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In Search of the Spin-Delocalization Effect from the Correlation Analysis of Relative Rates of the Trichloromethyl-Bromo-Addition Reactions to Fourteen p-Y-Substituted Phenylacetylenes

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Abstract: A rigorous procedure was applied to the measurement of the relative rates, i.e., $k_r(Y) = k_Y/k_H$, of trichloromethyl-bromo-addition reactions to fourteen p-Y-substituted phenylacetylenes (**1-Y**, with **Y** = **F**, **Cl**, **Br**, **Me**, **t-Bu**, **OMe**, **SMe**, **SiMe$_3$**, **CF$_3$**, **CN**, **NO$_2$**, **SOMe**, **COMe** and **CO$_2$Me**). The reaction was run in cyclohexane under nitrogen atmosphere at 65±0.5°C. All products were derived from the intermediate $YC_6H_4\dot{C}{=}CHCCl_3$ adduct radicals. Correlation analysis of these rate data seems to suggest that both a polar and a spin-delocalization effect are operating at the transition state.

INTRODUCTION

In recent years, we have developed a rigorous kinetic methodology for measuring the relative rates of radical reactions and for solving the question of whether the single-parameter equation or the dual-parameter equation should be applied.[1, 2] It has been found that the dual-parameter equation is needed for the correlation analysis of radical addition reactions to styrenes and α-methylstyrenes,[2a,b] while the single-parameter equation is good enough for the correlation analysis of the hydrogen-atom abstraction reaction of isopropylbenzenes.[2c] In the latter case, however, the dual-parameter equation seems to improve the correlation and the existence of the spin effect may be revealed by examination of the individual and total deviations from the regression lines.[2c] Consequently, an urgent task would be to find out whether the triple bond in phenylacetylenes behaves just like the double bond in styrenes, or rather, the aforesaid triple bond behaves in a manner similar to the benzylic C-H bonds. The latter possibility was visualized because of the consideration of the difference between the nature of the sp-carbon and that of the sp^2-carbon, e.g., the difference in electrophilicity. Therefore, it would be highly interesting and worthwhile to study the substituent effects on the trichloromethyl-bromo-addition reactions to p-Y-substituted phenylacetylenes (**1-Y**) by our newly established rigorous kinetic methodology.[2]

On the question of whether the single-parameter equation or the dual-parameter equation should be used for the correlation analysis in radical chemistry, we are inclined to formulate our views as follows.[2d] In the absence of measurable steric effects, the chemical and spectral properties of radical or radicaloid species are always affected, albeit to different degrees, by both polar and spin-delocalization effects. Therefore, in correlation analyses of these properties (designated as variable in eq 1 to eq 3), the applicability of the dual-parameter eq 3 should always be tested. In these equations, $\rho^x\sigma^x$ and $\rho^{\cdot}\sigma^{\cdot}$ respectively stand for the contributions of the polar and spin-delocalization effects. The $|\rho^x/\rho^{\cdot}|$ ratio may serve as a rough measure of the relative importance of the polar effect and the spin effect.[1a, 1c] For a more direct comparison of various data, it might be preferable to use the same ρ^x and $\rho^{\cdot}$ in this ratio, e.g., use ρ_{mb} and $\rho_{JJ}^{\cdot}$ values derived from the application of σ_{mb} and $\sigma_{JJ}^{\cdot}$ scales, or, if $(\sigma_p + \sigma_{JJ}^{\cdot})$ yields the best correlation, use also ρ_p and $\rho_{JJ}^{\cdot}$ values derived from the application of σ_p and $\sigma_{JJ}^{\cdot}$ scales. In general, four categories of possible circumstances may exist. (i) When both polar and spin effects are important, the $|\rho^x/\rho^{\cdot}|$ values might fall in the range of (very) roughly 0.2 to 0.8, e.g., in radical additions to, and fluorescence spectra of, styrenes.[2a-b, 2f] Under these circumstances, the necessity of using the dual-parameter eq 3 can be easily established because it yields much better correlation results than those of single-parameter equations. (ii) When polar effects dominate, this ratio might be around or greater than unity, e.g., in hydrogen-atom abstraction reactions and EPR data of some phenyl nitroxides.[2c, 2e, 2i] Under these circumstances, using eq 3 instead of eq 1 may not improve, or only slightly improve, the correlation result, and the necessity of applying eq3 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 data from the regression lines of eq 1 and eq 3. A case in point is the hydrogen-atom abstraction reaction of isopropylbenzenes, or the EPR of disubstituted diphenyl nitroxides.[2c] (iii) When spin-delocalization effect dominates, then eq 2 easily applies, and the use of eq 3 does not improve or does not greatly improve the correlation result. Very recently discovered examples are the UV spectra of some aromatic compounds, such as styrenes and phenylacetylenes, etc.[2d, 2g] (iv) When there are other complicating and interacting factors or effects, as pointed out by previous workers for some of the UV studies, then none of the three equations may be successfully applied.[2d]

$$\text{variable} = \rho^x\sigma^x + \text{constant} \qquad (1)$$

$$\text{variable} = \rho^{\cdot}\sigma^{\cdot} + \text{constant} \qquad (2)$$

$$\text{variable} = \rho^x\sigma^x + \rho^{\cdot}\sigma^{\cdot} + \text{constant} \qquad (3)$$

Since the transition states of all radical reactions should possess some degree of radical character, we might expect that reliable rate data of all types of radical reactions in the absence of measurable steric effects could be correlated by the dual-parameter eq 4, rather than by the single-parameter eq 5. The $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ ratio

$$\log k_Y/k_H = \rho^x\sigma^x + \rho^{\cdot}\sigma^{\cdot} \tag{4}$$

$$\log k_Y/k_H = \rho^x\sigma^x \tag{5}$$

has been found to be 0.35 for the radical dimerization of substituted trifluoro-styrenes,[1a] 0.42 for the $CCl_3\cdot$ radical addition to styrenes,[2a] 0.37 for bromine atom addition to methylstyrenes,[2b] and 1.14 for the hydrogen-atom abstraction reaction of isopropylbenzenes ($|\rho_p/\rho_{JJ}^{\cdot}| = 2.01$).[2c] The above mentioned $|\rho^x/\rho^{\cdot}|$ ratios were all derived from a truly rigorous kinetic methodology which fulfilled the following requirements.[1, 2] (1) the measured rate should be the rate of the elementary step under study; (2) all products should be derived from the same measured step, thus it would be possible to measure accurately the k_Y/k_H ratios by only monitoring the $\ln\varphi_Y / \ln\varphi_H$ ratios, where φ represents the mole fraction of unreacted substrate at a particular time t, without worrying about the relative amounts of the products; (3) a rigorous procedure should be followed, for example, several (e.g. 9-12) measurements of the relative rates [$k_Y/k_H = k_r(Y)$] are performed over a reasonably wide range of the degree of conversion (extent of reaction), which can be inversely expressed in terms of φ values. The reliability of this kinetic methodology can be evaluated from the deviations of the 9-12 independently measured $k_r(Y)$ values from the averaged value (either the arithmetic average or that obtained from the regression line, see Experimental); and (4) at least 11-12 para substituents with well-distributed electronic properties should be used. Although fine works have been done previously on radical addition reactions to carbon-carbon triple bond,[3] to our knowledge there exist no $k_r(Y)$ data which are derived from a methodology that fulfills all the above-mentioned requirements. The present work, therefore, aims to address this problem.

We have chosen the trichloromethyl-bromo-addition reactions of p-Y-substituted phenylacetylenes (**1-Y**) with CCl_3SO_2Br as the addendum, as the system for our study. It will be shown that for **1-H**, the reaction follows eq 6 to eq 12 described in the Scheme.

Scheme

$$CCl_3SO_2Br \longrightarrow Br\cdot + CCl_3SO_2\cdot \tag{6}$$

$$CCl_3SO_2\cdot \longrightarrow CCl_3\cdot + SO_2 \tag{7}$$

$$\underset{\textbf{1-H}}{Ph\text{-}C\equiv CH} + CCl_3\cdot \longrightarrow \underset{\textbf{2-H}}{Ph\text{-}\dot{C}{=}CH\text{-}CCl_3} \tag{8}$$

$$\textbf{2-H} + CCl_3SO_2Br \longrightarrow \underset{\textbf{3-H}}{Ph\text{-}CBr{=}CHCCl_3} + CCl_3SO_2\cdot \tag{9}$$

$$\textbf{2-H} + CCl_3SO_2Br \longrightarrow \underset{\textbf{4-H}}{Ph\text{-}CCl{=}CHCCl_3} + \cdot CCl_2SO_2Br \tag{10}$$

$$\textbf{2-H} \xrightarrow{\text{H-abstraction from solvent}} \underset{\textbf{5-H}}{\text{Ph-CH=CHCCl}_3} \qquad (11)$$

$$\begin{array}{ccc} \text{Ph-CX=CH-CCl}_3 & \xrightarrow{\text{trace } H_2O} & \text{Ph-CX=CHCOOH} \\ \textbf{3-H, 4-H, 5-H} & & \textbf{6-H, 7-H, 8-H} \\ (\text{X=Br, Cl , H}) & & (\text{X=Br, Cl , H}) \end{array} \qquad (12)$$

In short, the above reactions can be described by eq 13.

$$\begin{array}{ccccccccc} \textbf{1-H} + \text{CCl}_3\text{SO}_2\text{Br} & \xrightarrow{65\pm0.5°\text{C, 18h}} & \textbf{1-H} & + & \text{Ph-CBr=CHCCl}_3 & + & \text{Ph-CCl=CHCCl}_3 & + & \text{Ph-CH=CHCCl}_3 \\ & 97.3\% & (21.0\%) & & \textbf{3-H}\ (65.0\%) & & \textbf{4-H}\ (3.5\%) & & \textbf{5-H}\ (2.8\%) \end{array}$$

$$\begin{array}{cccccc} + & \text{Ph-CBr=CHCOOH} & + & \text{Ph-CCl=CHCOOH} & + & \text{Ph-CH=CHCOOH} \\ & \textbf{6-H}\ (3.2\%) & & \textbf{7-H}\ (1.0\%) & & \textbf{8-H}\ (0.8\%) \end{array} \qquad (13)$$

EXPERIMENTAL SECTION

Boiling-points and melting-points were uncorrected. ^{1}H NMR spectra were obtained at 60MHz on a Varian EM-360A spectrometer with TMS as the external standard. IR spectra were recorded on a Shimadzu IR-440 spectrometer. Mass Spectrometry (MS) was carried out using a HP5989A MS instrument. GC analysis were performed on a HP5890 Gas Chromatography with nitrogen as the carrier gas.

Typical GC conditions were : oven temperature: from 50 to 250°C at a rate of 10°C/min; injection temperature: 260°C; detection temperature: 220°C; and carrier gas pressure: 380 kpa.

Commercial cyclohexane and $CF_2ClCFCl_2$ (F-113) were washed with conc. H_2SO_4 and H_2O, dried over $CaCl_2$ for several days and distilled prior to use.

The addendum $\mathbf{CCl_3SO_2Br}$ was prepared as described previously.[2a, 4]

Phenylacetylene (**1-H**) was purchased from Fluka Co. and vacuum-distilled before use (50 - 52°C / 30 torr). Acetylenes **1-Ys** with **Y=Cl**, **Br**, **t-Bu**, **Me**, **OMe**, **CN** and **F** were prepared according to a previously described method.[5] Acetylenes **1-Ys** with **Y** = $\mathbf{SiMe_3}$, $\mathbf{NO_2}$, **COMe**, **SMe**, $\mathbf{NMe_2}$, $\mathbf{CF_3}$ and $\mathbf{CO_2Me}$ were prepared by procedures[6, 7] derived from the well-known Heck reaction.[8] The sulfoxide **1-SOMe** was prepared from **1-SMe** by $NaIO_4$ oxidation.[9]

All **1-Y** substrates are known compounds and were further identified by **^{1}H NMR**, **IR** and **MS** spectroscopy. Boiling points or melting points of **1-Ys** prepared in our lab are as follows: **1-Cl**, mp: 42-44°C (lit.[10] 43.5-44°C); **1-Br**, mp: 64-65°C (lit.[10] 63.5-63.7°C); **1-t-Bu**, bp: 68-69°C / 2 torr (lit.[11] 67°C /1.7torr); **1-Me**, bp: 164-166°C (lit.[10] 168°C); **1-OMe**, bp: 86-88°C / 9 torr (lit.[12] 73-74°C / 2 torr); **1-CN**, mp: 154-155°C (lit.[12] 153°C); **1-F**, bp: 45-49°C / 6.5 torr (lit.[13] 34-35°C / 10 torr); **1-SiMe$_3$**, bp: 72-75°C / 4 torr (lit.[14] 65-66°C / 2.5 torr); **1-NO$_2$**, mp: 148-149°C (lit.[13] 149-150°C) ; **1-COMe**, mp: 67.5-68.5°C (lit.[7] 69 - 70°C); **1-CF$_3$**, bp: 58-60°C /30torr (lit.[12] 47 - 48°C / 20 torr); **1-CO$_2$Me**, mp: 92 - 93°C (lit.[6] 92.5 -93.5°C). (**1-SMe**[12] and **1-SOMe** were viscous compounds which could not be vacuum distilled).

Reaction of 1-H with CCl_3SO_2Br

In a three-necked round bottom flask (100ml), a solution of **1-H** (5 mmol), **CCl_3SO_2Br** (20 mmol) and internal GC standard (150 μl) in cyclohexane (50 ml) was vigorously stirred at 65±0.5°C under nitrogen atmosphere. After 18 h, the crude reaction solution was analysed by GC, seven compounds, i.e., **1-H**, **3-H**, **4-H**, **5-H**, **6-H**, **7-H** and **8-H**, were detected (eq 14). These were separated by chromatography and identified by ^{1}H NMR, IR and MS spectra. The yields were found to be: **1-H**, 21.0%; **3-H**, 65.0%; **4-H**, 3.5%; **5-H**, 2.8%; **6-H**, 3.2%; **7-H**, 1.0% and **8-H**, 0.8% (total yield 97.3%).

Kinetic competition procedure[2a-c]

In a three-necked round bottom flask (25 ml), a solution of **1-Y** (1 mmol), **1-H** (1 mmol), **CCl_3SO_2Br** (8 mmol) and internal GC standard (30-40 μl) in cyclohexane (15 ml) was vigorously stirred at 65±0.5°C under nitrogen atmosphere for eighteen to twenty-four hours until the degree of conversion of **1-H** or **1-Y** reached 50% (φ = 0.5) to 90% (φ = 0.1). During this time, nine to twelve samples (about 0.2ml each) were taken, usually at t = 1/12, 0.5, 1.0, 2.0, 4, 6, 8, 10, 12, 14, 16 and 18 hour intervals, and immediately injected into dry-ice-cooled tubes. They were sealed and then analyzed by GC.

GC internal standards were chosen according to the requirements of convenient retention times and no interference with the integration of substrate and product GC peaks. The internal standards used were decane for **1-H**, **1-Cl**, **1-Br**, **1-Me**, **1-F**, **1-CN**, **1-CF$_3$**, **1-SiMe$_3$** and **1-NO$_2$**, and tetradecane for **1-t-Bu**, **1-OMe**, **1-COMe**, **1-SMe**, **1-SOMe** and **1-CO$_2$Me**. Data from the aforementioned reaction of **1-H** with **CCl_3SO_2Br** (as summarized by eq 6-13) show that our chosen system is a very clean (chain) reaction, and all products formed therefore are derived from the same intermediate **2-H** generated in the same measured step (eq 8). This fact ensures the applicability of eq 14:[1,15] in which φ is defined as the mole fraction of unreacted substrate, i.e.,

$$k_r(\mathbf{Y}) = \frac{k_Y}{k_H} = \frac{\log\{[\mathbf{1\text{-}Y}]_t / [\mathbf{1\text{-}Y}]_0\}}{\log\{[\mathbf{1\text{-}H}]_t / [\mathbf{1\text{-}H}]_0\}} = \frac{\log \varphi_Y}{\log \varphi_H} \qquad (14)$$

$[\mathbf{1}]_t / [\mathbf{1}]_0$, for the calculation of relative rate constants $k_r(\mathbf{Y})$. As the GC peaks of **1-F** and **1-H** overlap with each other, k_r (**F**) cannot be measured by direct competition between **1-F** and **1-H**. However, direct competition between **1-F** and **1-Br** was experimentally feasible, hence the k_r (**F**) value in Table 1 was calculated by the equation $k_F/k_H = (k_F/k_{Br}) \times (k_{Br}/k_H)$.

RESULTS AND DISCUSSION

According to eq 14, if a set of φ values (1.0-0.2) were measured over a wide range of reaction times which correspond to a wide range of the extent of reaction (0-80%), then a linear relationship of ln φ_Y (time t) with ln φ_H (time t) would be obtained if all the products were derived from the same rate-determining step and if the adopted kinetic methodology was reliable.

In fact, we obtained 14 excellent linear plots [see correlation coefficient (r) values in **Table 1**] on the basis of 14 sets of ln φ_Y vs. ln φ_H plots with the φ value falling mainly in the range of 1.0-0.2. These 14 sets correspond to 14 pairings of **1-Y** with **1-H**. A typical example is illustrated in **Figure 1** for the kinetic competition between **1-Cl** and **1-H**, with the corresponding φ and ln φ values listed in **Table 2**. Both **Table 2** and **Figure 1** demonstrate that the k_r(**Cl**) values are not affected by the degree of conversion of the substrates.

Table 1 shows that the k_r(**Cl**) value from the regression analysis is 0.771 ± 0.018 with $r = 0.9991$. The k_r(**Y**) values summarized in **Table 1** are the averaged k_r(**Y**) values obtained from regression analysis of the 9-12 independently measured k_r values at 9-12 consecutive time intervals. The number of these measurements is designated as *n* in **Table 1** and is illustrated by the twelve points in **Figure 1**. These k_r(**Y**) values are almost the same as all the k_r(**Y**) values obtained by simply averaging the *n* independently measured k_r values. These results demonstrate that the chosen reaction system fulfills our proposed requirements and that the adopted kinetic methods are truly reliable. The total spread of relative rates in radical chemistry is usually small.[1a] It is roughly 10 in the present work, similar to that for the hydrogen-atom abstraction reaction of isopropylbenzenes.[2c]

Before systematic evaluation of the fourteen k_r (**Y**) values by the standard procedure described above with the molar ratio of the reactants of **1-H** and **1-Y** fixed at 1 : 1 and in the same solvent of cyclohexane, the reliability of the methodology was further cross-checked by measuring the k_r (**Cl**) values at different **1-H** / **1-Cl** molar ratios in cyclohexane. The k_r (**Cl**) value was also measured in a different solvent, F-113. The results are summarized in **Table 3**, which shows that within experimental uncertainty, neither the molar ratio nor the solvent will change the k_r (**Cl**) values. This is also in harmony with the general observation that the solvent-dependence of substituent effect on the relative rates of a radical reaction under competitive conditions, e. g., hydrogen-atom abstraction or addition, is relatively small.[16a,b]

As described above and summarized in **Table 1**, our methodology has provided a reliable set of $k_r(Y)$ values for 14 substituents. These k_r values are not affected by the degree of conversion of the substrates (**Table 2**) or the different molar ratios of the two substrates, or the nature of solvents (**Table 3**). The precision of the k_r measurements is clearly reflected in the r values in **Table 1**. The usual experimental uncertainty ($\Delta k_r/k_r$) and S, the experimental uncertainties of $\log k_r$ values, calculated by the equation: $S = [\log(k_r + \Delta k_r) - \log k_r]$ or $S = [\log(k_r - \Delta k_r) - \log k_r]$, are shown in **Table 1**. In this table are also listed the values of D-1, which represents the standard deviation from the regression line of **Figure 2**, and D-2, which represents the standard deviation from the regression line of **Figure 3**.

Table 1. Relative Rates [k_r (**Y**)] of Trichloromethyl-Bromo-Additioon System at 65 ± 0.5°C and a **1-Y$_1$** / **1-Y$_2$** Molar Ratio of ca. 1 : 1

Y_1/Y_2	k_r+Δk_r	$\Delta k_r/k_r$	S[b]	D-1[c]	D-2[c]	n	r
Cl/H	0.771±0.018	2.4%	0.011	-0.006	0.024	12	0.9991
Br/H	0.784±0.076	9.7%	0.041	0.029	0.026	9	0.9968
t-Bu/H	1.807±0.034	1.9%	0.009	0.111	-0.048	11	0.9990
Me/H	1.682±0.030	1.8%	0.008	0.045	0.010	10	0.9993
OMe/H	2.446±0.077	3.2%	0.014	-0.115	0.031	10	0.9979
CN/H	0.301±0.014	4.7%	0.020	-0.037	-0.072	11	0.9989
F/Br	1.040±0.031	2.9%	0.013			11	0.9991
F/H[a]	0.815±0.107	13.2%	0.054	-0.105	0.012		
NO_2/H	0.240±0.019	8.0%	0.034	-0.046	-0.021	10	0.9971
$SiMe_3$/H	1.218±0.033	2.8%	0.012	0.132	-0.119	10	0.9986
COMe/H[d]	0.740±0.055	7.5%	0.032			10	0.9995
CO_2Me/H	0.499±0.025	5.1%	0.022	0.066	-0.010	10	0.9983
CF_3/H	0.269±0.016	6.0%	0.026	-0.120	-0.005	9	0.9985
SOMe/H[d]	0.608±0.043	7.1%	0.030			10	0.9954
SMe/H	2.236±0.109	4.9%	0.021	-0.030	0.044	11	0.9963

[a] $k_F/k_H = (k_F/k_{Br}) \times (k_{Br}/k_H) = 0.815$. [b] S stands for the experimental uncertainties of $\log k_r$ values as defined in the text. [c] D-1 or D-2, as defined in the text, stands for the deviation of the $\log k_r$ values from the regression lines of **Figure 2** ($\log k_r$ vs. σ^+) or **Figure 3** ($\log k_r$ vs. $\sigma_p + \sigma_{JJ}{}^{\cdot}$) respectively; $\Sigma|\text{D-1}| = 0.842$, $\Sigma|\text{D-2}| = 0.422$. [d] The σ^+ values for **Y=COMe, SOMe** are unavailable.

Table 2. φ and ln φ Values of **1-Cl** and **1-H** in Kinetic Competition Reaction at Twelve Successive Time Intervals (Molar Ratio ca. 1 : 1)

t(hr)	φ_H	$-\ln\varphi_H$	φ_{Cl}	$-\ln\varphi_{Cl}$
0.083	1.00	0	1.00	0
0.167	0.985	0.015	0.971	0.030
0.333	0.915	0.088	0.944	0.057
1	0.888	0.119	0.904	0.101
1.5	0.810	0.210	0.852	0.160
2	0.699	0.358	0.764	0.270
3	0.570	0.563	0.638	0.450
4	0.499	0.695	0.602	0.508
8	0.411	0.890	0.482	0.729
12	0.314	1.158	0.411	0.889
15	0.255	1.365	0.348	1.057
19	0.214	1.543	0.305	1.187

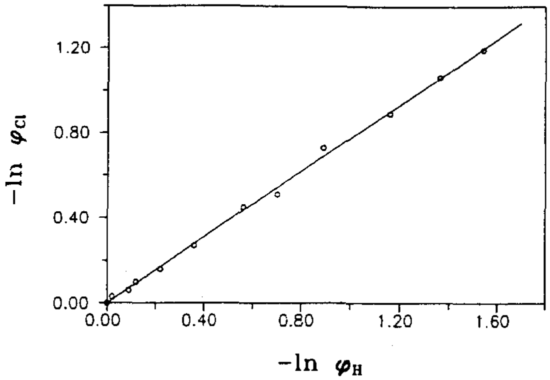

Figure 1. Plot of $-\ln\varphi_{Cl}$ vs. $-\ln\varphi_H$

Table 3. Measurement of k_r (Cl) Values at Different **1-H** / **1-Cl** Molar Ratios in cyclohexane or in F-113 (parenthesized value)

1-H[a]	1-Cl[a]	k_r(Cl)	n	r
1.13	3.06	0.783±0.017	11	0.9995
1.22	1.42	0.771±0.018	12	0.9991
3.85	1.24	0.757±0.016	9	0.9991
1.37	1.49	(0.742±0.022)	12	0.9991

[a] Unit: mmol.

For the correlation analysis of our data, values of σ^{x} and $\sigma^{\bullet}$ were taken from the following sources: σ_{mb}, Ref. 16c; σ_p and σ^{+}, Ref. 16d; $\sigma_{JJ}^{\bullet}$, Ref. 1a; $\sigma_{\alpha}^{\bullet}$, Ref. 17a-b; $\sigma_{C}^{\bullet}$, Ref. 17c-d. Correlation of our data with both eq 4 and eq 5 are summarized in **Table 4** in which ρ^{x}, $\rho^{\bullet}$, r or R, s, ψ, F and n values are listed. All possible combinations of ($\sigma^{x}+\sigma^{\bullet}$) had been tried, with $\sigma^{x} = \sigma_{mb}$, σ^{+} and σ_p, and $\sigma^{\bullet} = \sigma_{JJ}^{\bullet}$, $\sigma_{\alpha}^{\bullet}$ and $\sigma_{C}^{\bullet}$. The r, ψ and F values calculated for the single-parameter eq 5 indicate that reasonably good correlations can be obtained by application of the single-parameter equation. But the scatter of points in the plot of logk_r values versus $\sigma^{\bullet}$

Table 4. Values of ρ^X and $\rho^{\cdot}$ of Eq 4 and Eq 5 , and Corresponding Values of the Correlation Coefficients s, r or R, ψ and F-test for Correlation of $k_r(Y)$ Values of n 1-Y's with ρ^X and $\rho^{\cdot}$

σ^X or $\sigma^X+\sigma^{\cdot}$	ρ^X	$\rho^{\cdot}$	s	r or R	ψ	F[a]	n
σ_{mb}	-0.630		0.338	0.896	0.478	52.68	15[b]
σ^+	-0.686		0.194	0.971	0.259	183.47	13[c]
σ_p	-0.886		0.264	0.938	0.374	94.46	15[b]
$\sigma_{mb}+\sigma_{JJ}^{\cdot}$	-0.690	0.512	0.258	0.945	0.365	50.42	15[b]
$\sigma_{mb}+10\sigma_{\alpha}^{\cdot}$	-0.686	0.486	0.259	0.942	0.383	39.22	13[d]
$\sigma_{mb}+\sigma_{C}^{\cdot}$	-0.747	0.439	0.302	0.930	0.413	35.48	14[e]
$\sigma^+ +\sigma_{JJ}^{\cdot}$	-0.682	0.116	0.197	0.973	0.262	89.80	13[c]
$\sigma^+ +10\sigma_{\alpha}^{\cdot}$	-0.664	0.093	0.216	0.966	0.302	56.14	11[f]
$\sigma^+ +\sigma_{C}^{\cdot}$	-0.686	0.004	0.204	0.971	0.271	83.40	13[c]
$\sigma_p+\sigma_{JJ}^{\cdot}$	-0.977	0.543	0.106	0.991	0.149	329.97	15[b]
$\sigma_p+10\sigma_{\alpha}^{\cdot}$	-0.960	0.443	0.155	0.979	0.230	117.94	13[d]
$\sigma_p+\sigma_{C}^{\cdot}$	-1.034	0.439	0.200	0.970	0.274	87.93	14[e]

[a] Critical F values: $F_{0.001}$ (1, 13)=17.81, $F_{0.001}$ (1, 12)=18.64, $F_{0.001}$ (1, 11)=19.69, $F_{0.001}$ (1,9)=22.86, $F_{0.001}$ (2,12) = 12.97, $F_{0.001}$ (2,12)=13.81, $F_{0.001}$ (2, 10)=14.91, $F_{0.001}$ (2, 8)=18.49. [b] **Y= F, Cl, Br, Me, t-Bu, OMe, SMe, SiMe$_3$, (H), CF$_3$, CN, NO$_2$, SOMe, COMe** and **CO$_2$Me**. [c] **Y= F, Cl, Br, Me, t-Bu, OMe, SMe, SiMe$_3$, (H), CF$_3$, CN, NO$_2$** and **CO$_2$Me**. [d] **Y= F, Cl, Me, t-Bu, OMe, SMe, SiMe$_3$, (H), CF$_3$, CN, SOMe, COMe** and **CO$_2$Me**. [e] **Y= F, Cl, Br, Me, t-Bu, OMe, SMe, SiMe$_3$, (H), CF$_3$, CN, NO$_2$, SOMe** and **CO$_2$Me**. [f] **Y= F, Cl, Me, t-Bu, OMe, SMe, SiMe$_3$, (H), CF$_3$, CN** and **CO$_2$Me**.

(the best among the three) in **Figure 2** indicates that some substituents (**t-Bu**, **OMe**, **F**, **SiMe$_3$** and **CF$_3$**) deviate too much from the regression line. This is clearly indicated by comparison of the S, D-1 and D-2 values listed in **Table 1**, and by direct inspection of **Figure 2**. It is noteworthy that some |D-1| values (> 0.10) are much larger than their S values (< 0.06) (**Table 1**). We propose that, in performing a reliable correlation, these deviations should not be ignored[1c], because they might be the reflection of a certain deficiency in the particular approach (e.g., application of the single parameter equation).

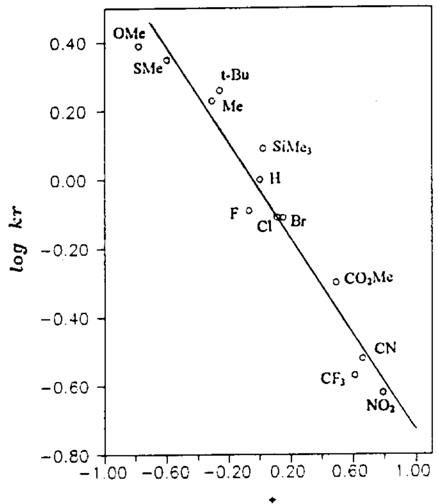

Figure 2. Plot of log k_r vs. σ^{+}

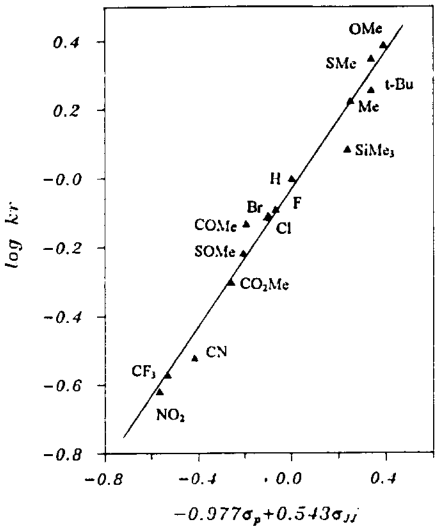

Figure 3. Plot of log k_r vs. $-0.977\sigma_p + 0.543\sigma_{JJ}^{\cdot}$

Application of the dual-parameter eq 4, as summarized in **Table 4,** shows that the three $(\sigma' + \sigma^{\cdot})$ combinations do not improve the correlation over that of the single-parameter correlation with σ^{+}. However, in likeness to the correlation results for the hydrogen-atom abstraction reaction from p-**Y**-substituted isopropylbenzenes,[2c] the $(\sigma_p + \sigma_{JJ}^{\cdot})$ combination improves the correlation, with $R = 0.991$, $\psi = 0.149$ and $F = 329.97$. Notably, for the sum of deviations, the $\sum|D\text{-}2|$ value (0.422) is much smaller than the $\sum|D\text{-}1|$ value (0.842). As **Figure 3** shows, for the dual-parameter correlation with $(\sigma_p + \sigma_{JJ}^{\cdot})$, almost all points fall on the regression line within experimental uncertainty (except **Y** = **SiMe$_3$**). This improvement does not seem to be a consequence of fortuity because (i) in recent years it has been established that σ^{x} and $\sigma^{\cdot}$ are independent parameters (cf. page 97 of Ref. 2b), and (ii) the "correlation coefficient" between σ_p and $\sigma_{JJ}^{\cdot}$ ($r = 0.092$, $n = 22$) is among the smallest known (r value between σ_{mb} and $\sigma_{JJ}^{\cdot}$ is even smaller, i. e., 0.075, $n = 22$).

One of the most interesting observations of the present work is that the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ and $|\rho_p/\rho_{JJ}^{\cdot}|$ values for our trichloromethyl-bromo-addition reactions to phenylacetylenes, i.e., 1.35 and 1.80 respectively, are rather similar to the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ and $|\rho_p/\rho_{JJ}^{\cdot}|$ values for the hydrogen-atom abstraction reactions of p-**Y**-substituted isopropylbenzenes, i. e., 1.14 and 2.01 respectively,[2c] but quite different from the $|\rho^{x}/\rho^{\cdot}|$ ratios for radical addition reactions to styrenes mentioned in the Introduction. This observation shows that the relative dominance of the polar effect over that of the spin-effect at the transition states of the trichloromethyl-bromo-addition reactions to phenylacetylenes (**1-Y**) resembles the relative importance of these effects for the hydrogen-atom abstraction reactions of isopropylbenzenes. In other words, the relative importance of the polar and spin effects appears to be different for radical additions to phenylacetylenes and styrenes. As experimentalists, we are not certain how these findings should be interpreted in theoretical terms, perhaps (as mentioned), when an electrophilic radical (such as $CCl_3\cdot$) attacks, the polar effect becomes more demanding when the attacked site is the more electrophilic sp carbon instead of the less electrophilic sp^2-carbon.[18] In other words, we may visualize that the transition states for radical additions to phenylacetylenes require more electrostatic assistance than those for the additions to styrenes. Incidentally, it is well known that the C≡C bond is stronger, shorter and more electron-deficient than C=C bond.[19] In conclusion, the correlation analysis of the trichloromethyl-bromo-addition reactions to p-Y-substituted phenylacetylenes (**1-Y**), in likeness to the hydrogen-atom abstraction reactions, seems to fall in the second category of our proposition presented in the Introduction, and both a polar effect and a spin-delocalization effect are operating at the transition state.

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