The chlorine radical cation containing only the ^{35}Cl isotope was generated and trapped. This ion was allowed to react with various aromatic compounds. As with $^{35}Cl^+$, the main reaction is electron transfer from the aromatic compound to $^{35}Cl_2^{\bullet+}$. Transfer of a substituent to an aromatic compound with simultaneous release of a neutral species is a common gas-phase reaction.[16,17] Reaction of $^{35}Cl_2^{\bullet+}$ with an aromatic compound could behave in an analogous fashion (eq 3). However, this reaction was not observed in our study.

The electron-rich aromatic cation radicals of anisole and toluene subsequently react with residual $^{35/37}Cl_2$ to form chlorine addition products which exhibit a standard chlorine isotope pattern. The other aromatic compounds studied show no chlorine addition products. The spectra of electron-deficient aromatic compounds benzaldehyde and nitrobenzene are dominated by ions resulting from fragmentation of the aromatic radical cation. These results support the mechanism of SET followed by subsequent chlorine addition; chlorine transfer to a aromatic compound does not appear to be viable competitive mechanism.

In solution, many alkenes and dienes undergo electrophilic addition with chlorine without catalysis. We have found, in general, that alkenes and dienes[18] do not form any chlorine addition products with either $^{35}Cl^+$ or $^{35}Cl_2^{\bullet+}$ in the gas phase. 1-Acetoxy-1,3-butadiene and hexachloro-1,3-butadiene formed small amounts of chlorine addition products. Again, the two factors which affect the reactivity of alkenes and dienes with chloronium ion are the exothermicity of the charge transfer reaction and the ability of the electron donating substituents to stabilize the radical cation product. Resonance stabilization of the radical cation intermediate is necessary to increase the lifetime of this intermediate so that secondary reactions with neutral species can occur. Thus, addition does not generally follow the charge-transfer process. The mass spectra show a high degree of fragmentation even at "zero reaction time". This observed behavior also supports the proposed two-step mechanism.

As expected, $^{35}Cl^+$ and $^{35}Cl_2^{\bullet+}$ do not add directly to an aromatic compound in an electrophilic aromatic substitution process. Additionally, the aromatic chlorine addition product is not formed by transfer of $^{35}Cl^+$ from $^{35}Cl_2^{\bullet+}$. Our results indicate that the mechanism of chlorine addition in the gas phase involves two reactions resulting in a product similar to the σ-complex formed in solution. It is possible to explain the apparent substrate selectivity toward formation of the chlorine addition product based on thermodynamics and stability of the aromatic cation radical. It is also extremely interesting to observe the similarities in the mechanism of the usual chlorination of hexachloro-1,3-butadiene in solution phase observed by Olah[19] and in this gas phase study. In both cases, SET is the initial reaction followed by quenching of the radical cation by neutral species.

Supplementary Material Available: Procedures for calculating the heats of reaction (ΔH) and tables comparing known and calculated ΔH_fs for relevant compounds (18 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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A Self-Consistent and Cross-Checked Scale of Spin-Delocalization Substituent Constants, the $\sigma^{\bullet}_{JJ}$ Scale

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On the basis of the ^{19}F NMR data of substituted α,β,β-trifluorostyrenes and the rate constants of their thermal cycloaddition reactions, a self-consistent and cross-checked scale of spin-delocalization substituent constants $\sigma^{\bullet}_{JJ}$ is proposed for 21 para-substituents and for 10 meta-substituents. By means of adopting different ρ_{mb} values, three methods for the calculation of the $\sigma^{\bullet}_{JJ}$ values at five different temperatures and their averaged values are presented. It has been shown that at each temperature and within a range of ρ_{mb} values from −0.20 to −0.40 the same set of $\sigma^{\bullet}$ constants are obtained from these three methods. There are seven advantages to the $\sigma^{\bullet}_{JJ}$ approach, including the fact that the reaction is exceptionally clean, a tailor-made polar parameter σ_{mb} is used in the dual-parameter equation, and the validity of the approach is strongly supported by the meta substituent effect which is independent of the polar effect. Some radical reactions, EPR data of substituted benzyl radicals, and bond dissociation energies are reexamined by using the $\sigma^{\bullet}_{JJ}$ in conjunction with polar σ constants in dual-parameter equations.

Understanding structure–property relationships and reaction mechanisms is the soul of chemistry, and much has been gained by application of the Hammett-type polar substituent parameters σ^X, i.e., σ_P, σ_m, σ_R, σ_F, σ_α, ..., etc.[1]

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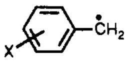
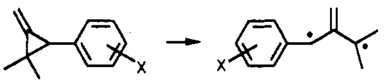
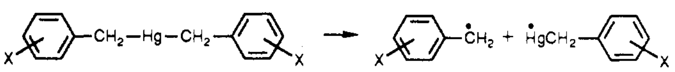
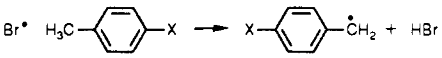
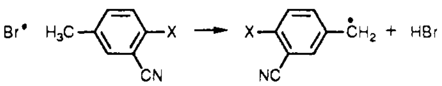
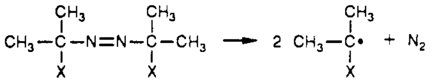
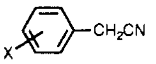
Table I. Different Approaches for Setting Up the $\sigma^\bullet$ Scale and Related Scales

designation	reaction or system	property measured	ref
Anrold's $\sigma^\bullet_\alpha$		hfc α-H	3b
Creary's $\sigma^\bullet_C$		rate constants	3c
Jackson's $\sigma^\bullet_J$		rate constants	3d
Fisher		rate constants	3e
Fisher (CN)'s $\sigma^\bullet_F$		rate constants	3e
Timberlake	 $CH_3-\underset{X}{\overset{CH_3}{C}}-N=N-\underset{X}{\overset{CH_3}{C}}-CH_3 \rightarrow 2\ CH_3-\underset{X}{\overset{CH_3}{C}}\bullet + N_2$	rate constants	3f
Bordwell's BDE		pK_{HA}, E_{ox}	3g
Viehe's RRS[a]	$RRS_H = 0, \frac{RRS_{Ph} + RRS_{vinyl}}{2} = 12$		3h

[a] Relative radical stabilization.

Radical chemists, however, have to face a much more formidable task because of the difficulty in separating polar (including resonance-polar) (σ^X) and spin-delocalization ($\sigma^\bullet$) effects which always come hand in hand. In the absence of measurable steric effects, if the transition state (TS) of the rate-determining step is not perfectly symmetrical, or is not such that polar effects greatly predominate over the spin-delocalization effect, then both effects will be expressed in the TS. Therefore, for structure–reactivity correlations the use of a dual-parameter equation, e.g., eq 1, appears to be appropriate. Consequently, the establishment of a reliable and rigorously checked $\sigma^\bullet$ scale has been sought.[2]

$$\log k_Y/k_H = \rho^X\sigma^X + \rho^\bullet\sigma^\bullet \qquad (1)$$

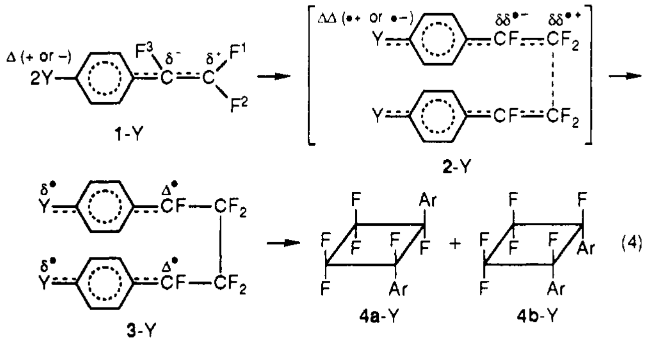
Extensive efforts have been dedicated to the setting up of $\sigma^\bullet$ scales, and results of these efforts have been thoroughly reviewed.[2,3] Among the various approaches, those of Arnold,[3b] Creary,[3c] Jackson,[3d] Fisher,[3e] and Viehe[3h] are of particular interest and are summarized in Table I. However, most approaches are not completely free from difficulties. For instance, in the single-parameter approaches of Arnold and Creary, polar effects are clearly manifested in the $\sigma^\bullet_\alpha$ and $\sigma^\bullet_C$ values for meta substituents (vide infra)[3c,4], i.e.

$$\sigma^\bullet_\alpha(\text{meta}) = -0.039\sigma_m + 0.0023,\ r = 0.962,\ n = 9 \qquad (2)$$

$$\sigma^\bullet_C(\text{meta}) = -0.21\sigma_m + 0.02,\ r = 0.964,\ n = 8 \qquad (3)$$

On the other hand, although both Fisher and Jackson have advocated dual-parameter approaches and made important contributions to the $\sigma^\bullet$ problem, Fisher's $\sigma^\bullet_F$ values for meta substituents[5] also seem to be related to polar effects,[6] and Jackson studied only a limited number of reactions. Furthermore, all previous $\sigma^\bullet$ constants for *p*-F, except that of Jackson, would suggest[3b,c,e] that the α-F of $FCH_2^\bullet$ should be a "spin-destabilizing" substituent, in direct contradiction to recent experimental measurements.[3k,7]

Our $\sigma^\bullet_{JJ}$ approach based on the thermal cycloaddition reaction (eq 4) of Y-substituted α,β,β-trifluorostyrenes, first communicated in part in 1984,[3a] is unique in that it possesses a number of advantageous features. They are as follows: (1) The reaction is exceptionally clean, no side reaction has ever been detected for the dimerization reaction of 32 para- and meta-substituted trifluorostyrenes in the temperature range (80–160 °C) used for the rate constant measurements. (2) The TS of this reaction has a "symmetry in polarity", and the degree of polarization of the π-bond in the TS is smaller than that of the ground state; thus there will be no additional polar interaction during the process of transition-state formation.[8,9] (3) The



(4)

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(8) We have already observed "extra polar interactions" in heterocycloaddition reactions between Y^1–TFS's and Y^2–TFS's, where Y^1 and Y^2 are donor and acceptor para-substituent groups.[9]

Table II. Values of $\sigma^{\bullet}_{JJ}$ for Para-Substitutents and $\sigma^{\bullet}_{m}$ for Meta-Substituents Based on Different ρ_{mb} Values (Parentheses) for Different Temperatures and the Averaged $\sigma^{\bullet}_{JJ}$ Constants Recommended for General Use

Y	110 °C (−0.38)	120 °C (−0.40)	140 °C (−0.30)	150 °C (−0.37)	160 °C (−0.30)	avg $\sigma^{\bullet}_{JJ}$	ref
H	0	0	0	0	0	0	3a
p-NMe$_2$	1.15	1.07	1.00	0.89	0.91	1.00 ± 0.11	16f
p-SMe	0.52	0.56	0.59	0.71	0.71	0.62 ± 0.09	16d
p-COMe	0.59	0.55	0.50	0.59	0.49	0.54 ± 0.05	16b
p-SOMe	0.53	0.47	0.47	0.48	0.54	0.50 ± 0.03	16f
p-Ph	0.49	0.49	0.44	0.45	0.46	0.47 ± 0.02	16f
p-CN	0.43	0.45	0.36	0.47	0.39	0.42 ± 0.04	16e
p-COOH	0.44	0.42	0.34	0.34	0.37	0.38 ± 0.05	16e
p-CONH$_2$	0.39	0.40	0.37	0.40	0.33	0.38 ± 0.03	16e
p-SO$_2$Me	0.37	0.35	0.34	0.40	0.42	0.38 ± 0.03	16f
p-NO$_2$	0.40	0.41	0.32	0.40	0.29	0.36 ± 0.06	16e
p-CO$_2$Me	0.32	0.34	0.30	0.38	0.32	0.33 ± 0.03	16e
p-SiMe$_3$	0.33	0.32	0.29	0.31	0.38	0.31 ± 0.02	16b
p-c-Pr	0.37	0.30	0.27	0.25	0.25	0.29 ± 0.05	16d
p-*t*-Bu	0.23	0.25	0.30	0.23	0.30	0.26 ± 0.04	16d
p-OMe	0.28	0.24	0.23	0.21	0.20	0.23 ± 0.03	3a
p-Br	0.24	0.23	0.21	0.25	0.24	0.23 ± 0.02	16b
p-Cl	0.24	0.22	0.19	0.22	0.22	0.22 ± 0.02	3a
p-Me	0.16	0.14	0.14	0.14	0.15	0.15 ± 0.01	3a
p-Et	0.17	0.15	0.14	0.16	0.14	0.15 ± 0.01	16c
p-CF$_3$	−0.004	−0.004	−0.03	−0.02	−0.003	−0.01 ± 0.01	3a
p-F	0.02	−0.03	−0.04	−0.01	−0.05	−0.02 ± 0.03	3a
m-Me	0	0	0	0	0	0	3a
m-Br	0.16	0.17	0.07	0.01	0.08	0.12 ± 0.05	11
m-*t*-Bu	0.09	0.09	0.10	0.15	0.12	0.11 ± 0.03	11
m-CN	0.10	0.14	0.11	0.12	0.09	0.11 ± 0.02	11
m-OMe	0.11	0.09	0.09	0.11	0.08	0.10 ± 0.01	11
m-CO$_2$Me	0.10	0.05	0.12	0.10	0.12	0.10 ± 0.03	11
m-F	0.05	0.04	0.02	0.04	−0.001	0.03 ± 0.02	11
m-NO$_2$	−0.03	0.01	−0.01	0.03	0.003	0.001 ± 0.02	11
m-Cl	−0.04	−0.03	−0.09	−0.04	−0.06	−0.05 ± 0.02	11
m-CF$_3$	−0.05	−0.06	−0.10	−0.06	−0.08	−0.07 ± 0.02	11

range of the rate constant is large enough for accurate evaluation of the differences in rate constant values, and yet small enough for us not to worry too much about the subtle possibility of the effect of differences in the timing of the transition-state formation. (4) On the basis of ^{19}F NMR data, we have already obtained a tailor-made polar σ^{X} scale, the σ_{mb} scale,[10] for the evaluation of the polar effect on this reaction. The evaluation is based on the assumption that the relative degree of polarization of the π-bond ($\delta\delta^{+}$, $\delta\delta^{-}$) in the TS's is proportional to that of the π-bond in the ground states (δ^{+}, δ^{-}). The σ_{mb} constants are direct measures of the degree of π-bond polarization of the ground state. To our knowledge, ours is the only dual-parameter approach with a tailor-made polar σ^{X} parameter. Other dual-parameter approaches would have to "adopt" a σ^{X}, e.g., σ^{+}, which might not be best suited to the particular correlation analysis. (5) Although contribution from the polar effect decreases along the reaction coordinate whereas contribution from the spin–delocalization effect increases, both effects are important at the TS of our cycloaddition reactions, as evidenced by comparing the relative $|\rho^{X}/\rho^{\bullet}|$ values calculated for the results of different approaches made by various authors (vide infra).[3] Presumably, a "balanced" polar/spin contribution is beneficial to the reliable separation of polar and spin effects. (6) Our approach, like some others,[3b] can also be double-checked by studying the behavior of meta-substituted trifluorostyrenes. If our approach is sound, then the $\sigma^{\bullet}_{m}$ values obtained for all the meta substituents should be (i) small but not necessarily naught and (ii), perhaps more importantly, not correlatable with any of the polar σ^{X} scales for the meta substituents (vide supra). This double-check test has already been passed.[11] (7) We have five sets of $\sigma^{\bullet}$ constants based on rate measurements at five temperatures. Thus, a rarely used cross-checking test is now applicable; i.e., if our approach is good, then, as expected, the five independently obtained $\sigma^{\bullet}$ scales should be completely correlatable. This expectation has been borne out by our results (vide infra). To our knowledge, no other σ scale has been cross-checked in this manner.

The present work introduces for the first time our recommended values of 32 $\sigma^{\bullet}_{JJ}$ substituent constants (see penultimate column of Table II), among them are 21 para-substituent $\sigma^{\bullet}_{JJ}$ values which are directly pertinent to the spin-delocalizing abilities of the α-substituents of methyl radicals, i.e., directly applicable to structure–property correlation studies, because the para position is homologous to the α-position of methyl radicals. Values of these $\sigma^{\bullet}_{JJ}$ constants are derived from about 150 averaged rate constants which are calculated from about 3000 experimental measurements performed in the last 12 years.[12] This paper discusses in some detail the various methods for evaluating the $\sigma^{\bullet}$ parameters and shows how the cross-checking mentioned above (seventh point of preceeding paragraph) has been tested. Finally, some applications of the $\sigma^{\bullet}_{JJ}$ scale will be discussed.

Results and Discussion

The $\sigma^{\bullet}_{JJ}$ Approach. The dual-parameter eq 5 was used in our approach to the $\sigma^{\bullet}_{JJ}$ scale. The thermal cyclo-

$$\log k_{Y}/k_{H} = \rho_{mb}\sigma_{mb} + \rho^{\bullet}\sigma^{\bullet}_{JJ} \qquad (5)$$

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[9] Ji, G. Z.; Shi, Y. Q.; Jiang, X. K. *Acta Chim. Sin.* **1988**, *46*, 1139; *Engl. Ed.* **1988**, 364.

[10] Ji, G. Z.; Jiang, X. K.; Zhang, T. H.; Yuan, S. G.; Yu, C. X.; Shi, Y. Q.; Zhang, X. L.; Shi, W. T. *J. Phys. Org. Chem.* **1990**, *3*, 643.

[11] Jiang, X. K.; Ji, G. Z.; Zhang, X. L. Guo, H. X. *Chin. J. Chem.*, in press.

[12] Our experiments were always run in duplicate sets. In each set at a specific temperature, the conversion was measured at 10–12 time intervals. For each set an averaged *k* based on these 10–12 measurements was calculated. The two *k* values were then averaged to give the final averaged *k*'s.

Table III. σ_{mb} Values[10]

substit	σ_{mb}	substit	σ_{mb}	substit	σ_{mb}
p-NMe$_2$	−0.96	*p*-CH$_2$=CH	0.03	*m*-Me	−0.20
p-MeO	−0.77	*p*-C$_6$H$_5$	0.06	*m*-*t*-Bu	−0.20
p-PhO	−0.46	*p*-Cl	0.11	*m*-Et	−0.15
p-c-Pr	−0.31	*p*-Br	0.13	*m*-MeO	−0.11
p-Me	−0.29	*p*-SiMe$_3$	0.14	*m*-Cl	0.12
p-F	−0.24	*p*-SOMe	0.19	*m*-COOMe	0.21
p-*t*-Bu	−0.22	*p*-COOH	0.31	*m*-F	0.23
p-SMe	−0.18	*p*-COOMe	0.48	*m*-Br	0.36
H	0	*p*-CF$_3$	0.49	*m*-CF$_3$	0.39
		p-SO$_2$Me	0.55	*m*-NO$_2$	0.69
		p-COMe	0.56	*m*-CN	0.89
		p-CN	0.86		
		p-NO$_2$	0.86		

dimerization of substituted α,β,β-trifluorostyrenes (1-Y) was chosen as the radical reaction model. In this reaction, 1-Y thermally cyclodimerizes in a head-to-head fashion via the 1,4-diradical intermediate 3-Y to form roughly equal amounts of *cis*- and *trans*-1,2-diphenylhexafluorobutanes (4-Y), as shown by eq 4.[13]

The ease of homolysis of the π-bond in 1-Y is dependent on the degree of polarization of the double bond as well as on the ability of the aryl rings to stabilize the diradical 3-Y. Obviously, substituents on the phenyl ring will not only affect the polarization of the π-bonds but also affect the ability of the aryl group to stabilize the radical intermediate 3-Y or the transition state 2-Y.

In substituted trifluorostyrenes (1-Y), the chemical shifts of F^1 and F^2, as well as the differences of the chemical shifts of F^3 and F^1 (δ_{3-1}) or F^3 and F^2 (δ_{3-2}), reflect the degree of polarization of the double bond in the 1-Y; thus polar substituent effects on the π-bond of 1-Y can be evaluated by the ^{19}F chemical shifts.

In fact, we can use eq 6, where $\Delta\delta_{3-1} = (\delta_{3-1})_Y - (\delta_{3-1})_H$, to define a polar substituent parameter σ_{mb} which reflects

$$\sigma_{mb} = 0.16\Delta\delta_{3-1} - 0.09 \qquad (6)$$

the ability of a certain substituent Y to polarize the π-bond of the corresponding 1-Y in the ground state.[10] Values of σ_{mb} constants are summarized in Table III. On the basis of the fact that the polarization of the π-bond always decreases along the reaction coordinate and that the range of rate constants (vide supra) for our reaction (eq 4) is relatively small, we can first make a plausible presumption that the polar effects of the substituents on the transition states parallel those on the ground states. This presumption, which is actually the only specific presumption we made for our $\sigma^{\bullet}_{JJ}$ approach, will naturally allow us to employ eq 5 for the calculation of $\sigma^{\bullet}_{JJ}$ constants from our data collected during the last 12 years (vide infra) and its credibility can be tested by the applicability of the $\sigma^{\bullet}_{JJ}$ scale to other clean radical reactions in the future.[14]

In eq 5, the term $\rho_{mb}\sigma_{mb}$ represents the contribution of polar effects of the substituents on this reaction, and the term $\rho^{\bullet}\sigma^{\bullet}_{JJ}$ represents the contribution of their spin delocalization effects. The value of $\rho^{\bullet}$ can be arbitrarily taken as unity for our $\sigma^{\bullet}_{JJ}$ scale. In the initial stage of development of our $\sigma^{\bullet}_{JJ}$ approach,[3a] we had to search for an operable or "reasonable" value for ρ_{mb}. We therefore made a tentative assumption that the spin-delocalizing effect of the *m*-methyl group on the benzylic radicaloid TS is negligible; i.e., the $\sigma^{\bullet}_{JJ}$ value of *m*-Me is practically zero, whereupon eq 5 becomes eq 7

Table IV. Correlation Analysis of $\sigma^{\bullet}_{JJ}$ with Other $\sigma^{\bullet}$ Scales

$\sigma^{\bullet}$	correlation coefficient (*r*)	*n*	ref
$\sigma^{\bullet}_{\alpha}$ (para + meta)	0.886	21	3b
$\sigma^{\bullet}_{\alpha}$ (para)	0.887	14	3b
$\sigma^{\bullet}_{c}$	0.897	12	3c
$\sigma^{\bullet}_{F}$	0.831	10	3e
$\sigma^{\bullet}_{J}$	0.750	10	3d
Viehe's RRS	0.780	21	3h

$$\rho_{mb} = \log (k_{m\text{-Me}}/k_H)\sigma_{mb} \text{ for } m\text{-Me} \qquad (7)$$

which yields ρ_{mb} values (parenthesized values in Table II) for the different temperatures, if the corresponding $k_{m\text{-Me}}$, k_H, and σ_{mb} values[10] are substituted into eq 7. Once a ρ_{mb} is adopted, for a particular temperature, all $\sigma^{\bullet}_{JJ}$ values at that temperature can be calculated by eq 8 if the *k* and

$$\sigma^{\bullet}_{JJ} \text{ for Y} = \log k_Y/k_H - \rho_{mb}\sigma_{mb} \text{ for Y} \qquad (8)$$

σ_{mb} values of Y's have been accurately measured. They are listed in Table II together with the averaged value recommended for general use in the second to last column.

Interestingly, we found later that our $\sigma^{\bullet}_{JJ}$ scale is not sensitive to the exact ρ_{mb} value we choose, as long as it is within a certain range, e.g., from −0.20 to −0.40. For instance, we made another tentative assumption that $\sigma^{\bullet}_{JJ}$(m-NO$_2$) is equal to zero (instead of $\sigma^{\bullet}_{JJ}$(m-Me) = 0) and another five ρ_{mb}(m-NO$_2$) values for the five temperatures can be calculated. It was found then that another set of $\sigma^{\bullet}_{JJ}$ constants based on ρ_{mb}(m-NO$_2$) is completely correlatable with the $\sigma^{\bullet}_{JJ}$ scale based on ρ_{mb}(m-Me). Therefore, for our $\sigma^{\bullet}_{JJ}$ approach, it is not essential to assume that $\sigma^{\bullet}_{JJ}$(m-Me) = 0, and as long as we use ρ_{mb} values within an operable range from −0.20 to −0.40, basically the same set of $\sigma^{\bullet}_{JJ}$ will be obtained. The above statement has been cross-checked by two other methods of calculation. (1) If instead of using five ρ_{mb} values for five temperatures, we use only one averaged ρ_{mb} value of −0.35 together with all the rate constants of five temperatures, we can again obtain six sets of $\sigma^{\bullet}_{JJ}$ values that are completely correlatable with those of Table II. (2) We can use a single ρ_{mb} value of −0.30 (previously used for data at 140 °C) and obtain similar results. Notably, we tried these two methods of calculation because we were worried at first about the fact that our initial method of calculation (using five ρ_{mb}'s) depended heavily on the high precision of kinetic measurements of only one substituent (*m*-Me). Summing up all the above-mentioned observations, we can now conclude that we can use any ρ_{mb} values from −0.20 to −0.40 and obtain the same set of $\sigma^{\bullet}_{JJ}$ constants. In other words, we have now eliminated the necessity of adopting the tentative assumption of $\sigma^{\bullet}_{JJ}$ for *m*-Me = 0 (vide supra). As shown in Table II, the standard deviation of the $\sigma^{\bullet}_{JJ}$ values for most of the substituents are less than 0.05 units. This indicates that the $\sigma^{\bullet}_{JJ}$ values are little affected by the temperature and the precision (or repeatability) of the $\sigma^{\bullet}_{JJ}$ values is relatively good. If we cross-correlate the $\sigma^{\bullet}_{JJ}$ values of each temperature with each other, we will find that the correlatabilities are also good. In other words, rate data collected at five temperatures form a self-consistent whole; they conform to one pattern, i.e., one $\sigma^{\bullet}_{JJ}$ scale. To our knowledge, no Hammett-type σ parmeters have been cross-checked in this manner even though such a result might have been expected. Finally, we would like to recommend the averaged $\sigma^{\bullet}_{JJ}$ values of the second to last column of Table II as the $\sigma^{\bullet}$ values to be used in future applications. Certainly, this $\sigma^{\bullet}_{JJ}$ parameter does not correlate with any of the polar substituent parameters. The

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[14] In fact, we have most recently very successfully applied the combination of $\sigma^{\bullet}_{JJ}$ and σ_{mb} constants (eq 5) to two exceptionally clean radical addition reactions to 24 substituted styrenes, and in the meantime demonstrated that single parameter correlations with any of the polar σ^X constants do not work.

Table V. Application of $\sigma_{\mathrm{JJ}}^{\bullet}$ Constants to Other Approaches by Using eq 9

approach[a]	σ^{X}	$\rho^{\bullet}$	ρ^{X}	$\lvert\rho^{\mathrm{X}}/\rho^{\bullet}\rvert$	R[b]	F[c]	n[d]	ref
Jiang and Ji	σ_{mb}	1.0	−0.30	0.30	(1.000)			this work
Arnold's a_1	σ^+	−1.83	0.06	0.03	0.954	50	13	3b
Creary	σ^+	0.83	0.08	0.10	0.924	22	12	3c
Jackson	σ^+	0.42	−0.41	0.98	0.971	33	7	3d
Fisher	σ^+	0.30	−1.44	4.8	0.995	376	9	3e
Fisher (CN)	σ^+	0.80	−1.21	1.51	0.984	108	9	3e
Bordwell's ΔAOP	σ^+	−1.28	1.63	1.27	0.998	710	7	3g
Viehe's RRS	σ^+	16.80	2.82	0.18	0.956	30	18	3h
Timberlake	σ^+	14.40	1.71	0.12	0.931	20	9	3i

[a] Cf. Table I. [b] Correlation coefficient. [c] F-test value. [d] Number of data.

results of cross correlation of $\sigma_{\mathrm{JJ}}^{\bullet}$ values with other $\sigma^{\bullet}$-type parameters are shown in Table IV. It shows that the $\sigma_{\mathrm{JJ}}^{\bullet}$ scale is different from other $\sigma^{\bullet}$ scales.

Other Evidence for the Reliability of the $\sigma_{\mathrm{JJ}}^{\bullet}$ Approach. One weakness of any single-parameter approach is that even though the spin-delocalization effect greatly predominates over the polar effect (ca. $\lvert\rho^{\mathrm{X}}/\rho^{\bullet}\rvert$ ratios in Table V), for a few substituents with very strong polar effect, the polar effect will still be reflected in the measurement of a certain property (rate or EPR) of that molecule with this particular substituent. In other words, a completely clean separation of spin-delocalization effect from polar effects may not have been achieved. For instance, Arnold's elegent works yielded the $\sigma_{\alpha}^{\bullet}$ scale, perhaps the most important $\sigma^{\bullet}$ scale now available. Arnold pointed out, however, that his $\sigma_{\alpha}^{\bullet}$ constants for the meta-substituents correlate very well with Hammett's polar constants (see eq 2).[4] Clearly, the same mechanism that allows the expression of polar effect of meta-substituents should be also operating for the para-substituents, except that for most all of them the polar effects are overpowered by the spin-delocalizing effects, as implicated by the $\lvert\rho^{\mathrm{X}}/\rho^{\bullet}\rvert$ value of 0.03 (cf. Table V). However, two substituents, i.e., p-F and p-CF_3, cannot do this because their spin-stabilizing abilities are extremely weak, but they are not necessarily "destabilizing" as the $\sigma^{\bullet}$ values of Arnold, Creary, Fisher, and Viehe might have implied.[2] In fact, it has already been experimentally demonstrated that the α-F in the $CFH_2^{\bullet}$ radical is weakly stabilizing.[3j,7] This very weak spin-delocalizing effect is expected to be attenuated by the benzene ring in the p-fluorobenzyl radicals, as our near-zero value for the $\sigma_{\mathrm{JJ}}^{\bullet}$ of p-F might have suggested. Another interesting observation is that our $\sigma_{\mathrm{JJ}}^{\bullet}$ values for p-SOMe and p-SO_2Me differ quite a bit, in accordance with the expectation that the $\sigma^{\bullet}$ values should be related to the bond orders of the S–O bonds, whereas the $\sigma^{\bullet}$ values of these two substituents evaluated by both Arnold and Creary are almost the same.[3c,15]

The arguments presented above would suggest another good test for the trustworthiness of our $\sigma_{\mathrm{JJ}}^{\bullet}$ approach; namely, if our approach is sound, then the $\sigma_{\mathrm{JJ}}^{\bullet}$ values for meta-substituents should, unlike those of the previous workers (vide supra), (1) not be correlatable with any of the Hammett-type polar σ^{X}'s and (2) be all very small but not necessarily zero. Both criteria of this test has now been met.[11]

Application of the $\sigma_{\mathrm{JJ}}^{\bullet}$ Scale. If the spin delocalization parameter $\sigma_{\mathrm{JJ}}^{\bullet}$ scale is reliable and truly reflects the ability of the substituents to delocalize the spin, then in combination with the polar substituent parameter σ^{X}, this scale should be able to correlate reliable kinetic or thermodynamic data of radical reactions and systems.[14] Furthermore, the relative importance of polar and spin delocalization effects in the radical reactions or systems may be assessed by comparing the relative magnitudes of the $\lvert\rho^{\mathrm{X}}/\rho^{\bullet}\rvert$ ratios derived from eq 9.

$$\log k_{\mathrm{Y}}/k_{\mathrm{H}} = \rho^{\mathrm{X}}\sigma^{\mathrm{X}} + \rho^{\bullet}\sigma_{\mathrm{JJ}}^{\bullet} \qquad (9)$$

In eq 9, a polar σ^{X} that gives the best correlation is used. The correlation results and the $\lvert\rho_{\mathrm{X}}/\rho^{\bullet}\rvert$ ratios are shown in Table V. Clearly, our $\sigma_{\mathrm{JJ}}^{\bullet}$ scale together with some suitable polar substituent parameter σ^{X} can be used satisfactorily to correlate Creary's, Jackson's, and Fisher's kinetic data, Bordwell's bond dissociation energy of 4-substituted aryl acetonitriles, Arnold's EPR data, and Viehe's data. It appears that the most interesting feature of Table V is the relative magnitudes of the $\lvert\rho^{\mathrm{X}}/\rho^{\bullet}\rvert$ ratios, which reflects the relative importance of the polar and spin-delocalization effects. For instance, they show that Arnold's $\sigma_{\alpha}^{\bullet}$ constants for the para substituents are almost free from polar effects (except for F and CF_3, vide supra). The fact that Fisher's reaction of substituted toluene without the m-CN has a $\lvert\rho^{\mathrm{X}}/\rho^{\bullet}\rvert$ ratio of 4.8 is also noteworthy. Finally, it is worthy of note that both Arnold's and Creary's data are well-correlated by the dual-parameter approach with our $\sigma_{\mathrm{JJ}}^{\bullet}$ scale.

Experimental Section

Instruments. Boiling and melting points were not corrected. ^{19}F NMR spectra were obtained at 56 MHz on a Varian EM-360 or at 188 MHz on a Varian XL-200, with trifluoroacetic acid as the external standard. UV/vis absorption spectra were taken on Perkin-Elmer 559. MS were taken on Finnigan 4021 or Shimadzu QP-1000 at 70 eV in EI mode. IR spectra were recorded on a Shimadzu IR-400. GC analysis were done on a Shanghai 102 GD gas chromatograph with a flame ionization detector.

Kinetic Measurements. Rate constants of the thermal cyclodimerization of 1-Y's in n-hexane in the temperature range of 110–160 °C were measured by previously described methods.[12,16]

Preparation of p-(Dimethylamino)-α,β,β-trifluorostyrene (1-NMe_2).[12f] A solution of 32 g (0.16 mol) of p-(dimethylamino)bromobenzene in 50 mL of THF was added to a mixture of 3.85 g (0.16 mol) of Mg in 50 mL of THF. After all the bromide had been added, stirring and refluxing were continued until the Mg disappeared. The solution was transferred to a 500-mL stainless steel reactor, which was cooled in a dry ice–acetone bath and evacuated; tetrafluoroethene (48 g, 0.48 mol) was then added. In a water bath, the horizontally placed reactor was shaken at 50 °C for 4 h. After the solution was cooled, excess C_2F_4 was released and the liquid was hydrolyzed with ice–water, extracted with ether, washed to neutral with water, and dried over anhydrous sodium sulfate. After the solvents were removed, the crude product was obtained by column chromatography on silica gel with 3:1 petroleum ether (bp 30–60 °C)/ether as the eluent. Further purification was accomplished by preparative gas chromatography (7.5% OV-101): ^{19}F NMR (n-hexane) δ 29.35 (F^1),

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44.36 (F^2), 100.05 (F^3) ppm; J 83.0 (J_{12}); 32.0 (J_{13}); 109.9 (J_{13}) Hz. Anal. Calcd for $C_{10}H_{10}NF_3$: C, 59.70; H, 5.01; N, 6.96; F, 28.33. Found: C, 59.56; H, 4.96; N, 7.03; F, 28.60.

Preparation of *p*-Phenyl-α,β,β-trifluorostyrene (1-Ph).[16f] The procedure was similar to that described previously for the preparation of 1-NMe_2. The crude product (21.0 g, 45%) was obtained from 46.6 g of 4-bromobiphenyl. Purification of the product was performed by column chromatography on silica gel with petroleum ether as the eluent: mp 62.5–64 °C. IR (KBr) 1745, 1275, 1140, 1110, 830, 755, 714, 685, cm^{-1}; ^{19}F NMR (THF) δ 24.53 (F^1), 39.64 (F^2), 101.63 (F^3) ppm; J 73.9 (J_{12}), 33.15 (J_{13}), 108.80 (J_{23}) Hz; UV (EtOH) λ_{max} 267 nm. Anal. Calcd for $C_{14}H_9F_3$: C, 71.79; H, 3.87; F, 24.33. Found: C, 71.88; H, 3.82; F, 24.10.

Preparation of *p*-(Methylsulfinyl)- and *p*-(Methylsulfonyl)bromobenzenes.[16f,19] *p*-Bromothioanisole (20.12 g, 0.1 mol) was dissolved in 100 mL of acetic acid, 10 mL of 30% hydrogen peroxide solution was added, and the solution was then refluxed for 4 h. After removal of the solvent, crude products were separated by column chromatography on silica gel with petroleum ether as the eluent. *p*-(Methylsulfonyl)bromobenzene was first obtained with 1:5 ethylacetate/petroleum ether as the eluent, and then *p*-(methylsulfinyl)bromobenzene, mp 86–87 °C (lit.[17] mp 86–87 °C), was collected with 2:5 ethylacetate/petroleum ether as the eluent. *p*-(Methylsulfonyl)bromobenzene (mp 104–105 °C, cf. ref 18) was characterized by the following analytical data: MS m/z 236 (M + H, 78), 234 (M^+, 89), 221 (42), 219 (73), 173 (81), 171 (100); ^1H NMR ($CDCl_3$) δ 7.87 (s, 4 H), 3.00 (s, 3 H) ppm; IR (KBr) 1570, 1462, 1385, 1305, 1270, 1145, 1085, 966, 768 cm^{-1}. Anal. Calcd for $C_7H_7BrO_2S$: C, 35.76; H, 3.00; Br, 33.99; S, 13.64. Found: C, 35.27; H, 2.72; Br, 34.64; S, 13.76.

Preparation of *p*-(Methylsulfinyl)-α,β,β-trifluorostyrene (1-SOMe).[16f,19] Trifluorovinylzinc bromide solution was prepared by the method of Coulson.[20] This zinc reagent (100 mL), 13.2 g of *p*-(methylsulfinyl)bromobenzene (60 mmol), and 1.38 g of $Pd(PPh_3)_4$ (1.2 mmol) were added into a dry 500-mL flask containing a magnetic stirbar. The reaction mixture was stirred and heated at 70 °C for 1 h. At this time, ^{19}F NMR analysis indicated that the conversion was complete. The excess trifluorovinylzinc reagent was hydrolyzed with 150 mL of 5% aqueous HCl. The mixture was extracted with petroleum ether (3 × 100 mL). After the solvent was evaporated, the crude product was column chromatographed on silica gel with petroleum ether as the eluent to yield 1.0 g of product (7.7%): mp 60–62 °C. MS m/z 221 (24), 220 (47), 205 (69), 204 (100), 173 (27), 157 (20), 145 (19); IR (KBr) 2976, 1755, 1290, 1150, 1105 cm^{-1}; ^{19}F NMR (THF) δ 22.73 (F^1), 37.30 (F^2), 100.63 (F^3); J 76.0 (J_{12}), 38.0 (J_{13}), 120.0 (J_{23}) Hz; UV (EtOH) λ_{max}, 259.4 nm. Anal. Calcd for $C_9H_7F_3OS$: C, 49.09; H, 3.20; F, 25.88; S, 14.57. Found: C, 48.94; H, 2.93; F, 26.01; S, 14.82.

Preparation of *p*-(Methylsulfonyl)-α,β,β-trifluorostyrene (1-SO_2Me).[16f] The procedure was similar to that described previously for the preparation of **1-SOMe**. From 4.0 g of *p*-(methylsulfonyl)bromobenzene was obtained 2.4 g (60%) of the product: mp 77–78 °C; MS m/z 237 (31), 236 (97), 204 (31), 173 (100), 157 (87), 145 (50); IR (KBr) 2990, 1755, 1340, 1146, 1107 cm^{-1}; ^{19}F NMR (THF) δ 20.83 (F^1), 35.33 (F^2), 101.00 (F^3) ppm; J 70.0 (J_{12}), 40.0 (J_{13}), 120.0 (J_{23}) Hz; UV (EtOH) λ_{max}, 254 nm. Anal. Calcd for $C_9H_7F_3O_2S$: C, 45.77, H, 2.99; F, 24.13; S, 13.57. Found: C, 45.27; H, 2.78, F, 24.72; S, 13.45.

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Registry No. 1-NMe_2, 134959-15-2; 1-Ph, 6999-04-8; 1-SOMe, 143307-87-3; 1-SO_2Me, 143307-88-4; *p*-$MeSOC_6H_4Br$, 934-71-4; *p*-$MeSO_2C_6H_4Br$, 3466-32-8; *p*-$Me_2NC_6H_4Br$, 586-77-6; $F_2C{=}CF_2$, 116-14-3; MeS-*p*-C_6H_4Br, 104-95-0; $F_2C{=}C(F)ZnBr$, 105417-08-1.

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Notes

Anomeric Effect and Hardness

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It has been observed that in reactions of the general type exemplified in eq 1, for all combinations of X, Y = F, OH and NH_2, the right hand side (RHS) of the equation is thermochemically more stable than the left hand side (LHS).[1] The stabilization on the RHS has been attributed

$$CH_3X + CH_3Y = CH_4 + XCH_2Y \tag{1}$$

to a special type of stereoelectronic effect operating in XCH_2Y compounds which is generally called the "anomeric effect". Some examples of reaction 1 are given in Table I (entries i–vi). However, the central atom can also be an element other than carbon,[1-3] as shown in example vii in Table I. Molecular orbital studies at the ab initio level implicate $n(X) \rightarrow \sigma^*(C{-}Y)$-type interactions as being responsible for the anomeric effect. Such interactions are expected to shorten the C–X bond, lengthen the C–Y bond, and widen the X–C–Y angle, all of which have been confirmed experimentally.[1-3] In fact, Brockway's observation[4] that C–F bonds are shortened by 0.06 Å on going from CH_3F to CF_4 could be said to be the first recognition of the anomeric effect. However, there are other reactions (examples viii–xviii in Table I) in which the anomeric effect is also revealed. It should be noted that in each of the reactions given in Table I, the number of bonds of each type is preserved.

Recently Pearson has tried to explain the anomeric effect in terms of "hardness".[5] The hardness (η) of a species is defined by eq 2 where IP and EA are the ionization

$$\eta = (IP - EA)/2 \tag{2}$$

potential and electron affinity of the species, respectively. In molecular orbital terms, this means that for a closed-

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