ELSEVIER

Journal of Fluorine Chemistry 79 (1996) 133–138

JOURNAL OF FLUORINE CHEMISTRY

The electrophilic trifluoromethyl radical $CF_3\cdot$ Application of the dual-parameter equation to the correlation analysis of relative rates of the trifluoromethylbromo addition reactions to 14 *p*-Y-substituted phenylacetylenes

Xi-Kui Jiang *, Guo-Zhen Ji *, John Rong-Yuan Xie

Shanghai Institute of Organic Chemistry, Academia Sinica, 354 Feng-Lin Lu, Shanghai 200032, China

Received 15 December 1995; accepted 17 April 1996

Abstract

A rigorous procedure was applied to the measurement of the relative rates, i.e., $k_r(Y) = k_Y/k_H$, of the trifluoromethylbromo addition reactions to 14 *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_2Me**). The reaction was run in cyclohexane under nitrogen at 55 ± 0.5 °C and was initiated by di-t-butylperoxy-oxalate. Correlation analysis of the data suggests that a spin effect is also operating at the transition state of this addition reaction and that the dual-parameter equation is applicable to this reaction.

Keywords: Radical addition to C≡C bond; Relative rates; Trifluoromethylbromo addition reactions; *p*-Y-substituted phenylacetylenes; Correlation analysis; Spin effect; Dual-parameter equation

1. Introduction

In recent years, the electrophilic nature and unique reactivity of the trifluoromethyl radical ($CF_3\cdot$) and other n-perfluoroalkyl radicals ($R_f\cdot$) have been studied and reported [1]. Dolbier, Ingold, Lusztyk and their coworkers have confirmed the strongly electrophilic character of the $R_f\cdot$ radicals by the negative sign of the ρ value of the following reaction [1c]

$$n\text{-}C_8F_{17}\cdot + CH_2{=}CHC_6H_4\text{-}p\text{-}X \longrightarrow n\text{-}C_8F_{17}CH_2\dot{C}HC_6H_4\text{-}p\text{-}X$$

(X = H, CF_3, Cl, CH_3 and OCH_3)

$$\log(k_X/k_H) = -0.53\sigma,\ r = 0.99,\ n = 5$$

and by the correlation between log k_{add} of $R_f\cdot$ and the ionization potentials (*IP* values) of terminal alkene ($r = 0.94$ $n = 7$; $r = 0.97$, $n = 13$; both with negative ρ values, but the exact values were not given) [1b,1c]. Their Hammett study for H-atom transfer from arene thiols with $n\text{-}C_7F_{15}\cdot$ also gave a negative ρ value ($\log k_{rel} = -0.56\sigma^+$, $r = 0.986$, $n = 5$) [1f]. In the meanwhile, we have developed a rigorous kinetic methodology for measuring the relative rates of radical reactions and for addressing the question of whether the single-parameter equation (Eq. (1) or Eq. (2)) or the dual-parameter equation (Eq. (3)) should be applied to the correlation analysis of the kinetic and spectral data in radical chemistry. In these equations, σ^x and $\sigma^\cdot$ respectively stand for the polar and spin-delocalization substituent constants. The $|\rho^x/\rho^\cdot|$ ratio may serve as a rough measure of the relative importance of the polar effect and the spin effect [2,3]. Variable represents $\log(k_Y/k_H)$.

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

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

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

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 [3a,3b,3h]. 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

* Corresponding authors.

PII S0022-1139(96)03482-3

unity, e.g., in hydrogen-atom abstraction reactions, in radical additions to phenylacetylenes and EPR data of some phenyl nitroxides [3c,3d,3g,3i]. 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 Eq. (3) 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). (iii) When the 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. [3e,3f]. (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 [3f].

We have also found that in the trichloromethylbromo addition reactions, the triple bond in phenylacetylenes behaves in a manner similar to the benzylic C–H bonds, rather than to the double bond in styrenes [3d]. In other words, the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ and $|\rho_p/\rho_{JJ}^{\cdot}|$ values for the aforesaid addition reactions are 1.35 and 1.80 respectively [3d], whereas the $|\rho_{mb}/\rho_{JJ}^{\cdot}|$ and $|\rho_p/\rho_{JJ}^{\cdot}|$ values are 0.42 and 0.65 for the $CCl_3\cdot$ radical addition to styrenes [3a], and 0.37 and 0.58 for bromine atom addition to methylstyrenes [3b], respectively. Therefore, it would be interesting to study the substituent effects on the addition reactions of $CF_3\cdot$ to *p*-Y-substituted-phenylacetylenes (**1-Y**) to find out how the triple bond behaves in this reaction system and whether the polar effect again predominates over the spin effect.

We have chosen the trifluoromethylbromo addition reactions of *p*-Y-substituted phenylacetylenes (**1-Y**) with CF_3SO_2Br as the addendum as the system for our study. It will be shown that for **1-H** the reaction follows Eq. (4) to Eq. (9) described in Scheme 1.

$$(^t\text{BuOOCO})_2 \xrightarrow{\Delta} 2\,^t\text{BuO}\cdot + 2CO_2 \quad (4)$$

$$CF_3SO_2Br + {}^t\text{BuO}\cdot \longrightarrow {}^t\text{BuOBr} + CF_3SO_2\cdot \quad (5)$$

$$CF_3SO_2\cdot \longrightarrow CF_3\cdot + SO_2 \quad (6)$$

$$\underset{\textbf{(1-H)}}{\text{Ph–C}\equiv\text{CH}} + CF_3\cdot \longrightarrow \underset{\textbf{(2-H)}}{\text{Ph–}\dot{\text{C}}\text{=CH–}CF_3} \quad (7)$$

$$\textbf{2-H} + CF_3SO_2Br \longrightarrow \underset{\textbf{(3-H)}}{\text{Ph–CBr=CH}CF_3} + CF_3SO_2\cdot \quad (8)$$

$$\textbf{2-H} \xrightarrow{\text{H-abstraction from solvent}} \underset{\textbf{(4-H)}}{\text{Ph–CH=CH}CF_3} \quad (9)$$

Scheme 1.

In short, the above reactions can be described by Eq. (10)

$$\textbf{1-H} + CF_3SO_2Br \xrightarrow[95.6\%]{(^t\text{BuOOCO})_2,\ 55\pm0.5\ ^\circ\text{C},\ 3.5\ \text{h}} \underset{\textbf{(3-H)}}{\textbf{1-H} + \text{Ph–CBr=CH}CF_3} + \underset{\textbf{(4-H)}}{\text{Ph–CH=CH}CF_3} \quad (10)$$

(67.9%) (4.4%)

2. Experimental details

2.1. General methods and materials

Boiling points and melting points were uncorrected. ^{1}H NMR spectra were obtained at 56.4 MHz on a Varian EM-360A spectrometer with TMS as the external standard. ^{19}F NMR spectra were obtained at 60 MHz on a Varian EM-360 spectrometer with trifluoroacetic acids as 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 °C to 250 °C at a rate of 10 °C min^{-1}; injection temperature, 260 °C; detection temperature, 220 °C; carrier gas pressure, 380 kPa.

The addendum CF_3SO_2Br was prepared as previously described [4]. All **1-Y** substrates are known compounds. They were further identified by ^{1}H NMR and IR spectroscopy, and mass spectrometry, as reported in detail in Ref. [3d].

2.2. Reaction of *1-H* with CF_3SO_2Br

In a three-necked round bottom flask (100 ml), a solution of **1-H** (5 mmol), CF_3SO_2Br (20 mmol), $(^t\text{BuOOCO})_2$ (0.2 mmol) and internal GC standard (150 μl) in cyclohexane (50 ml) was vigorously stirred at 55 ± 0.5 °C under a nitrogen atmosphere. After 3.5 h, the crude reaction solution was analyzed by GC when three compounds, i.e., **1-H, 3-H** and **4-H**, were detected (Eq. (14)). These were separated by chromatography and identified by their ^{1}H NMR, ^{19}F NMR, IR and MS spectra. Their yields were found to be: **1-H**, 23.3%; **3-H**, 67.9%: and **4-H**, 4.4% (total yield 95.6%).

2.3. Kinetic competition procedure [2a,2f,2g,3]

In a three-necked round-bottom flask (25 ml), a solution of **1-Y** (1 mmol), **1-H** (1 mmol), CF_3SO_2Br (8 mmol), $(^t\text{BuOOCO})_2$ (0.08 mmol) and internal GC standard (30–40 μl) in cyclohexane (15 ml) was vigorously stirred at 55 ± 0.5 °C under a nitrogen atmosphere for 4–5 h until the degree of conversion of **1-H** or **1-Y** reached 40% ($\varphi = 0.6$) to 80% ($\varphi = 0.2$). During this time, nine to 11 samples (about 0.2 ml each) were taken, usually at times (t) of 0.083, 0.167,

Table 1
Relative rates [k_r(Y)] of trifluoromethylbromo addition reaction at 55 ± 0.5 °C and a **1-Y$_1$/1-Y$_2$** molar ratio of ca. 1:1

Y_1/Y_2	$k_r \pm \Delta k_r$	$\Delta k_r/k_r$ (%)	s [b]	$D-1$ [c]	$D-2$ [c]	n	r
Cl/H	0.713 ± 0.039	5.5	0.023	−0.031	0.001	10	0.9979
Br/H	0.722 ± 0.087	12.1	0.0049	−0.011	−0.016	10	0.9969
^{t}Bu/H	1.981 ± 0.224	11.4	0.047	0.143	−0.038	9	0.9973
Me/H	1.756 ± 0.183	10.5	0.043	0.067	0.023	9	0.9976
OMe/H	2.654 ± 0.278	10.5	0.043	−0.149	0.006	10	0.9989
CN/H	0.301 ± 0.020	6.7	0.028	−0.004	−0.040	10	0.9972
F/Cl	1.205 ± 0.084	7.0	0.029			10	0.9991
F/H [a]	0.859 ± 0.123	14.4	0.058	−0.091	0.035		
NO_2/H	0.218 ± 0.033	15.2	0.061	−0.076	−0.044	10	0.9970
$SiMe_3$/H	1.296 ± 0.099	7.7	0.032	0.177	−0.104	10	0.9988
COMe/H [d]	0.659 ± 0.065	9.9	0.041			11	0.9969
CO_2Me/H	0.529 ± 0.075	14.2	0.058	0.098	0.015	11	0.9981
CF_3/H	0.279 ± 0.038	13.7	0.055	−0.120	0.007	10	0.9974
SOMe/H [d]	0.622 ± 0.072	11.6	0.048			10	0.9981
SMe/H	2.466 ± 0.236	9.6	0.040	−0.041	0.041	10	0.9980

[a] $k_F/k_H = (k_F/k_{Cl}) \times (k_{Cl}/k_H) = 0.859$.
[b] s stands for the experimental uncertainties in the log k_r values as defined in the text.
[c] $D-1$ or $D-2$, as defined in the text, stand for the deviation of the log k_r values from the regression lines of Fig. 2 (log k_r versus σ^+) or Fig. 3 (log k_r versus σ_{JJ}^+), respectively; $\Sigma|D-1| = 1.045$, $\Sigma|D-2| = 0.401$.
[d] The σ^+ values for Y = COMe, SOMe are unavailable.

0.333, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 h respectively, 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 standard 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_2Me**. Data from the above-mentioned reaction of **1-H** with CCl_3SO_2Br [as summarized by Eqs. (3)–(9)] show that our chosen system is a very clean (chain) reaction, and all products formed are therefore derived from the same intermediate **2-H** generated in the same measured step (Eq. (7)). This fact ensures the applicability of Eq. (11) [2,3d] in which φ is defined as the mole fraction of unreacted substrate, i.e. $[\mathbf{1}]_t/[\mathbf{1}]_0$, for the calculation of relative rate constants k_r(Y)

$$k_r(Y) = \frac{k_Y}{k_H} = \frac{\log\{[\mathbf{1\text{-}Y}]_t/[\mathbf{1\text{-}Y}]_0\}}{\log\{[\mathbf{1\text{-}H}]_t/[\mathbf{1\text{-}H}]_0\}} = \frac{\log \varphi_Y}{\log \varphi_H} \qquad (11)$$

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-Cl is experimentally feasible, hence the** k_r(F) value in Table 1 was calculated by the equation $k_F/k_H = (k_F/k_{Cl}) \times (k_{Cl}/k_H)$.

3. Results and discussion

According to Eq. (11), if a set of φ values (1.0–0.2) are measured over a wide range of reaction times that correspond to a wide range of extent of reaction (0%–80%), then a linear relationship between 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 listed in Table 1] on the basis of 14 sets of ln φ_Y versus ln φ_H plots, with the φ value falling mainly in the range 1.0–0.2. These 14 sets correspond to 14 pairings of **1-Y** with **1-H**. A typical example is illustrated in Fig. 1 for the kinetic competition between **1-Br** and **1-H**, with the corresponding φ and ln φ values listed in Table 2.

Table 1 shows that the k_r(Br) value from the regression analysis is 0.722 ± 0.087 with $r = 0.9969$. The k_r(Y) values summarized in Table 1 are the averaged k_r(Y) values obtained from regression analysis of the 9–11 independently measured k_r values at 9–11 consecutive time intervals. The

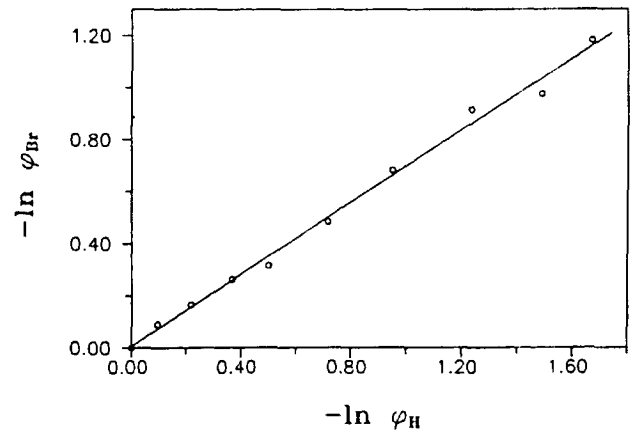

Fig. 1. Plot of $-\ln \varphi_{Br}$ versus $-\ln \varphi_H$.

Table 2
Values of φ and ln φ for **1-Br** and **1-H** in the kinetic competition reaction at 12 successive time intervals (molar ratio ca. 1:1)

Time, t (h)	φ_H	$-\ln \varphi_H$	φ_{Br}	$-\ln \varphi_{Br}$
0.083	1.00	0	1.00	0
0.167	0.908	0.096	0.915	0.089
0.333	0.804	0.219	0.848	0.165
1.0	0.692	0.369	0.770	0.262
1.2	0.604	0.503	0.730	0.315
2.0	0.488	0.718	0.617	0.483
2.5	0.386	0.953	0.505	0.682
3.0	0.290	1.239	0.401	0.913
3.5	0.225	1.490	0.378	0.974
4.0	0.188	1.670	0.307	1.180

number of these measurements is designated as n (Table 1) and is illustrated by the 12 points in Fig. 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 (cf. Refs. [3b] and [3c]) and that the adopted kinetic methods are truly reliable.

Before systematic evaluation of the 14 k_r(Y) values obtained by the standard experimental procedure described above with the molar ratio of the reactants of **1-H** and **1-Y** fixed at 1:1 and in the same cyclohexane solvent, the reliability of the methodology was further cross-checked by measuring the k_r(Br) values at different **1-H/1-Br** molar ratios (1:3, 1:1 and 3:1) in cyclohexane. The k_r(Br) 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(Br) values. Furthermore, both Table 2 and Fig. 1 demonstrate that the k_r(Br) values are not affected by the degree of conversion of the substrates.

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 independent of the degree of conversion of the substrates (Table 2) and not much affected by the molar ratios of the two substrates, or the nature of the 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 from the equation $s = [\log(k_r + \Delta k_r) - \log k_r]$ or $s = [\log(k_r - \Delta k_r) - \log k_r]$,

Table 3
Measurement of k_r(Br) values at different **1-H** and **1-Br** molar ratios in cyclohexane or in F-113 (parenthesized value)

1-H [a]	*1-Br* [a]	k_r(Br)	n	r
1.07	3.32	0.739 ± 0.110	9	0.9960
1.85	1.69	0.722 ± 0.087	10	0.9969
4.24	1.38	0.688 ± 0.047	10	0.9983
1.56	1.42	(0.704 ± 0.093)	10	0.9972

[a] Units: mmol.

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 Fig. 2, and $D-2$, which represents the standard deviation from the regression line of Fig. 3.

For the correlation analysis of our data, values of σ^x and $\sigma^\cdot$ were taken from the following sources: σ_{mb}, Ref. [5a]; σ_p and σ^+, Ref. [5b]; $\sigma_{JJ}^\cdot$, Ref. [2a]; $\sigma_\alpha^\cdot$, Ref. [6a,6b]; $\sigma_C^\cdot$, Ref. [6c,6d]. Correlation of our data with both Eq. (1) and Eq. (3) are summarized in Table 4 in which ρ^x, $\rho^\cdot$, r or R, s, ψ, F and n values are listed. All possible combinations of $(\sigma^x + \sigma^\cdot)$ have been tried, with $\sigma^x = \sigma_{mb}$, σ^+ and σ_p, and $\sigma^\cdot = \sigma_{JJ}^\cdot$, $\sigma_\alpha^\cdot$ and $\sigma_C^\cdot$. The r, ψ and F values calculated for the single-parameter Eq. (1) indicate that reasonably good correlations can be obtained by application of the single-

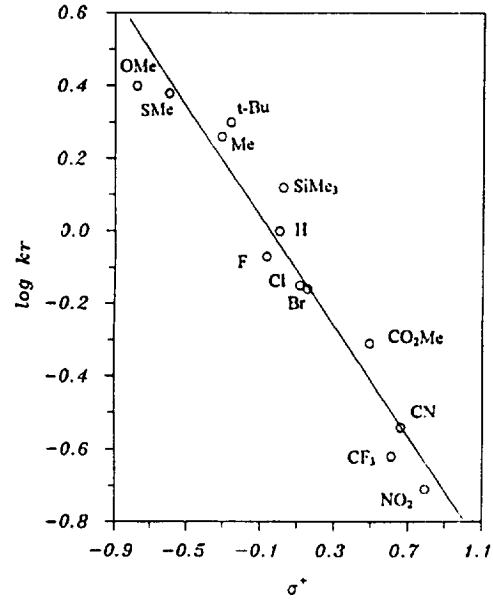

Fig. 2. Plot of log k_r versus σ^+.

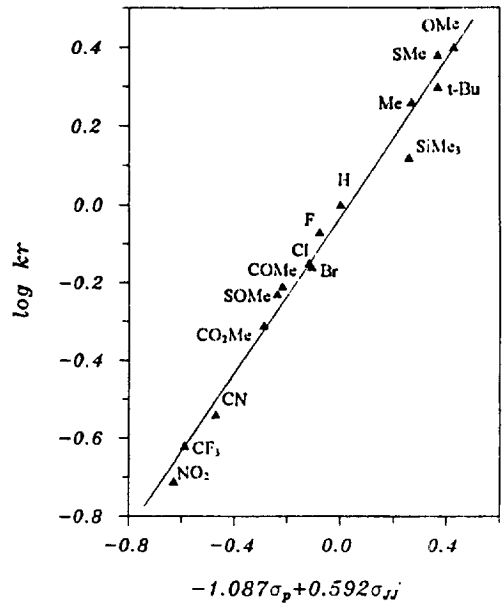

Fig. 3. Plot of log ^k_r versus $-1.087\sigma_p + 0.592\sigma_{JJ}^\cdot$.

Table 4
Values of ρ^x and $\rho^\cdot$ of Eq. (1) and Eq. (3), and the corresponding values of the correlation coefficients s, r or R, ψ and F-test

σ^x or $\sigma^x+\sigma^\cdot$	ρ^x	$\rho^\cdot$	s	r or R	ψ	F	n
σ_{mb}	−0.696		0.167	0.891	0.488	50.13	15 [b]
σ^+	−0.756		0.101	0.973	0.243	196.92	13 [c]
σ_p	−0.988		0.124	0.942	0.362	101.93	15 [b]
$\sigma_{mb}+\sigma_{JJ}^\cdot$	−0.764	0.552	0.132	0.938	0.387	44.22	15 [b]
$\sigma_{mb}+\sigma_\alpha^\cdot$	−0.746	0.520	0.131	0.934	0.408	34.09	13 [d]
$\sigma_{mb}+\sigma_C^\cdot$	−0.819	0.441	0.153	0.923	0.435	31.61	14 [e]
$\sigma^+ + \sigma_{JJ}^\cdot$	−0.753	0.099	0.103	0.976	0.249	119.19	13 [c]
$\sigma^+ + 10\sigma_\alpha^\cdot$	−0.723	0.087	0.111	0.967	0.291	63.46	11 [f]
$\sigma^+ + \sigma_C^\cdot$	−0.752	−0.035	0.104	0.975	0.251	107.07	13 [c]
$\sigma_p+\sigma_{JJ}^\cdot$	−1.087	0.592	0.045	0.993	0.132	426.97	15 [b]
$\sigma_p+10\sigma_\alpha^\cdot$	−1.056	0.478	0.069	0.982	0.213	138.56	13 [d]
$\sigma_p+\sigma_C^\cdot$	−1.145	0.452	0.093	0.972	0.264	95.24	14 [c]

[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, Me_3Si, (H), CF_3, CN, NO_2, SOMe, COMe and CO_2Me.
[c] Y = F, Cl, Br, Me, ^{t}Bu, OMe SMe, Me_3Si, (H), CF_3, CN, NO_2 and CO_2Me.
[d] Y = F, Cl, Me, ^{t}Bu, OMe, SMe, Me_3Si, (H), CF_3, CN, SOMe, COMe and CO_2Me.
[e] Y = F, Cl, Br, Me, ^{t}Bu, OMe, SMe, Me_3Si, (H), CF_3, CN, NO_2, SOMe and CO_2Me.
[f] Y = F, Cl, Me, ^{t}Bu, OMe, SMe, Me_3Si, (H), CF_3, CN and CO_2Me.

parameter equation. The correlation results, e.g., for σ_p, $\rho_p=-0.988$, $r=0.942$, $n=15$; for σ^+, $\rho^+=-0.756$, $r=0.973$, $n=13$, clearly reflect the strongly electrophilic nature of the $CF_3\cdot$ radical. This result is in accord with the results of Dolbier et al., e.g., for σ_p, $\rho_p=-0.53$, $r=0.99$, $n=5$ [1c]. But the scatter of points in the plot of log k_r values versus σ^+ (the best among the three) in Fig. 2 indicates that some substituents (^{t}Bu, OMe, F, $SiMe_3$, CO_2Me 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 Fig. 2. It is noteworthy that some $|D-1|$ values ($\leqslant 0.09$) are larger than their s values (<0.061) (Table 1). We propose that in performing a reliable correlation these deviations should not be ignored [2c] because they might be the reflection of a certain deficiency in the particular approach (e.g., application of the single parameter equation).

Application of the dual-parameter Eq. (3), 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 [3c], the ($\sigma_p+\sigma_{JJ}^\cdot$) combination clearly improves the correlation, with $R=0.993$, $\psi=0.132$ and $F=426.97$. Notably, for the sum of deviations, the $\Sigma|D-2|$ value (0.401) is much smaller than the $\Sigma|D-1|$ value (1.045). As Fig. 3 clearly 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 = $SiMe_3$).

Of particular interest is a comparison of the behaviour of $CF_3\cdot$ with that of $CCl_3\cdot$ in their addition reactions to phenylacetylenes. The $|\rho_{mb}/\rho_{JJ}^\cdot|$ and $|\rho_p/\rho_{JJ}^\cdot|$ values for the trichloromethylbromo addition reactions to p-Y-substituted phenylacetylenes are 1.35 and 1.80, respectively [3d], whereas the ρ ratios for our trifluoromethylbromo addition reactions are 1.38 and 1.84, respectively. This shows that the $CF_3\cdot$ radical behaves quite similarly to $CCl_3\cdot$ in its addition reactions. In short, our results clearly show that, just like the trichloromethylbromo addition reactions to phenylacetylenes [3d], the relative dominance of the polar effect over that of the spin effect in the transition states of the trifluoromethylbromo addition reactions to p-Y-substituted phenylacetylenes (**1-Y**) resembles the relative importance of these effects for the hydrogen-atom abstraction reactions of isopropylbenzenes (the $|\rho_{mb}/\rho_{JJ}^\cdot|$ and $|\rho_p/\rho_{JJ}^\cdot|$ values are 1.14 and 2.01, respectively) [3c]. In other words, the relative importance of the polar and spin effects is different for radical additions to phenylacetylenes and styrenes [3d]. It is well known that the C≡C bond is stronger, shorter and more electron-deficient than the C=C bond [7]. Apparently, when an electrophilic radical (such as $CF_3\cdot$ or $CCl_3\cdot$) 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 [8]. 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. In conclusion, the correlation analysis of the trifluoromethylbromo addition reactions to p-Y-substituted phenylacetylenes (**1-Y**), similar to the hydrogen-atom abstraction of isopropylbenzenes and the trichloromethylbromo addition reactions to phenylacetylenes, falls in the second category of the proposition presented in our Introduction.

Acknowledgment

We are grateful to the National Natural Science Foundation of China for financial support for this work.

References

[1] (a) M.A. McClinton and D.A. McClinton, *Tetrahedron, 48* (1992) 6555; (b) D.V. Avila, K.U. Ingold, J. Lusztyk, W.R. Dolbier, Jr. and H.Q. Pan, *J. Am. Chem. Soc., 115* (1993) 1577, and references cited therein; (c) D.V. Avila, K.U. Ingold, J. Lusztyk, W.R. Dolbier, Jr., H.Q. Pan and M. Muir, *J. Am. Chem. Soc., 116* (1994) 99; (d) X.X. Rong, H.Q. Pan, W.R. Dolbier, Jr. and B.E. Smart, *J. Am. Chem. Soc., 116* (1994) 4521; (e) W.R. Dolbier, Jr. and M.A. McClinton, *J. Fluorine Chem., 70* (1995) 249; (f) W.R. Dolbier, Jr. and X.X. Rong, *J. Fluorine Chem., 72* (1995) 235.

[2] X.-K. Jiang and G.-Z. Ji, *J. Org. Chem., 57* (1992) 6051, and references cited therein; (b) X.-K. Jiang, G.-Z. Ji and D.Z.-R. Wang, *J. Fluorine Chem., 66* (1994) 187; (c) X.-K. Jiang, G.-Z. Ji and J.R.-Y. Xie, *J. Chem. Res. S,* (1995) 422; (d) H.G. Viehe, Z. Janousek and R. Merenyi, *Substituent Effects in Radical Chemistry,* Reidel, Dordrecht, 1986; (e) D.R. Arnold, in Ref. [2d], pp. 171–188; (f) A.S. Dneprovskii and A.L. Iz'yurov, *Zh. Org. Khim., 24* (1988) 2498; (g) A.S. Dneprovskii, E.V. Eliseenkov and T.A. Osmonov, *Zh. Org. Khim., 30* (1994) 375.

[3] (a) G.H.-X. Guo, S.S.-X. Sun, G.-Z. Ji and X.-K. Jiang, *J. Chem. Res S,* (1993) 166; *J. Chem. Res. M,* (1993) 1123; (b) X.-K. Jiang, W.W.-Z. Liu and S.-H. Wu, *J. Phys. Org. Chem., 7* (1994) 96; (c) X.-K. Jiang, W.W.-Z. Liu and S.-H. Wu, *Tetrahedron, 50* (1994) 7503; (d) X.-K. Jiang, G.-Z. Ji and J.R.-Y. Xie, *Tetrahedron, 52* (1996) 3017; (e) X.-K. Jiang, G.-Z. Ji and D.Z.-R. Wang, *J. Phys. Org. Chem., 8* (1995) 143; (f) X.-K. Jiang, G.-Z. Ji, D.Z.-R. Wang and J.R.-Y. Xie, *J. Phys. Org. Chem., 8* (1995) 143; (g) Y.-H. Zhang, B Jiang, C.-M. Zhou and X.-K. Jiang, *Chin. J. Chem., 12* (1994) 516; (h) Y.-H. Zhang, G.H.-X. Guo, X.-S. Jin, B.-B. Jiang, Y.-H. Fu and X.-K. Jiang, *J. Photochem. Photobiol. (Chem. Sect.), 88* (1995) 11; (i) Y.-H. Zhang, W.F.-X. Ding, C.-M. Zhou, J.-F. Chen and X.-K. Jiang, *J. Chem. Res. S,* (1996) 88; (j) X.-K. Jiang, Y.-H. Zhang and W.F.-X. Ding, *J. Chem. Soc. Perkin Trans. 2,* submitted.

[4] (a) W.-Y. Huang, W. Wang and B.N. Huang, *Acta Chim. Sinica, 43* (1985) 409; *ibid., 44* (1986) 45; (b) W.-Y. Huang and J.-L. Chen, *Acta Chim. Sinica, 45* (1987) 445; *Engl. Ed.,* (1986) 381.

[5] (a) G.Z. Ji, X.-K. Jiang, Y.H. Zhang, S.G. Yuan, C.X. Yu, Y.Q. Shi, X.L. Zhang and W.T. Shi, *J. Phys. Org. Chem., 3* (1990) 643; (b) C. Hansch, A. Leo and R.W. Taft, *Chem. Rev., 91* (1991) 165.

[6] (a) J.M. Dust and D.R. Arnold, *J. Am. Chem. Soc., 105* (1983) 1221; (b) D.D.M. Wayner and D.R. Arnold, *Can. J. Chem., 62* (1984) 1164; *ibid., 63* (1985) 2378; (c) X. Creary, in H.G. Viehe, Z. Janousek and R. Merenyi (eds.), *Substituent Effects in Radical Chemistry,* Reidel, Dordrecht, 1986, pp. 245–262; (d)X. Creary, M.E. Mehrsheikh-Mohammadi and S. McDonald, *J. Org. Chem., 52* (1987) 3254.

[7] (a) R.T. Morrison and R.N. Boyd, *Organic Chemistry,* 6th edn., Prentice-Hall, Englewood Cliffs, NJ, 1992, pp. 425–440; (b) T.H. Lowry and K.S. Richardson, *Mechanism and Theory in Organic Chemistry,* 2nd edn., Harper & Row, New York, 1981, pp 19–30, 506–513.

[8] Y. Amiel, in S. Patai and Z. Rappoport (eds.), *The Chemistry of Functional Groups, Supplement C,* John Wiley & Sons, Chichester, UK, 1983, pp. 341–348.