.23 ± 0.02	0.13
SMe	0.62 ± 0.09	-0.18	NO ₂	0.36 ± 0.06	0.86	Cl	0.22 ± 0.02	0.11
COMe	0.54 ± 0.05	0.56	MeC(O)O	0.35 ± 0.07	-0.14	Me	0.15 ± 0.01	-0.29
SOMe	0.50 ± 0.03	0.19	CO ₂ Me	0.33 ± 0.03	0.48	CF ₃	-0.01 ± 0.01	0.49
Ph	0.47 ± 0.02	0.06	SiMe ₃	0.31 ± 0.02	0.14	F	-0.02 ± 0.03	-0.24
CN	0.42 ± 0.04	0.86	<i>c</i> -Pr	0.29 ± 0.05	-0.31			

will provide an answer to this question by proposing that there are four possible categories (I–IV, vide infra) of correlation results based on the applicability of eqs 1–3,

$$\log(k_Y/k_H) \text{ (or spectral data)} = \rho^x \sigma^x + \rho^* \sigma^* + C \quad (1)$$

$$\log(k_Y/k_H) \text{ (or spectral data)} = \rho^x \sigma^x + C \quad (2)$$

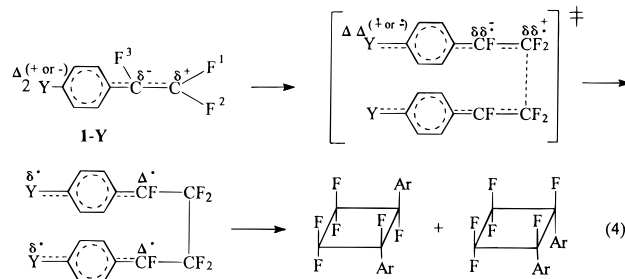
$$\log(k_Y/k_H) \text{ (or spectral data)} = \rho^* \sigma^* + C \quad (3)$$

and on the $|\rho^x/\rho^*|$ ratio from eq 1 which should always be tested. To be noted is that successful correlation by eq 2 does not necessarily signify the absence of the spin effect. A breakthrough in the correlation of UV data of some model aromatic compounds will also be described.

Establishment of the σ_{JJ}^* Scale

As mentioned, we take σ^* as a measure of the ability of an α substituent (Y) to delocalize a spin. The simplest example is the ability of Y to delocalize the spin of the YCH_2^* radical. However, data derived from YCH_2^* or its precursor, YCH_2Z , may be complicated by steric and polar effects. Therefore, like some other workers,⁵ we set up our σ^* scale by assessing the spin-delocalizing ability of Y in *p*-Y-substituted benzyl radicals in order to avoid complications from steric effects. Notably, σ^* as defined above is different from any other measure derived directly from bond dissociation energy (BDE).⁴ As Wu has pointed out,¹⁸ it is conceptually misleading to evaluate radical-stabilizing abilities of substituents directly from BDE data without considering polar (and steric) effects on BDE.

Our approach was to find an exceedingly clean reaction which would give rise to the benzylic radical in the rate-determining step. The reaction should be one for which the polar and spin effects on its rate were separable. Luckily we found the thermal cycloaddition reactions of Y-substituted α,β,β -trifluorostyrenes (**1-Y**), as shown in eq 4. These reactions can proceed in *n*-hexane at rates which



are accurately measurable in the temperature range 110–160 °C. They have been carefully studied and shown to proceed through 1,4-biradical intermediates.^{7,8}

Since the ease of homolysis of the π -bond in **1-Y** depends on both the degree of polarization of the π -bond (δ^+ and δ^- in **1-Y**) and the radical-stabilizing ability of Y, rate constants (k_Y) of the cycloaddition reaction are affected by both of these effects, i.e., polar ($\rho^x \sigma^x$ in eq 1) and spin delocalization ($\rho^* \sigma^*$). In other words, these rate constants increase not only with increasing spin-delocalizing ability of the Y substituents (ρ^* is positive) but also with increasing electron-pair donating abilities of the Y substituents (ρ^x is negative) and vice versa.^{5a,7a,8d}

The σ_{JJ}^* scale is unique in the sense that it is based on two independently measured data, i.e., k_Y values and ¹⁹F NMR data of the three F atoms of **1-Y**. The difference between the chemical shifts of F³ and F¹ (δ_{3-1}), or F³ and F² (δ_{3-2}), reflects the degree of polarization of the π bond in the ground state of **1-Y** (δ^+ and δ^- of **1-Y**). By means of eq 5, where $\Delta\delta_{3-1} = (\delta_{3-1})_Y - (\delta_{3-1})_H$, a scale of polar

$$\sigma_{mb} = (0.16)\Delta\delta_{3-1} - 0.09 \quad (5)$$

substituent constants, the σ_{mb} scale, was set up.¹⁹ It is not only a tailor-made scale for the σ_{JJ}^* approach, but also is expected to be applicable to systems in which the substituent Y interacts with a multiple bond. Values of σ_{mb} are summarized in Table 1.²⁰

To use σ_{mb} as a measure of the polar effect in the cycloaddition of **1-Y**, we assumed that the polar effects of the Y's on the transition states (TS's) parallel those on the ground states. In fact, this is the only theoretical assumption that had to be made for setting up the σ_{JJ}^* scale after it had been demonstrated that ρ_{mb} (ρ^x of eq 1) could be any value in a range of approximately -0.20 to -0.40.^{7a,b} In other words, if we arbitrarily set $\rho^* = 1$, and use a ρ_{mb} value of -0.35, then the σ_{JJ}^* value of any Y can be calculated by eq 6. Furthermore, five similar or

$$\sigma_{JJ}^* \text{ for Y} = \log k_Y/k_H - \rho_{mb}\sigma_{mb} \text{ for Y} \quad (6)$$

mutually correlatable sets of σ_{JJ}^* scales, each derived from data measured at a specific temperature (110, 120, 140, 150, and 160 °C) had been obtained.^{7a,b} It is noteworthy that no other σ scale (σ^x or σ^*) had been cross-checked in this manner, and seven advantageous features have been claimed for the σ_{JJ}^* scale.^{7a,c} Precision and reliability of our rate measurements have been strongly supported by the existence of an isokinetic relationship (IKR) involving a total of 32 **1-Y**'s.²¹ The isokinetic temperature is 378 K. This relationship appears to be the only IKR for a reaction

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Table 2. Values of r for Correlations by $\log k_R(Y) = \rho^x \sigma^x$ and Values of R , ρ^x , ρ^* and ρ_{mb}/ρ_{JJ}^* for Correlations by $\log k_R(Y) = \rho_{mb}\sigma_{mb} + \rho_{JJ}^*\sigma_{JJ}^{*a}$

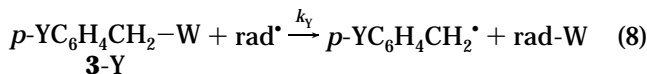
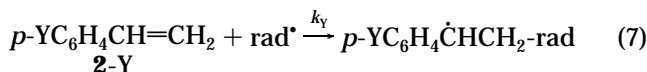
entry no.	r (σ^x)	R	n	$\rho_{mb}(\rho_p)$	ρ_{JJ}^*	ρ_{mb}/ρ_{JJ}^* (ρ_p/ρ_{JJ}^*)	ref
4		(1.00)	21	-0.35	1.00	-0.35	7a,b
10	0.938 (σ^+)	0.935 ^b	12	-0.673	0.733	-0.92	9
11	0.747 (σ^+)	0.992	12	-0.626	1.488	-0.42	9
12	0.898 (σ^+)	0.990	15	-0.53	0.62	-0.85	16
13	0.743 (σ^+)	0.997	11	-0.168	0.449	-0.37	10
14	0.971 (σ^+)	0.945 (0.991)	15	-0.690 (-0.977)	0.512 (0.543)	-1.35 (-1.81)	13
15	0.973 (σ^+)	0.938 (0.993)	15	-0.764 (-1.087)	0.552 (0.592)	-1.38 (-1.85)	14
16	0.901 (σ_p)	0.980 (0.997)	11	-0.699 (-0.995)	0.613 (0.494)	-1.14 (-2.01)	11
17	0.941 (σ_p)	0.893 (0.993)	14	-0.259 (-0.399)	0.237 (0.238)	-1.09 (-1.68)	12
18	0.868 (σ_p) ^c	0.910 (0.977)	13	0.245 (0.314)	0.229 (0.273)	1.07 (1.15)	15

^a Parenthesized values are for correlations by $\log k_R(Y) = \rho_p\sigma_p + \rho_{JJ}^*\sigma_{JJ}^{*}$ (σ^+ , σ_{JJ}^*): $R = 0.953$. ^c σ^- : $r = 0.892$.

involving 1,4-biradical intermediates. Recommended σ_{JJ}^* values are summarized in Table 1.²²

Testing the Dual-Parameter Equation and the σ_{JJ}^* Scale by Kinetic Data Measured by a Rigorous Methodology

The trustworthiness of a σ^* scale should not rely solely on the rigor of the methodology of its establishment. Its credibility needs to be evaluated on the basis of its applicability to reliable kinetic data, because in the absence of measurable steric effects, rates of formation of benzylic radicals in an essentially inert solvent are affected by polar (σ^x) and spin-delocalization (σ^*) effects. Some spectral data might be complicated by other factors.^{23,24} We therefore proposed the following requirements for acquiring truly reliable kinetic data to be used in the correlation analysis of substituent (Y) effects on the rates of formation of *p*-Y-substituted benzylic radicals from their precursors **2**-Y and **3**-Y, as shown in eq 7 and eq 8.^{9-11,13}



(1) The reaction should be exceptionally clean, in the sense that almost all products are derived from the same measured step. This step, with k_Y as the rate constant for the formation of benzylic radicals from **2**-Y or **3**-Y, is rate-determining and essentially irreversible. Most likely, this reaction is an effective chain reaction.

(2) The relative rate, k_Y/k_H or $k_r(Y)$, is based on direct competition between **2**-Y and **2**-H and is calculated by the well-known eq 9,²⁵ in which **2**-Y can be replaced by **3**-Y. In eq 9, $[\mathbf{2}\text{-Y}]_t$ represents the concentration of unreacted **2**-Y at time t , and φ_Y stands for the mole

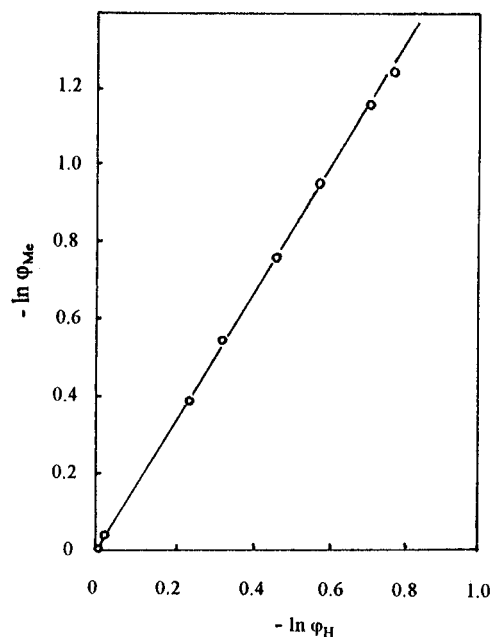


FIGURE 1. Plot of $-\ln \varphi_{Me}$ vs $-\ln \varphi_H$ for the H-atom abstraction reaction from *p*-Y-substituted isopropylbenzenes by Br[•] in reaction 16.

fraction of unreacted substrate **2**-Y or **3**-Y. Use of eq 9 allows measurement of k_Y/k_H ratios without worrying about the relative amounts of the products.

$$k_r(Y) = \frac{k_Y}{k_H} = \frac{\log\{[\mathbf{2}\text{-Y}]_t/[\mathbf{2}\text{-Y}]_0\}}{\log\{[\mathbf{2}\text{-H}]_t/[\mathbf{2}\text{-H}]_0\}} = \frac{\log \varphi_Y}{\log \varphi_H} \quad (9)$$

(3) A rigorous kinetic procedure is followed, i.e., at least 5~12 independent measurements of the k_Y/k_H [i.e., $k_r(Y)$] values are made over a wide range of conversions (extent of reaction 0~80% or 0~90%).

(4) Each $k_R(Y)$ value (capital R) is derived from regression analysis of a $\log \varphi_Y$ -vs- $\log \varphi_H$ plot; each plot should be an almost perfect straight line with a slope = $k_R(Y)$. This is illustrated by Figure 1, in which $-\ln \varphi_{Me}$ is plotted against $-\ln \varphi_H$, for H-atom abstraction by Br[•] from 11 *p*-Y-substituted isopropylbenzenes (eq 16). Criteria for the reliability and precision of the $k_R(Y)$ values are the following: (i) This $k_R(Y)$ value should be about the same as the arithmetically averaged k_Y/k_H value of at least 5~12 independent measurements. (ii) The $k_R(Y)$ value should be independent of the **2**-Y/**2**-H or **3**-Y/**3**-H mole ratios. Establishment of the constancy and reliability of the $k_R(Y)$ values serves to show that the requirements have been satisfied.

(22) The σ_{JJ}^* and σ_{mb} values for the **MeSO**₂- group in ref 7a should be corrected to 0.41 ± 0.04 and 0.64, respectively (see ref 7b).

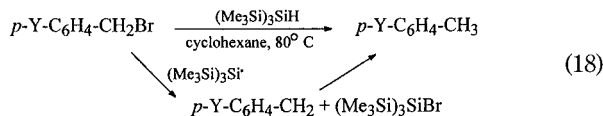
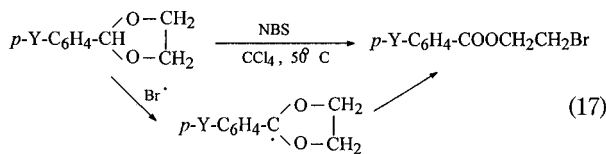
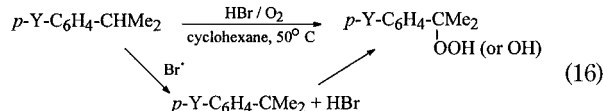
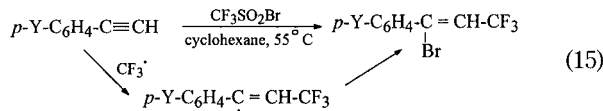
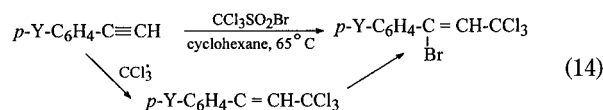
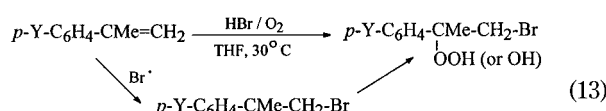
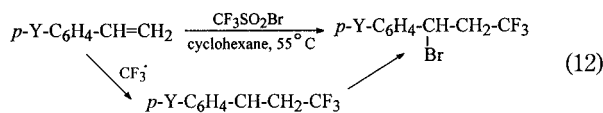
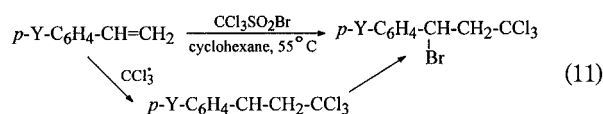
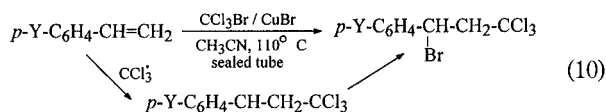
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(5) At least 11–12 para substituents with well-distributed electronic properties should be used to avoid any fortuitous “parallelism” between a limited number of σ^x and σ^y constants (cf. ref 8d).

Since, to our knowledge, previously reported k_I/k_H data for correlation analysis have not been acquired by a methodology that fulfills all of our proposed requirements, we sought exceptionally clean reactions, and then conducted our investigation of those for which all the above-mentioned requirements were fulfilled. Besides the cycloaddition reaction shown by eq 4, nine other such reactions were found, as described in terms of their rate-determining step by eqs 10–18.^{9–16} These equation



numbers are given as the entry numbers in Table 2. Main products are also given in these reactions, with the understanding that total yield of the main products and minor products (if any) derived from the same rate-limiting step fall in the range of 94~98% for all nine reactions.

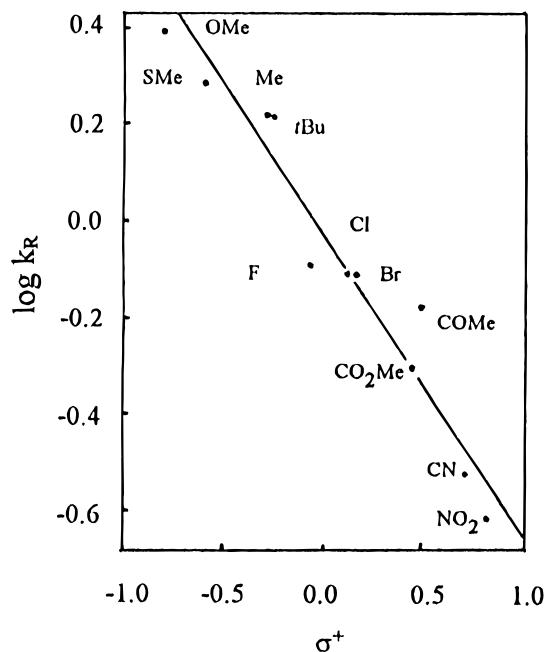


FIGURE 2. Plot of $\log k_R$ vs σ^+ for the H-atom abstraction reaction from *p*-Y-substituted isopropylbenzenes by $\text{Br} \cdot$ in reaction 16.

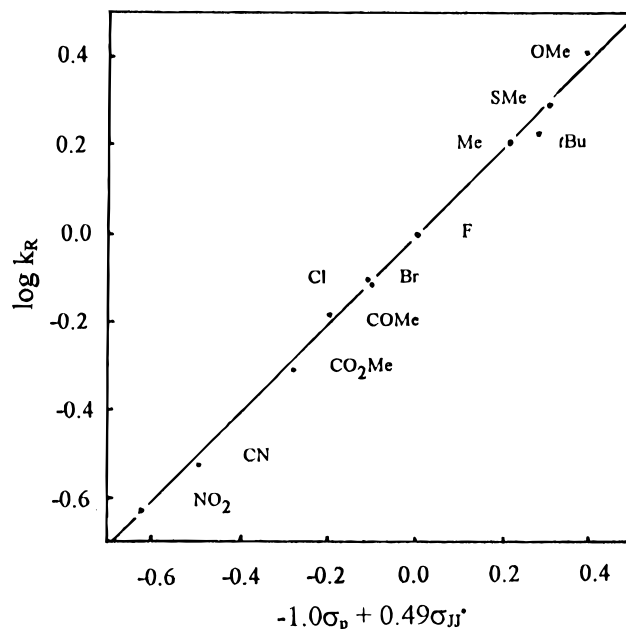


FIGURE 3. Plot of $\log k_R$ vs $(-1.0\sigma_p + 0.49\sigma_{JJ}^*)$ for the H-atom abstraction reaction from *p*-Y-substituted isopropylbenzenes by $\text{Br} \cdot$ in reaction 16.

The number of Y substituents used was at least 11–12 (and sometimes 13–15) for all of these studies. The results of correlation by the single-parameter eq 2, with $\sigma^x = \sigma_p$, σ^+ , or σ_{mb} , were compared with those by the dual-parameter eq 1, with $\sigma^* = \sigma_\alpha^*$, σ_C^* , or σ_{JJ}^* . In other words, all nine possible pairings of (σ^x, σ^y) were always tried. The values of ρ^x and ρ^y can be easily evaluated by applying multiple linear regression with the aid of a computer.^{2a} Figures 2 and 3 are given as illustrations for such comparisons. For the H-atom abstraction reaction described by eq 16, Figure 2 shows a $\log k_R$ -vs- σ^+ plot and Figure 3 gives the $\log k_R$ -vs- $(\sigma_p, \sigma_{JJ}^*)$ plot. Figure 2 clearly shows that there are many sizable deviations of the k_R values from the single-parameter regression line for some sub-

stituents. Thus the regression line based on the dual-parameter correlation in Figure 3 is very likely a more realistic representation of the actual state of affairs, i.e., existence of the spin effect. Our ρ^* values derived from applications of eq 1 always turned out to be positive for all nine reactions, i.e., all Y substituents delocalize the spin at the transition state. Our ρ^x values were all negative, except that for reaction 18, because the attacking radicals involved are all electrophilic radicals, except the silyl radicals of reaction 18.

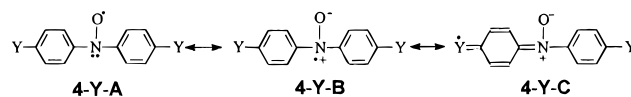
It has been pointed out previously (see, e.g., ref 7a) that the relative magnitude of the $|\rho^x/\rho^*|$ value may serve as an approximate indicator of the relative importance of the polar and spin-delocalization effects at the TS, especially when the same σ^x (e.g., σ_p or σ_{mb}) and σ^* (e.g., σ_{JJ}^*) are used in comparisons.^{23b} Only the ρ_{mb}/ρ_{JJ}^* or ρ_p/ρ_{JJ}^* values, with the latter in parentheses, are summarized in Table 2, because either the $(\sigma_{mb}, \sigma_{JJ}^*)$ pairing or the $(\sigma_p, \sigma_{JJ}^*)$ combination gave the best correlation results. This observation lends support to our belief that the σ_{JJ}^* scale is the most self-consistent and trustworthy σ scale now available. It is to be noted that $|\rho_p/\rho_{JJ}^*|$ values are a bit larger than the corresponding $|\rho_{mb}/\rho_{JJ}^*|$ values.

One of the most significant observations of our results is revealed by the "best" r values derived from application of a certain σ^x scale (parenthesized) to the single-parameter eq 2, as given in the second column of Table 2. With the exception of most of the addition reactions to styrenes (entries 11, 12, and 13) and the Br-atom abstraction reaction (entry 18), all other reactions (10, 14, 15, 16, and 17) can be quite well correlated by eq 2 with either σ^+ or σ_p , with r values greater than 0.90 ($n > 11$). This observation is certainly in harmony with a large number of literature reports.⁶ We declined, however, to use Occam's razor in a simplistic manner, i.e., we proposed that, even though the $k_R(Y)$ data could be very well correlated by eq 2 with σ^x alone, it should not be interpreted to mean the absence of the spin effect (σ^*). Furthermore, we suggested that it would be good practice to do two things:^{11-14,26,27} (1) try the dual-parameter eq 1 and evaluate the correlation results in terms of R , ψ , and F -test values^{2a,36} and (2) examine the individual deviations of $\log k_R$ values of the $\log k_R$ -vs- σ^x and $\log k_R$ -vs- (σ^x, σ^*) plots. Obviously, the latter would become very important if improvements achieved by applying eq 1 were not as definitive as those found for reactions 11-13.

After carrying out the above-mentioned practices, the following observations or facts have been established: (1) Correlation by eq 1 [by one of the three possible $(\sigma^x, \sigma_{JJ}^*)$ combinations] always leads to an improvement over correlation by eq 2, albeit to different degrees. (2) For all the nine entries (10-18), the R values are at least 0.95 (see entry 10, note a). More significantly, seven of them (11-17) have R values greater than 0.99 and ψ values smaller than 0.17.^{2a} Taking into account the number of substituents ($n > 11$), these appear to be excellent dual-parameter correlation results. (3) For entries 10, 14, 15,

16, and 17, the improvement over the single-parameter correlations cannot be regarded as definitive because the $\rho^x\sigma^x$ term alone suffices for good correlation results. Under these circumstances, careful examination of the individual deviations (compare, e.g., Figure 2 with Figure 3) always suggests the existence of the spin effect, even though it is overshadowed by the polar effect and thus cannot clearly reveal itself by simple comparison of correlation results based on eq 2 and eq 1.

A case in point is correlation analysis of the EPR a_N values of 12 symmetrically *para*-disubstituted diphenyl nitroxides 4-Y.²⁶ Application of eq 2 with σ_p yielded an r



value of 0.981 ($\psi = 0.21$), thus the improvement ($R = 0.988$, $\psi = 0.18$) made by application of eq 1 with the $(\sigma_p, \sigma_{JJ}^*)$ combination cannot be regarded as definitely meaningful. However, large negative deviations of the a_N values of two almost nonpolar but effective spin-stabilizing groups, i.e., SMe ($\sigma_p = 0.00$; $\sigma_{JJ}^* = 0.62$) and SiMe₃ ($\sigma_p = -0.07$; $\sigma_{JJ}^* = 0.31$), from the regression line of the a_N -vs- σ_p plot indicate that the spin-delocalization effects of the substituents are also in operation (cf. structure 4-Y-C). Similar results have been obtained for the EPR data of 13 *p*-Y-substituted benzoyl *tert*-butyl nitroxides.²⁷

The Four Categories of Possible Circumstances

After pondering our findings presented above, we came to realize that, for correlation analysis in radical chemistry, four categories of possible circumstances might be visualized in the absence of measurable steric effects,^{12-14,23b} with the understanding that there are also borderline cases. Our "four-categories" proposition is intended to answer the puzzling questions raised in the introduction of this Account. The answer is the following: previously reported successful applications of eq 2 could simply be cases conforming to category-II behavior.

(I) When both polar and spin effects are important, the $|\rho_{mb}/\rho_{JJ}^*|$ values might fall in the range of (very) roughly 0.2-0.8, e.g., in radical additions to styrenes (eqs 11-13). Under these circumstances, the necessity of using the dual-parameter eq 1 can be easily established because it yields much better correlation results than those from eq 2. Correlation results of the fluorescence spectral data of substituted styrenes and α -methylstyrenes,²⁸ and UV data of some phenylhydrazones (vide infra),²⁹ have also been found to fall in this category.

(II) When polar effects dominate, this ratio might approach or be larger than unity, e.g., in reactions described by eqs 10 and 14-17, as well as for the correlation of EPR data previously mentioned.^{26,27} Under these circumstances, using eq 1 instead of applying eq 2

(26) Zhang, Y. H.; Jiang, B.; Zhou, C. M.; Jiang, X. K. *Chin. J. Chem.* **1994**, *12*, 516.

(27) Zhang, Y. H.; Ding, W. F. X.; Zhou, C. M.; Chen, G. F.; Jiang, X. K. *J. Chem. Res. (S)* **1996**, 88; (*M*) **1996**, 0679.

(28) Zhang, Y. H.; Guo, G. H. X.; Jin, X. S.; Jiang, B. B.; Fu, Y. H.; Jiang, X. K. *J. Photochem. Photobiol. A: Chem.* **1995**, *88*, 11.

(29) (a) Ding, W. F. X. Ph.D. Dissertation, Shanghai Institute of Organic Chemistry, 1996. (b) Xie, J. R. Y. Ph.D. Dissertation, Shanghai Institute of Organic Chemistry, 1996.

may not improve the correlation result much, and the necessity of applying eq 1 cannot be established in a definitive manner. However, the existence of the spin effect can still be revealed by careful examination of the individual and total deviations of the experimental data from the regression lines of eqs 1 and 2 (vide supra).^{11–15,26,27} Incidentally, correlation results for reaction 18, the bromine-atom abstraction by a silyl radical,¹⁵ may be looked upon as on the borderline between categories I and II.

(III) When the spin-delocalization effect dominates, then eq 3 should apply. Application of eq 1 might yield a $|\rho_{mb}/\rho_{II}^*|$ ratio of less than about 0.2. A small $|\rho^x/\rho^*|$ value suggests the dominance of the spin effect, but it does not necessarily signify the absence of the polar effect. This category-III behavior will be illustrated by correlation results for some UV data to be discussed later.²³

(IV) When there are other complicating and interacting factors or effects, as pointed out by previous workers for some of the UV studies,^{23b,24} then none of the three equations may be applicable. For instance, for EPR a_N values of seven *p*-Y-substituted α -fluoro- α -bromodifluoromethylbenzyl *tert*-butyl nitroxides, there is no meaningful correlation by either eq 2 ($r = 0.54–0.79$) or eq 1 ($R = 0.62–0.89$).²⁷

The four-categories proposition has already revealed some interesting aspects of radical chemistry. For instance, it might have been expected that phenylacetylenes would behave rather similarly to styrenes in radical addition reactions. Now we have found that they do not, because electrophilic radical additions to phenylacetylenes (eqs 14 and 15) fall in category II, just like the H-atom abstraction reactions (eqs 16 and 17), whereas additions to styrenes (eqs 11 and 12) fall in category I. Perhaps, when an electrophilic radical (CCl_3^* or CF_3^*) attacks, the polar effect becomes more demanding when the attacked site is the more electrophilic sp carbon instead of the less electrophilic sp² carbon. In other words, the transition states for additions to phenylacetylenes might require more electrostatic assistance than those for the additions to styrenes.

Another interesting aspect of radical chemistry revealed by the four-categories notion and the comparison of $|\rho^x/\rho^*|$ values is the role played by the spin-delocalization effect at the transition state. We expected that, for the same type of reaction, perhaps a larger spin effect at the transition state will result in a smaller $|\rho^x/\rho^*|$ ratio. From this speculative perspective, it is satisfying to observe that the $|\rho_{mb}/\rho_{II}^*|$ ratio (1.09) for the H-atom abstraction reaction involving a dialkoxy benzylic radical (eq 17) is smaller than the $|\rho_{mb}/\rho_{II}^*|$ ratio (1.14) for a similar reaction involving a dialkyl radical (eq 16). This result is in harmony with the magnitude of the spin effects of the alkyl and alkoxy groups based on the σ_{II}^* scale (σ_{II}^* for Me, 0.15; for MeO, 0.23). Entry 18 is worthy of note. It is the first example of a reaction with a positive ρ^x (thus a positive ρ^x/ρ^* ratio) assessed by the dual-parameter eq 1 based on kinetic data derived from our rigorous methodology.

Finally, on the basis of the $|\rho_{mb}/\rho_{II}^*|$ value (0.92) and the category-II classification of the $CCl_3Br/CuBr$ reaction

(entry 10), we are tempted to generalize that radicals coordinated to metal or metal ions [e.g., $(CCl_3, M)^*$] may demand more polar assistance from substituents at the TS's than the same truly *free* radicals (e.g., free CCl_3^*) do.

A Delightful Revisit to the Task of the Correlation of UV Data

Searching for a good correlation of UV data on simple aromatic compounds with substituent constants had not been a very successful endeavor. For instance, Brownlee and Topsom commented that “previously claimed simple relationships between UV frequency and substituent electronic properties are mostly unfounded”.^{23b,24} Since the excited state might possess radicaloid character because it possesses two half-occupied molecular orbitals,^{28,30} we have been intrigued by the puzzle of why no one has reported an attempt to correlate the UV data on simple aromatic compounds by using eq 1, or even eq 3. The necessity of testing the applicability of the σ constants was further suggested by previous claims that some UV data could be “successfully” correlated by using two straight lines or the absolute values of σ^x (i.e., $|\sigma^x|$).^{23b} We therefore decided to embark on a simple research program, i.e., prepare a large number of *p*-Y-substituted simple model compounds with an easily identified UV absorption, and then try to correlate their ν_{max} values by using eq 1, 2, or 3. Preliminary results on the K bands of styrenes turned out to be unexpectedly encouraging.^{23a} Soon after, the UV spectra of some other classes of *p*-Y-substituted aromatic compounds were also found to fall in category III.²³ These *p*-Y-substituted compounds are the following: 17 styrenes, eight α -methylstyrenes, 20 α,β,β -trifluorostyrenes, 16 phenylacetylenes, and nine acetophenones. On the basis of our correlation results, three observations stand out in vivid contrast to previous reports. (1) The ν_{max} data are not related to the polar substituent constants σ^x by eq 2. (2) Good correlations, all with *F* values which correspond to confidence levels (CL's) greater than 99.9%, can be obtained by applying eq 3 with σ^* ; typical ν_{max} -vs- σ^x and ν_{max} -vs- σ^* plots are illustrated by Figure 4. (3) By using eq 1, all the nine pairings of (σ^x, σ^*) yield good correlations with CL > 99.9% and with $|\rho_{mb}/\rho_{II}^*|$ values smaller than 0.2.

A fourth significant observation is that all the ρ^* values of the above-mentioned correlations of ν_{max} values are negative. Since ν_{max} is a measure of the excitation energy, this suggests that the Y substituents can delocalize or stabilize the spin in the higher half-occupied orbital of the excited state and lower its energy and that the extent of this excited-state stabilization by the substituents parallels their stabilizing abilities in the ground state.

UV data of some other classes of compounds were also found to fall into category III,²⁹ namely, 15 *p*-Y-substituted phenyl α,α -ethylenedioxytoluenes, 11 *p*-Y-substituted benzaldehyde semicarbazones, 11 *p*-Y-substituted benzaldehyde 4-phenylsemicarbazones, 11 *p*-Y-substituted benzaldehyde tosylhydrazones, and 11 *p*-Y-substituted benzaldehyde phenylsulfonylhydrazones.^{23,29} By this time,

(30) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 3, 200.

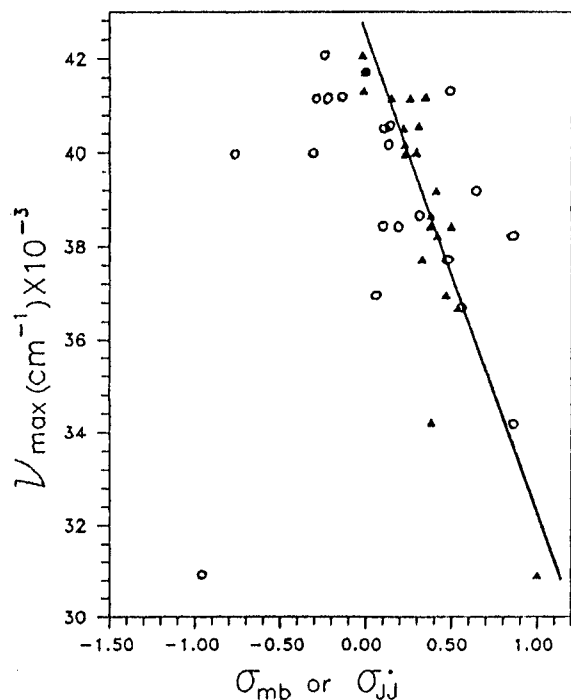


FIGURE 4. Plots of ν_{\max} (cm^{-1}) vs σ_{mb} (○) or σ_{JJ}^* (▲) for the UV of 21 α,β -trifluorostyrenes.

we had become more interested in searching for category-I behavior because category-I behavior would substantiate our belief that polar and spin effects always coexist. Indeed, examples for category-I behavior were soon found in the UV data of 12 *p*-Y-substituted benzaldehyde phenylhydrazones, 11 *p*-Y-substituted benzaldehyde (4-nitrophenyl)hydrazones, 13 *p*-Y-substituted benzaldehyde 2,4-dinitrophenylhydrazones,^{29a,31} and 11 *p*-Y-substituted benzaldehyde tosylimines.^{29b} We have also

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 (32) Streitwieser, A., Jr.; Perrin, C. *J. Am. Chem. Soc.* **1964**, 86, 4938.
 (33) Wu, Y. D.; Wong, C. L. *J. Org. Chem.* **1995**, 60, 821.
 (34) Cheng, J. P.; Zhao, Y. Y.; Huan, Z. W. *Sci. China (B)* **1995**, 38, 1417.
 (35) Wu, Y. D.; Lai, D. K. W. *J. Org. Chem.* **1996**, 61, 7904.
 (36) As described in ref 2a, *r* and *R* are basically of similar nature; the former is the correlation coefficient for simple regression, and the latter is the multiple correlation coefficient for multiple regression, e.g., a dual-parameter correlation. The ψ value is a measure of the goodness of fit which takes into account the number of substituents for correlation analysis of substituent effects. A smaller ψ value signifies a better fit. From the *F* value, i.e., the *F*-test value, the confidence level (CL) of a correlation analysis can be assessed (see, e.g., Box, G. E.; Hunter, W. G.; Hunder, J. S. *Statistics for Experimenters. An Introduction to Design, Data Analysis and Model Building*; John Wiley: New York, 1978).

demonstrated that many previously reported "successful" correlations of UV data are actually examples of either category I or category III.^{24b} Finally, we would like to mention that (1) Ding has found category-I behavior for the oxidation potentials by cyclic voltammetry of 12 *p*-Y-substituted benzaldehyde phenylhydrazones and 11 *p*-Y-substituted benzaldehyde 4-nitrophenylhydrazones^{29a,32} and (2) Xie has found category-II behavior for the reduction potentials by cyclic voltammetry of 16 *p*-Y-substituted phenylacetylenes, 11 *p*-Y-substituted benzaldehyde tosylimines, and 11 *p*-Y-substituted benzaldehyde tosylhydrazones.^{29b,32}

Concluding Remarks

In conclusion, we believe that both the σ^* scale and the dual-parameter eq 1 will be of basic importance to radical chemistry. We are pleased to note that some theoreticians have also made use of the σ^* scales in checking their calculations.^{18,33} We also hope that future workers will note our proposition that, even though the $k_{\text{R}}(\text{Y})$ data were correlated by eq 2 with σ^* alone, it should not be taken to mean the absence of the spin effect.

In closing, we note that all the chemistry discussed in this Account is of carbon radicals. Oxygen and nitrogen radicals may behave differently in various ways. In fact, recently, both Cheng and Wu have studied the substituent effects on these so-called "Class-O" radicals.^{34,35} We would like to offer hereby a crude "memory-aid" to these substituent effects: The unshared electron pair and the spin seem to be fighting for living space around the oxygen (or nitrogen) radical. An electron-pair donor substituent Y will tend to keep the lone pair on the oxygen (by repulsion), and thus it will tend to increase the delocalization of the spin. In other words, a donor Y will stabilize the oxygen (or nitrogen) radical. Conversely, an acceptor Y will destabilize the oxygen (or nitrogen) radical. Certainly, this state of affairs is in direct contrast to carbon-radical chemistry which features stabilization by both donor and acceptor substituents.

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