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The Nucleophilic Silyl Radical: Dual-Parameter Correlation Analysis of the Relative Rates of Bromine-Atom Abstraction Reactions as Measured by a Rigorous Methodology

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Abstract: the relative rates [$k_R(Y)$ values] of bromine-atom abstraction reactions of 13 *p*-Y-substituted benzyl bromides (1-Y's : Y = H, Et, tBu, Me₃Si, MeS, Ph, F, Cl, Br, CF₃, CN, CO₂Me, SO₂Me) by tris(trimethylsilyl) silyl radicals [(Me₃Si)₃Si^{*}] in cyclohexane at 80 °C have been measured by a rigorous methodology. Correlation analysis of the kinetic data by the dual-parameter equation (log $k_Y / k_H = \rho^x \sigma^x + \rho^* \sigma^*$) shows that the silyl radical is distinctly nucleophilic and the transition states of the bromine-atom abstraction reactions are affected by both the polar and spin-delocalization effects of the Y-substituents. Comparison of the $|\rho_p / \rho_{JJ}|^*$ values suggests that the contribution of the spin-delocalization effects in this Br-atom abstraction reactions. © 1997 Elsevier Science Ltd.

Introduction

It has been well-established that the transition states (TS's) of H-atom abstraction reactions by electrophilic radicals (e.g., Br[•], Cl[•], CCl₃[•], ROO[•] and tBuO[•]) are dominated by polar effects of the substituents (Y's).¹ Correlation analyses with the Hammett equation (log $k_Y/k_H = \rho^x \sigma^x$) give negative ρ^x values. On the other hand, the question of whether alkyl radicals are truly nucleophilic has aroused intense

variable =
$$\rho^{x}\sigma^{x} + \rho^{\bullet}\sigma^{\bullet}$$
 (1)

variable =
$$\rho^{x}\sigma^{x}$$
 (2)

variable = $\rho \cdot \sigma^{\bullet}$ (3)

interests among radical chemists.^{2,3} On the basis of his competitive kinetic data on H-atom abstraction reactions of *p*-**Y**-substituted toluenes, Pryor has concluded that the t-butyl radical is nucleophilic because the ρ^x value of the Hammett correlation is positive (+0.49).²¹ Metal and metalloid radicals (e.g., R₃Sn[•], R₃Ge[•] and R₃Si[•]), however, have been readily demonstrated to be nucleophilic by the fact that single-parameter correlation analyses of the relative rates of halogen-atom abstraction reactions by these radicals give positive ρ^x values.⁴ To our knowledge, these metal or metalloid radical reactions have not been studied by an exceptionally rigorous kinetic methodology together with the use of at least 11-12 well-distributed **Y**-substituents. Furthermore, they have never been carefully analysed by the dual-parameter eq 1, with variable = log k_Y / k_H , and with $\rho^x \sigma^x$ and $\rho^* \sigma^*$ representing the contributions of polar effects and spin-delocalization effects of the substituents respectively.⁵⁻⁷ The present work is an attempt to perform such a task with the silyl as the metalloid radical.

Our recent works on substituent effects in radical reactions as measured by a rigorous methodology have shown that the TS's of the rate-determining steps which are characterized by attacks by electrophilic radicals are affected by both polar effects and spin-delocalization effects of the Y-substituents.⁵ We proposed that the dual-parameter eq 1 should always be tested and compared with correlation results based on application of the single-parameter eq 2. It has also been pointed out that the $|\rho^x / \rho^*|$ ratio derived from the dual-parameter eq 1 may serve as a rough measure of the relative importance of the polar and the spin effect.⁷ Our results have established that the dual-parameter eq 1 is needed for the correlation analysis of the rate data of CCl_3^* or Br[•] radical addition reactions to styrenes^{5b} and α -methylstyrenes,^{5c} while the single-parameter eq 2 is good enough for the correlation analysis of the electrophilic radical (e.g., CCl_3^{\bullet} or CF_3^{\bullet}) addition reactions to phenylacetylenes^{5e,5h} and the H-atom abstraction reactions of isopropylbenzenes^{5d} or α, α -ethylenedioxy toluenes^{5g} by Br[•] radicals. But even in those cases where the polar effects dominate in the TS's, the dualparameter eq 1 can always improve the correlation results, albeit to different degrees. Furthermore, the existence of the spin effect may also be revealed by examination of the individual deviations from the regression lines. Consequently, an interesting and urgent task for us would be to find out whether the spindelocalization effects also exist at the transition states of halogen-atom abstraction reactions by nucleophilic radicals.

On the basis of our findings made in the last six years, we came to realize that four possible categories (I to IV) of possible circumstances might be visualized.^{5e-5h,6b} I. When both polar and spin effects are important, the $|\rho_{mb} / \rho_{JJ}|^{\bullet}|$ values might fall in the range of (very) roughly 0.2 to 0.8, e.g., in electrophilic radical additions to, and fluorescence spectra of, styrenes.^{5b,5c,6d} Under these circumstances, the necessity of using the dual-parameter eq 1 can be easily established because it yields much better correlation results than those of single-parameter equations. II. When polar effects dominate, this ratio might be around or greater than unity,

e.g., in H-atom abstraction reactions by electrophilic radicals,^{5d,5g} electrophilic radical addition reactions to phenylacetylenes,^{5e,5h} and EPR data of some phenylnitroxides.^{6c,6d} Under these circumstances, using eq 1 instead of eq 2 may not much improve the correlation result, and the necessity of applying eq 1 cannot be established in a definitive manner. However, the existence of the spin effect can still be revealed by careful examination of the individual deviations of the data from the regression lines of eq 1 and eq 2. III. When the spin-delocalization effect dominates, then eq 3 easily applies, and the use of eq 1 may not much improve the correlation result. Application of eq 1 might yield a $|\rho_{mb} / \rho_{JJ}|^{\bullet}$ ratio of less than 0.2. Very recently discovered examples are the UV spectra of some aromatic compounds, such as styrenes and phenylacetylenes, etc.^{6a,6b} IV. When there are other complicating and interacting factors or effects, then none of the three equations can be successfully applied.^{6a}

We proposed that truly reliable correlation analysis in radical chemistry should be based on a rigorous kinetic methodology which fulfills all the following requirements.⁵ (1) The reaction should be exceptionally clean, in the sense that almost all products are derived from the same rate-determining step for which the relative rate is measured. (2) The relative rate, k_Y / k_H or k_r (**Y**), is calculated by the well-known eq 4,^{5,8} in which $[1-Y]_t$ and $[1-Y]_0$ are the concentrations of 1-Y at time t and 0, and φ is defined as the mole fraction of unreacted substrate, i.e., $[1-Y]_t / [1-Y]_0$. (3) A rigorous kinetic procedure is followed, several (e.g 8-15) 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: 0 - 90%). (4) Each k_R (**Y**) value (capital R) is derived from the regression analysis of a ln φ_Y -vs.- ln φ_H plot, each plot should be an almost perfect straight line with a slope = k_R (**Y**), this k_R (**Y**) value should be about the same (within experimental uncertainty) as the arithmetically averaged k_Y / k_H value of several (e.g., 8-15) independent measurements. (4) At least 11-12 para substituents with well-distributed electronic properties should be used.

$$k_{r}(\mathbf{Y}) = \frac{k_{Y}}{k_{H}} = \frac{\ln \{ [\mathbf{1-Y}]_{i} / [\mathbf{1-Y}]_{0} \}}{\ln \{ [\mathbf{1-H}]_{i} / [\mathbf{1-H}]_{0} \}} = \frac{\ln \varphi_{Y}}{\ln \varphi_{H}}$$
(4)

Although quite a few fine works have been done previously on halogen-atom abstraction reactions by nucleophilic metal or metalloid radicals,⁴ to our knowledge, there exist no k_R (Y) data which are obtained from a methodology that fulfills all the above-mentioned requirements. The present work reports how we have tried to address this problem.

$$p-\mathbf{Y}-\mathbf{C}_{6}\mathbf{H}_{4}-\mathbf{C}\mathbf{H}_{2}\mathbf{B}\mathbf{r} + (\mathbf{M}\mathbf{e}_{3}\mathbf{S}\mathbf{i})_{3}\mathbf{S}\mathbf{i}\mathbf{H} \xrightarrow{\text{AIBN, 80°C}} p-\mathbf{Y}-\mathbf{C}_{6}\mathbf{H}_{4}-\mathbf{C}\mathbf{H}_{3} + (\mathbf{M}\mathbf{e}_{3}\mathbf{S}\mathbf{i})_{3}\mathbf{S}\mathbf{i}\mathbf{B}\mathbf{r} \quad (5)$$

$$1 - \mathbf{Y} \qquad \mathbf{2} \qquad \text{cyclohexane} \qquad \mathbf{3} - \mathbf{Y} \qquad \mathbf{4}$$

As described by eq 5, the reduction reactions of p-Y-benzyl bromides (1-Y's) by tris(trimethylsilyl) silane (2) have been chosen to be our target reactions for our investigation, because 2 has been reported to be an effective and highly selective reducing agent for organic halides,⁹ and the reduction reaction of eq 5 (with 1-Y = 1-H) is a very clean radical chain reaction (Scheme 1) which yields toluene (3-H) almost quantitatively. The above reaction has been reconfirmed in this laboratory, i.e., by GC comparison with an authentic sample of 3-H, and by the fact that the only product detected was 3-H. We, therefore, measured the k_R (Y) values for 13 *p*-Y-substituted benzyl bromides (1-Y's) by our above-mentioned kinetic methodology and carried out a systematic correlation analysis of our data, as described in the result and discussion section.

Scheme 1

$$(Me_{3}Si)_{3}SiH + In^{\bullet} \longrightarrow (Me_{3}Si)_{3}Si^{\bullet} + In-H$$

$$(6)$$

$$2 \qquad 2^{\bullet}$$

$$p-Y-C_{6}H_{4}-CH_{2}Br + (Me_{3}Si)_{3}Si^{\bullet} \longrightarrow p-Y-C_{6}H_{4}-CH_{2}^{\bullet} + (Me_{3}Si)_{3}SiBr$$

$$(7)$$

$$1-Y \qquad 2^{\bullet} \qquad 1-Y^{\bullet} \qquad 4$$

$$p-Y-C_{6}H_{4}-CH_{2}^{\bullet} + (Me_{3}Si)_{3}SiH \qquad \longrightarrow p-Y-C_{6}H_{4}-CH_{3} + (Me_{3}Si)_{3}Si^{\bullet}$$

$$(8)$$

$$1-Y^{\bullet} \qquad 2 \qquad 3-Y \qquad 2^{\bullet}$$

EXPERIMENTAL SECTION

Apparatus. ¹H NMR spectra were recorded at 60 MHZ on a varian EM-360 and at 90 MHZ on a FX-90Q spectrometer with TMS as the external standard. ¹⁹F NMR spectra were obtained at 60 MHZ on a varian EM-360 with trifluoroacetic acid as external standard. Mass Spectrometry (MS) were carried out using a HP 5989A MS instrument. GC analysis were performed on a HP-5890 Gas Chromatography, an OV-17 capillary column was used with a hydrogen flame detector and with nitrogen as the carrier gas.

Reagents and Substrates. Analytical grade cyclohexane was washed with conc. H_2SO_4 and H_2O , dried over CaCl₂ for several days and distilled prior to use. α, α -Azobisisobutyronitrile (AIBN) was recrystalised from acetone and used in the form of a 0.03 M cyclohexane solution kept at -20°C. Analytical grade and freshly fractionated (b.p. 83-85°C / 22 torr) benzyl bromide (1-H) was used. Analytical grade 4-nitrobenzyl bromide was recrystalised (m.p. 98 - 100°C) from mixed solution of n-hexane and ethyl acetate. Tris (trimethylsilyl) silane (2) was purchased from Tokyo Kasei and used as received.

All the *p*-Y-substituted benzyl bromides, i.e., 1-Y s with Y = F, Cl, Br, CN, CO₂Me, CF₃, Me, Et, tBu, Me₃Si, SO₂ Me, MeS and Ph) are known compounds and were prepared by previously reported methods.^{10, 11} They were further identified by ¹ H NMR (or ¹⁹ F NMR) and MS. Boiling points or melting points of 1-Y s prepared in our lab were as follow: 1-Cl, m.p. 49-50°C (lit.^{11a} 49.5-50.5°C); 1-Br, m.p. 60-61°C (lit.^{11a} 60.5-61°C); 1-CO₂Me, m.p. 54-55°C (lit.^{11a} 55-56°C); 1-Me, m.p. 34-35°C (lit.^{11a} 35°C); 1-CN, m.p. 114-115°C (lit.^{11a} 115-116°C); 1-Ph, m.p. 83.5-84°C (lit.^{11b} 83-84°C); 1-Me₃Si, b.p. 78-80°C / 1 torr (lit.^{11c} 76-80°C / 1 torr); 1-F, b.p. 90-92°C / 20 torr (lit.^{11d} 85°C / 15 torr); 1-MeS, m.p. 44 - 45°C (lit.^{11e} 44°C); 1-CF₃, b.p. 65-66°C / 5 torr (lit.^{11f} 37-40 / 1.5 torr); 1-tBu, b.p. 93-94°C / 1.5 torr, m.p. 14°C (lit.^{11g} m.p. 15.2°C); 1-SO₂Me, m.p. 95-96°C (lit.^{10a} 94-96°C); 1-Et, b.p. 87-88°C / 1 torr (lit.^{10b} 88°C / 1 torr).

Attempted Competition Reactions of p-Y-Substituted Toluenes (3-Y's, Y = CN, CO_2Me , MeS, SO_2Me and SOMe) with 1-H.^{4c} 1-H (0.04 mmol), 3-Y (0.04 mmol), 2 (0.10 mmol), n-C₁₅H₃₂ (1.5 µL) and 0.03 M AIBN (80 µL, 3 mol%) were added into a volumetric flask and diluted to 2 mL with cyclohexane. Eight aliquots (0.2 mL) of the solution were degassed by the freeze-thaw procedure three times and sealed in Pyrex ampoules. The ampoules were thermostated (80 ± 0.5°C) for 4h. GC analysis showed that within experimental uncertainty (5%), under conditions in which 90% of 1-H were reduced, none of the 3-Y's (except 3-SOMe) were reduced.

Kinetic Competition Procedure for 1-Y and 1-H.^{5b-5h} **1-H** (0.04 mmol), **1-Y** (0.04 mmol), **2** (0.10 mmol), n-C₁₅H₃₂ (1.5 μ L) and 0.03 M AIBN (80 μ L, 3 mol%) were added to a volumetric flask and diluted to 2 mL with cyclohexane. Sixteen aliquots (120 μ L) of the solution were degassed by the freezethaw procedure three times and sealed in Pyrex ampoules. The ampoules were immersed in the thermostat (80 \pm 0.5°C). Four hours later, the degree of conversion of **1-H** or **1-Y** could reach 50% ($\phi = 0.5$) to 90% ($\phi = 0.1$). During this time, 8-16 ampoules were taken out, usually at 15 min intervals, and kept in dry-ice. They were opened and analysed later by GC.

As the GC peaks of 1-F and 1-CF₃ overlap with that of 1-H, the k_R (F) and k_R (CF₃) cannot be measured by direct competition between 1-F or 1-CF₃ and 1-H. However, direct competition between 1-F or 1-CF₃ and 1-Cl is experimentally feasible, hence the k_R (F) or k_R (CF₃) values in Table 2 were calculated by the equation: $k_Y / k_H = k_Y / k_{Cl} \cdot k_{Cl} / k_H$, where Y was F or CF₃. The k_R (NO₂) value could not be measured because the mixture of 1-NO₂ and 1-H would not react under our experimental conditions. The k_R (Me) value could not be measured because the GC peaks of 1-Me and (Me₃Si)₃SiBr overlap with each other.

RESULTS AND DISCUSSION

Before we measure the relative rates of bromine-atom abstraction reactions of 1-Y's by $(Me_3Si)_3Si^{\bullet}$ radicals, possible side reactions involving the reduction of the para substituents must be considered. Benzyl bromide is known to be 200 times more reactive than benzyl chloride or bromobenzene,^{9a,9c} therefore, side reactions involving halogen substituents (i.e., **F**, **Cl** and **Br**) can be neglected. Furthermore, the bond energy of benzylic C-Br bond (248 kJmol⁻¹) is much smaller than that of the benzylic C-H bond (368.2 kJmol⁻¹).

while the bond energy of $(Me_3Si)_3Si$ -Br is expected not to differ too much from that of the $(Me_3Si)_3Si$ -H bond (330.5 kJmol⁻¹)^{12a} because the bond energy of Me_3Si -Br (359 kJmol⁻¹)^{12b} does not differ too much from that of Me_3Si -H (368 kJmol⁻¹)^{12b}. Thus the side reactions involving H-atom abstraction from the substituents **Me**, **Et**, **Ph**, **Me_3Si** and **MeO** are also negligible under our reaction conditions. In order to assess the possibility of side reactions of the reducible substituents, i.e., **MeS**, **CN**, **CO_2Me**, **SO_2Me** and **SOMe**, we have carried out competition reactions between *p*-Y-substituted toluenes (**3-Y's**, **Y** = **CN**, **CO_2Me**, **MeS**, **SO_2Me** and **SOMe**) and **1-H** with $(Me_3Si)_3SiH$ as the reducing agent, and found that when the conversion of **1-H** reached 90%, the **3-Y's** (except **Y** = **SOMe**) have not been reduced at all within experimental uncertainty (± 5 %). Consequently, the side reactions involving all the aforesaid substituents except **SOMe** may be disregarded, and the **SOMe** group was deleted from the list of substituents.

According to eq 4, if a set of φ values $(1.0 \sim 0.1)$ were measured over a wide range of reaction times which correspond to a wide range of the extent of reaction ($0 \sim 90\%$), then a linear relationship of $\ln \varphi_{\rm Y}$ (time t) with $\ln\varphi_{\rm H}$ (time t) would be obtained if all the products were derived from the same rate-limiting step and if the adopted kinetic methodology were reliable. Table 1 is a sample of a set of $\varphi_{\rm Y}$ versus $\varphi_{\rm H}$ data, with ${\bf Y} = {\bf Br}$, Fourteen samples taken at fourteen time intervals were measured for the φ values, and the $\ln \varphi_{\rm Br}$ vs. $\ln \varphi_{\rm H}$ plot turned out to be an almost perfect straight line with r = 0.999 (n = 14), as shown by Figure 1. Fourteen (three for ${\bf Y} = {\bf CI}$ at three different $1 - {\bf Y} / 1 - {\bf H}$ ratios) other sets of $\varphi_{\rm Y}$ versus $\varphi_{\rm H}$ data and $\ln \varphi_{\rm Y}$ -vs.- $\ln \varphi_{\rm H}$ straight line plots have been obtained. The r values listed in Table 2 are indicators of the reliability of our kinetic procedure. The k_R(${\bf Y}$) values summarized in Table 2 are the slopes of the

Table 1. Relative Reactivity of **1-H** and **1-Br** in the Bromine - Atom Abstraction Reaction by Tris (trimethylsilyl) silyl Radicals in Cycloheane at 80°C

t (h)	φн	ϕ_{Br}	-ln φ _H	-ln φ _{Br}
0	1	1	0	0
0.25	0.9451	0.9090	0.564	0.0955
0.50	0.7540	0.6911	0.2824	0.3695
0.75	0.7060	0.6141	0.3482	0.4876
1.00	0.6699	0.5973	0.4006	0.5154
1.25	0.6753	0.5838	0.3926	0.5382
1.50	0.6226	0.5209	0.4738	0.6521
1.75	0.5304	0.4337	0.6340	0.8355
2.00	0.4150	0.3273	0.8795	1.1168
2.25	0.4036	0.3094	0.9073	1.1732
2.50	0.4010	0.2929	0.9137	1.2280
3.00	0.3447	0.2529	1.0651	1.3749
3.50	0.2845	0.1957	1.2569	1.6313
4.00	0.2424	0.1640	1.4172	1.8076



Figure 1. Plot of $-\ln\varphi_{Br}$ vs. $-\ln\varphi_{H}$

Y ₁ / Y ₂	Ratio	$k_R \pm \Delta k_R$	r	n	D-1 p	D-1 _c	D-2 ^d
H / H		1			-0.110	-0.047	0.020
Cl / H	1:1	1.261 ± 0.044	0.996	11	-0.023	0.009	-0.011
Cl / H	1:2	1.266 ± 0.041	0.997	15			
Cl / H	2:1	1.270 ± 0.047	0.997	14			
Br / H	1:1	1.273 ± 0.021	0.999	14	-0.020	-0.001	-0.010
F / Cl	1 : 1	0.810 ± 0.037	0.998	13			
F / H ^a	1:1	1.021 ± 0.082			-0.059	-0.031	0.016
CF ₃ /Cl	1:1	1.108 ± 0.020	0.999	13			
CF_3 / H^a	1:1	1.397 ± 0.074			-0.082	-0.055	-0.002
SO ₂ Me/ H	1:1	1.993 ± 0.032	0.999	11	-0.000	-0.026	-0.032
CN / H	1:1	2.098 ± 0.066	0.997	12	0.055	0.040	0.020
CO ₂ Me / H	1:1	1.687 ± 0.065	0.996	16	0.030	0.004	0.016
t-Bu / H	1:1	0.882 ± 0.020	0.999	12	-0.036	-0.072	-0.043
MeS / H	1:1	1.505 ± 0.030	0.997	8	0.130	0.116	0.029
Ph / H	1:1	1.321 ± 0.051	0.998	10	0.076	0.069	0.016
Me ₃ Si / H	1:1	1.002 ± 0.018	0.999	13	-0.023		-0.042
Et / H	1:1	0.994 ± 0.018	0.999	10	-0.000	-0.006	0.024

 Table 2. Relative Rates of Bromine-Atom Abstraction of p-Y-Benzyl Bromides (1-Y) by

 Tris (trimethylsilyl) silyl Radicals in Cyclohexane at 80°C

 $a: k_{F/H} = k_{F/C1} \bullet k_{C1/H}; \quad \Delta k_{F/H} = \Delta k_{F/C1} \bullet k_{C1/H} + \Delta k_{C1/H} \bullet k_{F/C1}; \qquad k_{CF3/H} = k_{CF3/C1} \bullet k_{C1/H}; \\ \Delta k_{CF3/H} = \Delta k_{CF3/C1} \bullet k_{C1/H} + \Delta k_{C1/H} \bullet k_{CF3/C1} \qquad b: As defined in the text; \Sigma | D-1 |_{p} = 0.583$

c : As defined in the text; $\Sigma |D-1|_{\perp} = 0.476$. d: As defined in the text; $\Sigma |D-2| = 0.281$.

regression lines of 8-16 independently measured $\ln \phi_{\rm Y}$ -vs.- $\ln \phi_{\rm H}$ data at 8-16 consecutive intervals. Within the experimental uncertainty (± 5 %), they are almost the same as the averaged $k_{\rm Y} / k_{\rm H}$ values of the n-1 independent measurements, where n is the number of tubes taken out for analysis. The first tube taken at time-zero gave no $k_{\rm Y}/k_{\rm H}$ value, but it served as a standard for $\phi_{\rm Y} = 1$ and $\phi_{\rm H} = 1$.

The reliability of our methodology has been further cross-checked by measuring the k_R (Cl) values at three different 1-Cl / 1-H molar ratios, i.e., at molar ratios of roughly 1 : 1, 1 : 2 and 2 : 1, as shown by the first three entries of Table 2. The data show that within experimental uncertainty, the k_R (Cl) values are not affected by the reactant molar ratios.

$\sigma^{x} \text{ or } \sigma^{\bullet} \text{ or}$ $(\sigma^{x} + \sigma^{\bullet})$	ρ ^x	ρ	ρ ^x /ρ •	r or R	Ψ	S	F ^b	n ^a
σ_{p}	0.33			0.868	0.540	0.061	33.63	13
$\sigma^{^{+}}$	0.16			0.567	0.902	0.096	4.735	12
σ	0.23			0.892	0.495	0.057	39.01	12
σ _{IJ} ・		0.32		0.535	0.918	0.10	4.42	13
σ_{c}		0.43		0.634	0.841	0.096	7.39	13
$\sigma_p + \sigma_{JJ}$ •	0.31	0.27	1.15	0.977	0.243	0.028	104.7	13
$\sigma_p + \sigma_C$ •	0.29	0.32	0.91	0.979	0.231	0.026	117.4	13
$\sigma^+ + \sigma_{JJ}^{\bullet}$	0.22	0.39	0.56	0.881	0.547	0.058	15.57	12
$\sigma^+ + \sigma_C^{\bullet}$	0.16	0.42	0.38	0.898	0.508	0.054	18.80	12
$\sigma_{mb}^{+}\sigma_{JJ}^{\bullet}$	0.25	0.23	1.09	0.910	0.474	0.054	23.95	13
$\sigma^- + \sigma_{JJ}^{\bullet}$	0.21	0.22	0.95	0.965	0.305	0.035	60.19	12
$\sigma^{+}\sigma_{C}^{+}$	0.20	0.26	0.77	0.969	0.284	0.032	69.99	12

Table 3. Values of ρ^x and ρ^{\bullet} of eq 1, eq 2 and eq 3, and corresponding values of the correlation coefficient r or R, ψ , s and F-test for correlation of $k_R(Y)$ values of n 1-Y's with σ^x and σ^{\bullet}

a. n = 13, Y = H, Cl, Br, F, CF₃, SO₂Me, CN, CO₂Me, tBu, MeS, Ph, Me₃Si and Et. n = 12, for σ⁺ : Y = H, Cl, Br, F, CF₃, CN, CO₂Me, tBu, MeS, Ph, Me₃Si and Et; for σ⁻ : Y = H, Cl, Br, F, CF₃, SO₂Me, CN, CO₂Me, tBu, MeS, Ph and Et.

b. Critical F values: 15 F_{0.001} (1,11) = 19.69 ; F_{0.001} (1,10) = 21.04; F_{0.05} (1,11) = 4.84; F_{0.10} (1,11) = 3.23 ; F_{0.10} (1,10) = 3.29; F_{0.001} (2,10) = 14.91 ; F_{0.001} (2,9) = 16.39 ; F_{0.01} (2,9) = 8.02.

Results of correlation of k_R (Y) with substituent constants by both eq 1, eq 2 and eq 3 are summarized in Table 3, in which r or R, ψ , F, s, ρ^x , ρ^{\bullet} and ρ^x / ρ^{\bullet} values are listed. Seven combinations of ($\sigma^x + \sigma^{\bullet}$) are given with $\sigma^x = \sigma_p^{-13}$, σ^{+13} , σ_{mb}^{-5a} and $\sigma^{-,13}$ and $\sigma^{\bullet} = \sigma_{JJ}^{\bullet 5a}$ and $\sigma_C^{\bullet 14}$. The $\sigma_{\alpha}^{\bullet 11}$ scale have not been included because the numble of substituents for $\sigma_{\alpha}^{\bullet}$ is two less than the maximum numble of substituents (13) for σ_{JJ}^{\bullet} and σ_C^{\bullet} . Notably, for correlations by the single-parameter eq 2, the correlation by σ_{mb} is not included because the reaction center is not a multiple bond. However, for correlations by the dual-parameter eq 1, the combination ($\sigma_{mb}+\sigma_{JJ}^{\bullet}$) is included because a rough $\rho_{mb} / \rho_{JJ}^{\bullet}$ values derived therefrom might help us to classify this reaction according to our "four-category proposition" mentioned in the introduction. In fact, in order to make a systematic investigation, $\rho_{mb} / \rho_{JJ}^{\bullet}$ values have been evaluated for all our previous studies (cf., ref. 5f).

Results of single-parameter correlation by eq 2 show that both σ^- and σ_p yield fair results, i.e., for σ_p : r = 0.868, $\psi = 0.54$, n = 13; for σ^- : r = 0.892, $\psi = 0.50$, n = 12. Both ρ^x values are positive and not smaller than 0.23, while σ^- gives the better correlation than σ_p does as expected, because the attacking radical is distinctly

nucleophilic.⁴ Also expected is the fact that correlations by eq 3 show no meaningful relationship between $k_R(Y)$ and σ^* . On the contrary, correlations by the dual-parameter eq 1 yield clearly improved results. If we take those results based on the use of the maximum number of substituents (n = 13), then the ($\sigma_p + \sigma_{JJ}^{\bullet}$) and $(\sigma_p + \sigma_c^{\bullet})$ combinations come out as the best combinations with R values greater than 0.977 (ψ 's < 0.243). The $(\sigma_{mb} + \sigma_{JJ})$ combination also yields pretty good correlations (R = 0.910, $\psi = 0.474$) with the $|\rho_{mb}/\rho_{JJ}|$ value = 1.07, which is a bit smaller than the $|\rho_p / \rho_{JJ}|$ value of 1.15, as expected.^{5f} Therefore, judging by the fact that the dual-parameter correlation is clearly better than the single-parameter correlation is, our studied reaction may be classified as category - I. However, judging by the magnitude of the $|\rho_{mb} / \rho_{II}|$ value, it seems to belong to category-II.^{5e,5f,6b} We suggest that it be looked upon as a borderline case of category - I and - II. As proposed previously, $^{5d-5h, 6c, d}$ it would be good practice to examine the deviations of log $k_R(Y)$ values of the substituents from the regression lines. In Table 2, |D-1|, stands for the deviations from the regression line of $[\log k_R(Y) \text{ vs. } \sigma_0]$ (cf. Figure 2), $|D-1|_-$ represents the deviations from the regression line of [log $k_R(Y)$ vs. σ^-] (cf. Figure 2), and |D-2| represents the deviations from the regression line of $[\log k_R(\mathbf{Y}) \text{ vs. } (0.31\sigma_p + 0.27\sigma_{JJ}^{\bullet})]$ (cf. Figure 3). Notably, for $|D-1|_p$, there are six substituents (**H**, **F**, CF₃, CN, MeS and Ph) with $|D-1|_{p}$ larger than 0.050; for $|D-1|_{-}$, there are five substituents (H, CF₃, tBu, MeS and Ph) with |D-1| larger than 0.050, for |D-2|, however, there is no substituent with deviations larger than 0.050, although deviations of Me₃Si and tBu are about 0.040. Therefore, existence of the spin-delocalization effect at the TS's is clearly suggested.

The positive ρ^x values (e.g., $\rho_p = 0.31$ or 0.29) calculated from the successful correlation by eq 1 with the $(\sigma_p + \sigma^{\bullet})$ combinations demonstrate that $(Me_3Si)_3Si^{\bullet}$ radicals are distinctly nucleophilic. In other words, if we visualize the TS's of W-atom abstraction reactions by Z[•] radicals in terms of the resonance structures A - D,^{4,9a,16} then for our Br-atom abstraction by the silyl radicals, C carries more weight than D, whereas for H-atom abstraction reactions by electrophilic radicals, D is more important than C. The necessity of using the dual-parameter eq 1 for a truly good correlation demonstrates that structure B is of importance too.

In our previous studies on H-atom abstraction reactions, we have argued that a smaller $|\rho_p / \rho_{JJ}^{\bullet}|$ ratio may suggest a greater contribution of the spin-delocalization effect.^{5g} Therefore, it is noteworthy that the $|\rho_p / \rho_{JJ}^{\bullet}|$ ratio (1.15) of our Br-atom abstraction reactions is smaller than the $|\rho_p / \rho_{JJ}^{\bullet}|$ ratios of the Hatom abstraction reactions, i.e., 1.68 for H-atom abstraction reactions from *p*-**Y**-substituted α, α -ethylenedioxy toluenes by Br^{• 5g} and 2.01 for H-atom abstraction reactions from *p*-**Y**-substituted isopropylbenzene by Br^{•.5d} The aforesaid conclusion is also in harmony with the classification of the Br-atom abstraction reactions as a borderline case of category-I and category-II.

As a casual illustration of the necessity of testing the applicability of the eq 1, we may note that while Migita's data for the Br-atom abstraction reaction by the *p*-chlorophenyl radicals cannot be correlated by the

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single-parameter eq 2,¹⁷ it actually can be correlated by the dual-parameter eq 1 with the $(\sigma_p + \sigma_{JJ}^*)$ pairing (R = 0.974, $\psi = 0.15$, n = 5, $\rho_p = -0.066$, $\rho^* = 0.495$, $\rho_p / \rho_{JJ}^* = -0.13$). We believe in future studies it would be worthwhile to assess the degree of nucleophilicity of the alkyl and aryl radicals by assessing the ρ^x values derived from a successful and rigorous application of eq 1. On the basis of this approach, one might be able to show, e.g., that methyl radicals were not distinctly nucleophilic radicals. Finally, we hope that the degree of nucleophilicity of other metal radicals will also be studied by our methodology and approach.



Figure 2. Plot of $logk_{\mathbf{R}}$ vs. $\sigma_{\mathbf{p}}(\circ)$ or $\sigma^{-}(\times)$

Figure 3. Plot of $logk_R$ vs. $(0.31\sigma_p+0.27\sigma_{JJ})$



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Scheme 2

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