How does an alkoxy group at the benzylic carbon affect the transition state of the hydrogen-atom abstraction reaction? Correlation analysis of relative rates for 14 *p*-Y-substituted α,α-ethylenedioxytoluenes

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Correlation analysis of the relative rates for the H-atom abstraction reaction of 14 2-(4-Y-phenyl)dioxolanes (*p*-Y-substituted α,α-ethylenedioxytoluenes, 1-Y) by *N*-bromosuccinimide (NBS) shows that the spin-delocalization effect is also operating at the transition state of the H-atom abstraction reaction and that the ethylenedioxy group at the benzylic carbon makes the spin-delocalization more observable than do two methyl groups.

Introduction

Although it has been reported many times that the single-parameter eqn. (1) with polar substituent constants σ^x has been

$$\log k_r = \rho^x\sigma^x \qquad (1)$$

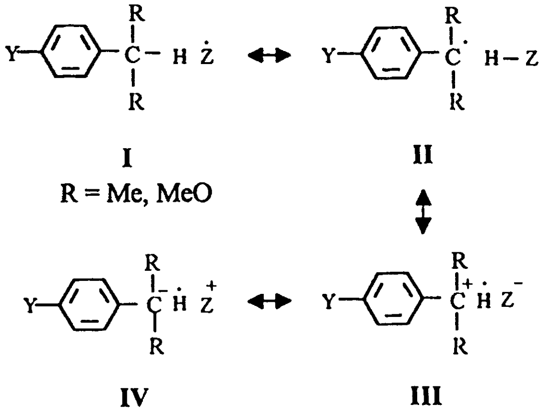
successfully applied to H-atom abstraction reactions,[1] we believe, in the absence of measurable steric effects, that the transition states (TS) of H-atom abstraction reactions are affected by both polar and spin-delocalization effects of the substituents. A recent study[2] on the H-atom abstraction reaction by bromine revealed that as long as the substituents are well distributed, reliable rate data measured by a rigorous competition kinetic method could be best correlated by the dual-parameter eqn. (2), where σ^x is the polar substituent

$$\log k_r = \rho^x\sigma^x + \rho^{\cdot}\sigma^{\cdot} \qquad (2)$$

constant and $\sigma^{\cdot}$ is the spin-delocalization substituent constant. The relative importance of the polar and spin-delocalization effects for radical abstraction reactions can be roughly evaluated by the $|\rho^x/\rho^{\cdot}|$ ratios.[3] The $|\rho_P{}^{\cdot}/\rho_{JJ}{}^{\cdot}|$ ratio has been found to be 2.01 for the H-atom abstraction of cumene [the $(\sigma_P{}^{\cdot} + \sigma_{JJ}{}^{\cdot})$ combination yields the best correlation].[2] This ratio shows that the spin-delocalization effect also exists, even though the polar effect predominates at the TS of that H-atom abstraction reaction.[2,3c,3f]

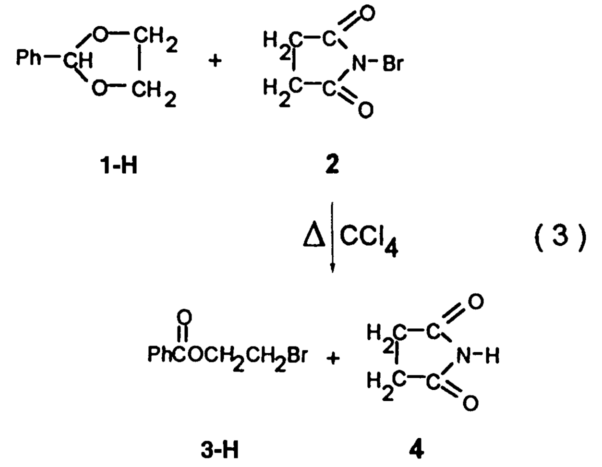
In general, substituent effects on the TS of H-atom abstraction reactions have been rationalized by the four imaginary resonance structures **I**, **II**, **III** and **IV**,[4] as shown in Scheme 1, in which Y represents a substituent, and $Z^{\cdot}$ the attacking radical. The susceptibility of the TS to spin-delocalization effects is suggested by **II**, and to polar influences by **III** and **IV**. When Z is electrophilic, **III** will carry more weight; when Z is nucleophilic, **IV** becomes more important. The above results on the H-atom abstraction reaction from cumene by the electrophilic bromine atom suggest that the detectability of the spin-delocalization effect may be attributed to the fact that **II** is not negligible, even though **III** is predominant.

Owing to the fact that we do not know precisely the timing of the TS of our H-atom abstraction reaction, it would be difficult to speculate on whether the polar effects of an α-alkoxy substituent would facilitate (by back-donation) or hinder (by field/inductive effect) the homolysis of the benzylic C–H bond, because the field/inductive effect and electron-pair back-donation effect of an α-alkoxy group operate in opposite directions. In other words, the relative relevance of the structures **I** and **III** is expected to depend on the timing of the appearance of the TS. In contrast, a larger spin-delocalization effect will always favour the homolysis of the benzylic C–H bond, even though the relative importance of structure **II** also depends on the timing of the TS.

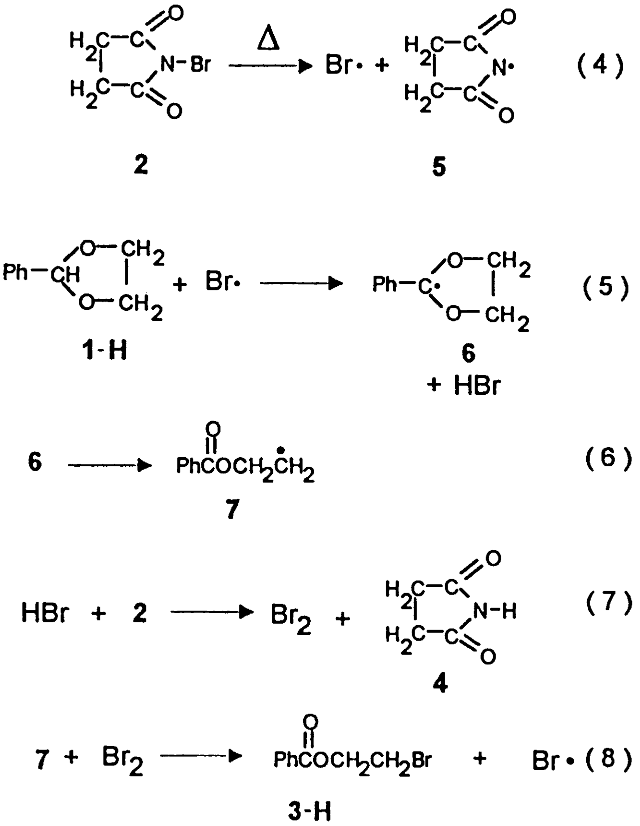


Scheme 1

An intriguing question now arises: is it possible to increase the relative importance of structure **II**, *i.e.*, reduce the magnitude of the $|\rho_P/\rho_{JJ}{}^{\cdot}|$ ratio by changing the two α-methyl substituents ($\sigma_{JJ}{}^{\cdot}$ = 0.15) of the Y-substituted cumenes to two other substituents? We thought the answer was yes, and chose the ethylenedioxy group to replace the two methyl groups of cumene, because it is known that the alkoxy group possesses greater spin-delocalizing ability than does the methyl, *e.g.*, $\sigma_{JJ}{}^{\cdot}$ for methoxy = 0.23. Therefore, efforts of the present work are dedicated to the correlation analysis of the H-atom abstraction reactions of 14 2-(4-Y-phenyl)dioxolanes (*p*-Y-substituted α,α-ethylenedioxytoluenes, **1**-Y) by our newly developed rigorous kinetic methodology. The reagent used was *N*-bromosuccinimide (NBS), which provides the bromine atoms as the attacking radicals. Bromination of ethylenedioxytoluene (**1**-H) with NBS has been found to be a very effective and useful method for synthesizing the 2-bromoethyl benzoate ester (**3**-H), as eqn. (3) shows.[5] Although the mechanism of NBS bromination has been somewhat controversial (see ref. 6 and references cited therein), it is nevertheless generally accepted that for bromination of benzylic hydrogens by NBS in CCl_4, a medium in which NBS has very low solubility ($\approx 10^{-3}$ mol dm^{-3}),[7] it is



the bromine atom that carries the chain, *i.e.*, that abstracts the benzylic hydrogen, as described by Scheme 2.[8] We have found



Scheme 2

that under the aforesaid standard conditions this reaction for 1-H is very clean, and only one product (3-H) can be detected (>90% yield). Therefore, by using our previously established rigorous methodology,[2,3c–e] we have performed a correlation analysis of our rate data for 14 *p*-Y-substituted α,α-ethylenedioxytoluenes (1-Y). As before, eqn. (9) was used for

$$k_r(\mathrm{Y}) = \frac{k_\mathrm{Y}}{k_\mathrm{H}} = \frac{\log\{[\mathbf{1}\text{-Y}]_t/[\mathbf{1}\text{-Y}]_0\}}{\log\{[\mathbf{1}\text{-H}]_t/[\mathbf{1}\text{-H}]_0\}} = \frac{\log\varphi_\mathrm{Y}}{\log\varphi_\mathrm{H}} \qquad (9)$$

the calculation of the relative rates $k_\mathrm{Y}/k_\mathrm{H}[k_r(\mathrm{Y})]$, in which $[\mathbf{1}\text{-Y}]_t$ and $[\mathbf{1}\text{-Y}]_0$ are the concentrations of 1-Y at time *t* and 0, and φ is defined as the mole fraction of unreacted substrate, *i.e.*, $[\mathbf{1}\text{-Y}]_t/[\mathbf{1}\text{-Y}]_0$.

Experimental

Apparatus

^{1}H NMR spectra were recorded at 60 MHz on a Varian EM-360 and at 90 MHz on an FX-90Q spectrometer with TMS as the external standard. ^{19}F NMR spectra were obtained at 60 MHz on a Varian EM-360 with trifluoroacetic acid as external standard. UV spectra were taken in 95% EtOH on a Perkin-Elmer Lambda 2. Mass spectrometry (MS) was carried out using an HP5989A MS instrument. GC analyses were performed on an HP-5890 Gas Chromatography, an OV-1 capillary colum was used with a flame ionization detector and with nitrogen as the carrier gas.

Reagents and substrates

Analytical grade CCl_4 was dried with CaH_2 and distilled prior to use. *N*-Bromosuccinimide was recrystallized from acetone. All the *p*-Y-benzaldehydes are commercially available, except for *p*-Me_3Si-benzaldehyde; this was prepared according to ref. 9. All the *p*-Y-substituted α,α-ethylenedioxytoluenes (**1**-Y) were prepared by a reported method.[8] **1**-Y with Y = H, OMe, Me, Br, Cl and NO_2 are known compounds,[10,11] further identified by ^{1}H NMR spectroscopy and MS. Boiling and melting points of **1**-Y are: **1**-H: bp 77–78 °C/4 torr (lit.,[10] 61–62 °C/1 torr); **1**-MeO: bp 97–98 °C/1.5 torr (lit.,[10] 97–98 °C/1.5 torr); **1**-Cl: bp 94.5–95 °C/2 torr (lit.,[10] 123.5 °C/11.5 torr); **1**-Me: bp 98–99 °C/5 torr (lit.,[10] 88 °C/2 torr); **1**-Br: bp 108 °C/2 torr (lit.,[11] 107 °C/2 torr), **1**-NO_2: mp 91 °C (lit.,[10] 90 °C).

Other **1**-Y are new compounds, physical data are: **1**-F: bp 78–79 °C/3.5 torr; $\delta_H(CCl_4$, 60 MHz) 7.35 (4 H, m, Ar), 5.89 (1 H, s, Ar-CH), 4.13 (4 H, s, $-OCH_2CH_2O-$); $\delta_F(CCl_4$, 60 MHZ) 35 (s); UV (95% EtOH) λ_{max}/nm 205.7 (ε/dm^3 mol^{-1} cm^{-1} 4.98 × 10^3); *m*/*z* 168 (M^+, 24%), 167 (100), 123 (40) and 95 (18) (Found: C, 64.07; H, 5.36, $C_9H_9FO_2$ requires C, 64.28; H, 5.39%); **1**-Bu^t: bp 108 °C/2 torr; $\delta_H(CCl_4$, 90 MHz) 7.30 (4 H, AB, Ar), 5.73 (1 H, s, Ar-CH), 4.00 (4 H, s, $-OCH_2CH_2O-$), 1.38 (9 H, s, Bu^t); UV (95% EtOH) λ_{max}/nm 216.5 (ε/dm^3 mol^{-1} cm^{-1} 9.15 × 10^3); *m*/*z* 206 (M^+, 25%), 205 (100), 191 (41), 161 (19), 149 (60) and 119 (81) (Found: C, 75.60; H, 8.80; $C_{13}H_{18}O_2$ requires C, 75.73; H, 8.74%); **1**-Me_3Si: bp 120 °C/2 torr; $\delta_H(CCl_4$, 90 MHz) 7.44 (4 H, s, Ar), 5.79 (1 H, s, Ar-CH), 4.04 (4 H, s, $-OCH_2CH_2O-$), 0.36 (9 H, s, Me_3Si); UV (95% EtOH) λ/nm 220.1 (ε/dm^3 mol^{-1} cm^{-1} 6.79 × 10^3); *m*/*z* 222 (M^+, 10%), 221 (45), 207 (100), 177 (28), 163 (46), 149 (86) and 135 (75) (Found: C, 64.75; H, 8.00; $C_{12}H_{18}O_2Si$ requires C, 64.81; H, 8.16%); **1**-CF_3: bp 95 °C/5 torr; $\delta_H(CCl_4$, 90 MHz) 7.46 (4 H, AB, Ar), 5.71 (1 H, s, Ar-CH), 3.92 (4 H, s, $-OCH_2CH_2O-$); $\delta_F(CCl_4$, 60 MHz) −15 (s); UV (95% EtOH) λ/nm 207.3 (ε/dm^3 mol^{-1} cm^{-1} 3.97 × 10^3); *m*/*z* 218 (M^+, 8%), 217 (32), 199 (32), 155 (20), 145 (12) and 105 (100) (Found: C, 54.83; H, 4.14; $C_{10}H_9F_3O_2$ requires C, 55.05; H, 4.13%); **1**-COOMe: bp 127–128 °C/1 torr; $\delta_H(CCl_4$, 90 MHz) 7.73 (4 H, AB, Ar), 5.80 (1 H, s, Ar-CH), 4.01 (4 H, s, $-OCH_2CH_2O-$), 3.90 (3 H, s, MeOOC–); UV (95% EtOH) λ/nm 233.1 (ε/dm^3 mol^{-1} cm^{-1} 9.25 × 10^3); *m*/*z* 208 (M^+, 18%), 207 (100), 193 (17), 163 (96), 149 (50) and 105 (71) (Found: C, 63.13; H, 5.95; $C_{11}H_{12}O_4$ requires C, 63.46; H, 5.81%); **1**-MeS: bp 107 °C/1 torr; $\delta_H(CCl_4$, 90 MHz) 7.00 (4 H, AB, Ar), 5.43 (1 H, s, Ar-CH), 3.71 (4 H, s, $-OCH_2CH_2O-$), 2.20 (3 H, s, MeS); UV (95% EtOH) λ/nm 258.3 (ε/dm^3 mol^{-1} cm^{-1} 7.99 × 10^3); *m*/*z* 196 (M^+, 62%), 195 (55), 151 (52), 149 (41) and 124 (100) (Found: C, 61.29; H, 6.35; $C_{10}H_{12}O_2S$ requires C, 61.22; H, 6.12%); **1**-CN: mp 46–47 °C; $\delta_H(CCl_4$, 90 MHz) 7.47 (4 H, AB, Ar), 5.67 (1 H, s, Ar-CH), 3.94 (4 H, s, $-OCH_2CH_2O-$); UV (95% EtOH) λ/nm 227.5 (ε/dm^3 mol^{-1} cm^{-1} 9.93 × 10^3); *m*/*z* 175 (M^+, 32%), 174 (100) and 130 (37) (Found: C, 68.60; H, 5.95; N, 7.94; $C_{10}H_9NO_2$ requires C, 68.56; H, 5.18; N, 8.00%); **1**-MeCOO: mp 47–48 °C; $\delta_H(CCl_4$, 90 MHz) 7.15 (4 H, AB, Ar), 5.70 (1 H, s, Ar-CH), 3.90 (4 H, s, $-OCH_2CH_2O-$), 2.20 (3 H, s, MeCOO–); UV (95% EtOH) λ/nm 207.9 (ε/dm^3 mol^{-1} cm^{-1} 5.51 × 10^3); *m*/*z* 208

Table 1 Relative reactivity of **1**-H and cumene in the H-atom abstraction reaction by atomic bromine in CCl_4 at 50 °C

Substrate	Mole ratios	$k_{1\text{-H}}/k_{\text{cumene}}$	n^a	r
	1:1	4.6 ± 0.2	8	0.9973
1-H/cumene	1:2	4.7 ± 0.2	8	0.9973
	1:5	4.6 ± 0.2	9	0.9989

[a] n is the number of measurements at successive time intervals.

(M^+, 3%), 207 (6), 165 (100), 149 (26) and 121 (55) (Found: C, 63.39; H, 5.86: $C_{11}H_{12}O_4$ requires C, 63.46; H, 5.81%).

Kinetic procedure for the competition between 1-H and 1-Y

To a round-bottom flask (25 cm^3) was added a solution of **1**-Y (0.5 mmol), **1**-H (0.5 mmol), internal GC standard (n-$C_{10}H_{22}$: 20 mm^3) in 20 cm^3 of CCl_4. The solution was vigorously stirred at 50 ± 0.5 °C under N_2 for 10 min and 1.1 mmol NBS was added. After 3 h the degree of conversion of **1**-H or **1**-Y could reach 50% ($\varphi = 0.5$) to 90% ($\varphi = 0.1$). During this time, 7–12 samples (about 0.10 cm^3 each) were taken at 5–10 min intervals into a 0.5 cm^3 tube, which was sealed immediately, cooled in dry ice and later analysed by GC. The ratio of **1**-Y/**1**-H could be changed (see Table 3).

Since the GC peaks of **1**-F and **1**-CF_3 overlap with **1**-H, whereas the peaks of **1**-MeO, **1**-Bu^t, **1**-Me_3Si, **1**-Br, **1**-CN overlap with the bromination product **3**-H, the relative rates k_Y/k_H (Y = F, CF_3, MeO, Bu^t, Me_3Si, Br and CN) cannot be measured by direct competition between **1**-Y and **1**-H; they were instead calculated from the equation: $k_Y/k_H = (k_Y/k_{Y'})\cdot(k_{Y'}/k_H)$, in which for Y = F, Y′ is Me; for Y = CF_3, Y′ is NO_2; for Y = MeO, Bu^t, Me_3Si, Br and CN, Y′ is Cl.

Kinetic procedure for the direct competition between 1-H and cumene

The procedure is based on one recently developed for the evaluation of the relative reactivity of styrene and α,β,β-trifluorostyrene, and that of α,β,β-trifluorostyrene and phenylacetylene,[12] it is also the same as that described above for the competition between **1**-H and **1**-Y. Dodecane was used as the internal GC standard. The ratio of **1**-H/cumene could be changed (see Table 1).

Results and discussion

In our previous study on the substituent (Y) effect on the reactivity of the benzylic C–H bond of *p*-Y-substituted cumenes, it was established that side-reactions involving C–H bonds of the substituents, *i.e.*, H-atom abstraction reactions from Bu^t, COMe, Me and SMe, can be neglected because the benzylic C–H bond of cumene is much more reactive than the reactivity of the C–H bonds of these substituents.[2] Therefore, if we could establish that the benzylic C–H bond of **1**-H is just as reactive as, or even more reactive than, the benzylic C–H bond of cumene, then H-atom abstraction side-reactions of the substituents of **1**-Y in the present study could also be legitimately neglected. Thus, we first evaluated the relative C–H bond reactivity of cumene and **1**-H by our recently-developed technique of direct competition between two types of substrates (*cf.* Experimental section). This technique has been successfully applied to the measurement of relative reactivities of styrene, α,β,β-trifluorostyrene and phenylacetylene.[12] From Table 1 the relative reactivity of **1**-H and cumene towards bromine is 4.6:1, and this ratio is independent of the **1**-H/cumene molar ratio (*i.e.*, at molar ratios of roughly 1:1, 1:2 and 1:5). In other words, the benzylic C–H of **1**-Y is undoubtedly much more reactive than that of *p*-Y-cumene, and within the limit of experimental precision, H-atom abstraction side-reactions of the substituents of **1**-Y may be disregarded.

Table 2 φ values for the reaction of **1**-Cl and **1**-H in competition for bromine atoms at 11 successive time intervals

t/min	φ_H	φ_{Cl}	$-\ln \varphi_H$	$-\ln \varphi_{Cl}$
0	1.000	1.000	0	0
5	0.783	0.811	0.244	0.210
15	0.674	0.711	0.395	0.340
30	0.494	0.542	0.706	0.613
40	0.458	0.514	0.780	0.665
50	0.370	0.442	0.993	0.817
60	0.288	0.353	1.244	1.042
70	0.204	0.270	1.589	1.309
80	0.145	0.201	1.931	1.606
90	0.114	0.164	2.172	1.807
110	0.086	0.122	2.451	2.102

Table 2 is a sample of a set of φ_Y *versus* φ_H data, with Y = Cl. Eleven samples taken at eleven time intervals were measured for the φ values, and the ln φ_Y *vs.* ln φ_H plot turned out to be an almost perfect straight line with $r = 0.998$ ($n = 11$). Fifteen (two for Y = NO_2 at different **1**-Y/**1**-H ratios) other sets of φ_Y *vs.* φ_H data and ln φ_Y *vs.* ln φ_H straight-line plots have been obtained. The r values listed in Table 3 are indicators of the reliabilty of our kinetic procedure. The k_r(Y) values summarized in Table 3 are the averaged k_r(Y) values obtained from regression analysis of 7–12 independently measured k_r(Y) values at 7–12 consecutive time intervals. They are almost the same as the k_r(Y) values obtained by simply averaging the n independently measured k_r values.

The reliability of our methodology has been further cross-checked by measuring the $k_r(NO_2)$ values at three different **1**-NO_2/**1**-H molar ratios, *i.e.*, at roughly 1:1, 2:1 and 1:2, as shown by the last three entries in Table 3. The data show that within experimental uncertainty, the $k_r(NO_2)$ values are not affected by the reactant molar ratios.

Correlation of our data with both eqn. (1) and eqn. (2) is summarized in Table 4, in which R, ψ, F, s, ρ^x and $\rho^{\cdot}$ values are listed. All possible combinations of ($\sigma^x + \sigma^{\cdot}$) were attempted with $\sigma^x = \sigma_P$,[13] σ^+[13] and σ_{mb},[3a] and $\sigma^{\cdot} = \sigma_{JJ}^{\cdot}$,[3a] $\sigma_{\alpha}^{\cdot}$[14] and $\sigma_C^{\cdot}$.[15] Unlike radical addition to styrenes,[3c,d] the σ_{mb} scale is no longer a 'tailor-made' polar substituent scale for the H-atom abstraction reaction. Thus, the σ_{mb} or ($\sigma_{mb} + \sigma^{\cdot}$) combination is not expected to yield the best correlation results among other σ^x or ($\sigma^x + \sigma^{\cdot}$) combinations.

The r and F values (0.941 and 93 for σ_P; 0.921 and 67 for σ^+) calculated on the basis of the single-parameter eqn. (1) indicate that reasonably good correlations can be obtained by the single-parameter eqn. (1) with σ_P. Application of the dual-parameter eqn. (2), as summarized in Table 4, shows that the correlations with $n = 14$ are not improved when $\sigma^x = \sigma^+$ or σ_{mb}. However, with $\sigma^x = \sigma_P$, the three correlations by the dual-parameter eqn. (2) lead to a noticeable improvement, *i.e.*, for the ($\sigma_P + \sigma_{JJ}^{\cdot}$) combination, $R = 0.993$, $\psi = 0.138$, $F = 363$, $n = 14$. The significance of applying the dual-parameter equation can also be shown by considering the deviations of the log k_r values of substituents from the regression line. As proposed in our previous work,[2,3d–i] in comparing correlation results by eqns. (1) and (2), it would be a good and useful practice to look at the deviations of the log k_r values of individual substituents from the regession lines, and these deviations (D values) might be compared with experimental uncertainties S_{exp}, as defined by the equation:[2] $S_{exp} = [\log(k_r + \Delta k_r) - \log k_r]$ or $S_{exp} = [\log k_r - \log(k_r - \Delta k_r)]$. For convenience, deviations from the regression line of (log k_r *vs.* σ_P) (Fig. 1) are designated as $|D - 1|$ in Table 3, and deviations from the regression line of [log k_r *vs.* $(-0.40\sigma_P + 0.24\sigma_{JJ}^{\cdot})$] (Fig. 2) are designated as $|D - 2|$. Notably, direct comparision of the $|D - 1|$ value of a certain substituent with the corresponding $|D - 2|$ value should not be made because they are derived from correlations with a

Table 3 Relative rates of NBS bromination of **1**-Y in CCl_4 at 50 °C

Y_1/Y_2	Ratio	$k_r \pm \Delta k_r$	n	r	S_{exp}[b]	D-1[c]	D-2[d]
MeO/Cl	1:1	1.67 ± 0.07	7	0.990			
MeO/H[a]		1.43 ± 0.09			0.027	0.014	0.009
MeS/H	1:1	1.43 ± 0.02	10	0.999	0.006	0.116	0.023
Bu^t/Cl	1:1	1.49 ± 0.05	8	0.997			
Bu^t/H[a]		1.27 ± 0.07			0.023	−0.010	−0.021
Me_3Si/Cl	1:1	1.44 ± 0.06	9	0.995			
Me_3Si/H[a]		1.23 ± 0.08			0.027	0.025	0.004
CH_3/H	1:1	1.20 ± 0.05	9	0.994	0.018	−0.024	−0.008
F/CH_3	1:1	0.76 ± 0.01	7	0.999			
F/H[a]		0.91 ± 0.04			0.005	−0.057	0.004
Br/Cl	1:1	1.01 ± 0.03	7	0.997			
Br/H[a]		0.86 ± 0.05			0.025	−0.018	−0.013
Cl/H	1:1	0.85 ± 0.02	11	0.998	0.010	−0.023	−0.016
MeC(O)O/H	1:1	0.85 ± 0.05	11	0.996	0.025	0.007	−0.015
CO_2Me/H	1:1	0.75 ± 0.02	12	0.998	0.011	0.006	−0.008
CN/Cl	1:1	0.82 ± 0.01	8	0.999			
CN/H[a]		0.70 ± 0.02			0.012	0.056	0.024
CF_3/NO_2	1:1	1.10 ± 0.03	7	0.997			
CF_3/H[a]		0.61 ± 0.03			0.021	−0.050	0.019
NO_2/H	1:1	0.55 ± 0.01	11	0.996	0.008	−0.004	−0.019
NO_2/H	2:1	0.56 ± 0.03	9	0.997			
NO_2/H	1:2	0.57 ± 0.03	7	0.993			

[a] Calculated from the equations: $k_Y/k_H = (k_Y/k_{Y'})\cdot(k_{Y'}/k_H)$ and $\Delta(k_Y/k_H) = (k_Y/k_{Y'})\cdot\Delta(k_{Y'}/k_H) + (k_{Y'}/k_H)\cdot\Delta(k_Y/k_{Y'})$. [b] S_{exp} stands for the experimental uncertainties of log k_r values as defined in the text. [c] D-1 stands for the deviations from the regression line of (log k_r *vs.* σ_P). [d] D-2 stands for the deviations from the regression line of [log k_r *vs.* $(-0.40\sigma_P + 0.24\sigma_{JJ}{}^{\bullet})$].

Table 4 Values of ρ^x and $\rho^{\bullet}$ of eqns. (1) and (2), and corresponding values of the correlation coefficient r (R), ψ, s and F-test for correlation of k_r (Y) values of n **1**-Y with σ^x and $\sigma^{\bullet}$ [a]

σ^x or ($\sigma^x + \sigma^{\bullet}$)	ρ^x	$\rho^{\bullet}$	r (R)	ψ	s	F[b]	n[a]
σ_P	−0.38		0.941	0.365	0.047	93.0	14
σ^+	−0.26		0.921	0.420	0.054	67.3	14
σ_{mb}	−0.24		0.836	0.592	0.076	27.9	14
$\sigma_P + \sigma_{JJ}{}^{\bullet}$	−0.40	0.24	0.993	0.138	0.018	363	14
$\sigma^+ + \sigma_{JJ}{}^{\bullet}$	−0.26	0.057	0.924	0.430	0.055	32.3	14
$\sigma_{mb} + \sigma_{JJ}{}^{\bullet}$	−0.26	0.24	0.893	0.509	0.065	21.6	14
$\sigma_P + 10\sigma_{\alpha}{}^{\bullet}$	−0.39	0.19	0.981	0.224	0.027	115	12
$\sigma^+ + 10\sigma_{\alpha}{}^{\bullet}$	−0.24	0.11	0.918	0.458	0.055	24.2	12
$\sigma_{mb} + 10\sigma_{\alpha}{}^{\bullet}$	−0.25	0.24	0.894	0.518	0.094	17.8	12
$\sigma_P + \sigma_C{}^{\bullet}$	−0.43	0.29	0.989	0.169	0.028	205	13
$\sigma^+ + \sigma_C{}^{\bullet}$	−0.27	0.029	0.948	0.362	0.048	44.7	13
$\sigma_{mb} + \sigma_C{}^{\bullet}$	−0.27	0.28	0.889	0.529	0.069	17.0	13

[a] n = 14, Y = H, CF_3, F, CN, Cl, Br, CO_2Me, MeCOO, NO_2, Me, MeO, MeS, Me_3Si and Bu^t. n = 13, Y = H, CF_3, F, CN, Cl, Br, NO_2, CO_2Me, Me, MeO, MeS, Me_3Si and Bu^t for $\sigma_c{}^{\bullet}$. n = 12, Y = H, CF_3, F, CN, Cl, CO_2Me, MeCOO, Me, MeO, MeS, Me_3Si and Bu^t for $\sigma_{\alpha}{}^{\bullet}$. [b] Critical F values[16]: $F_{0.001}$ (1,12) = 18.64, $F_{0.001}$ (2,11) = 13.81, $F_{0.001}$ (2,9) = 16.39, $F_{0.001}$ (2,10) = 14.9.

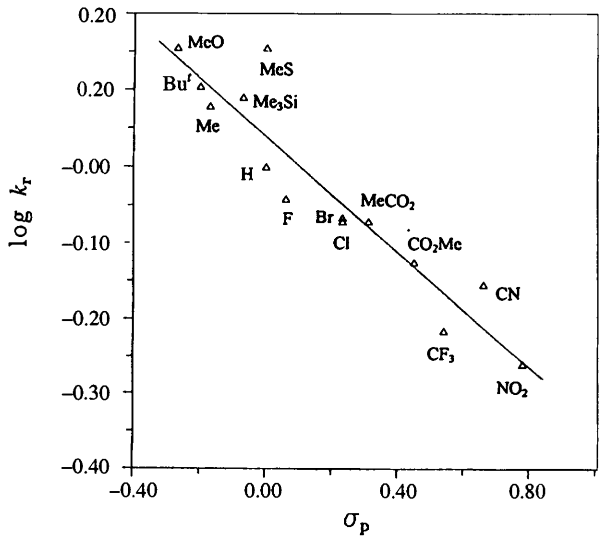


Fig. 1 Plot of log k_r *vs.* σ_P

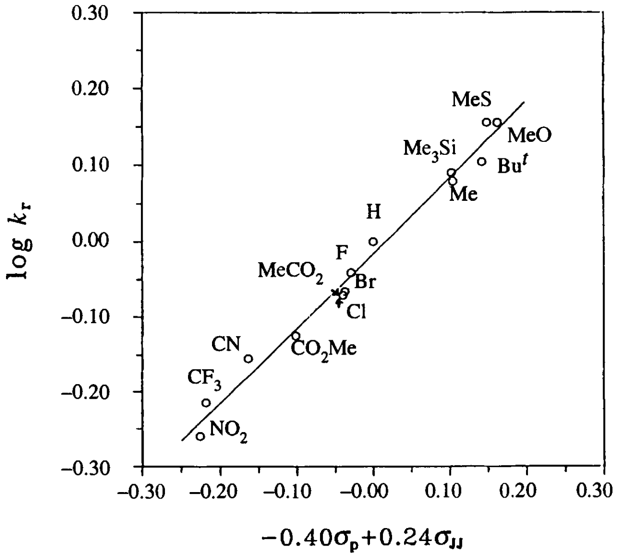


Fig. 2 Plot of log k_r *vs.* $(-0.40\sigma_P + 0.24\,\sigma_{JJ}{}^{\bullet})$

different number of degrees of freedom. They are listed in Table 3 only as an aid to making approximate comparisions with the S_{exp} values. Evidently, for the single-parameter correlation, there are four substituents (MeS, F, CN and CF_3) with log k_r values which clearly deviate from the regression line, *i.e.*, with their $|D|$-values much larger than their S_{exp} values, whereas for the dual-parameter correlation, there is only one substituent (MeS) with its $|D|$-values much larger than the corresponding S_{exp} value. The above-mentioned result suggests that, in addition to the polar effect, the spin-delocalization effect also affects the transition state of the H-atom abstraction reaction by the bromine atom.[2,3–3i] Furthermore, it is noteworthy that the $|\rho^x/\rho_{JJ}^{\bullet}|$ ratio (1.67 for $\rho^x = \rho_P$; 1.09 for $\rho^x = \rho_{mb}$) is smaller than that of the H-atom abstraction reaction from cumenes (2.01 for $\rho^x = \rho_P$; 1.14 for $\rho^x = \rho_{mb}$),[2] and even smaller than that of the $CCl_3^{\bullet}$ addition reaction to phenylacetylenes (1.80 for $\rho^x = \rho_P$; 1.35 for $\rho^x = \rho_{mb}$),[3e] but much larger than that of the $CCl_3^{\bullet}$ addition to styrenes (0.65 for $\rho^x = \rho_P$; 0.42 for $\rho^x = \rho_{mb}$)[3c] and of $Br^{\bullet}$ addition to α-methylstyrenes (0.58 for $\rho^x = \rho_P$; 0.37 for $\rho^x = \rho_{mb}$).[3d] These findings imply that the relative importance of the spin-delocalization effect at the TS of the aforesaid reactions increases in the following order: H-atom abstraction from cumenes < radical addition to phenylacetylenes < H-atom abstraction from **1**-Y < radical additions to styrenes and α-methylstyrenes. The fact that all ρ^x values are negative is in accord with the known electrophilic nature of the bromination, and the fact that all $\rho^{\bullet}$ values are positive is in harmony with expectation because all substituents are spin-stabilizers.[3a]

In conclusion, the relative rates of the H-atom abstraction reaction of bromine radicals from 14 *p*-Y-α,α-ethylenedioxytoluenes (**1**-Y) have been measured by a rigorous methodology. Good correlation can be obtained by using the single-parameter equation with σ_P, and application of the dual-parameter equation with $(\sigma_P + \sigma_{JJ}^{\bullet})$ leads to an improvement. Consideration of the deviations of substituents from the single-parameter and dual-parameter regression lines also shows that the spin-delocalization effect is operating at the transition state of this H-atom abstraction reaction. Notably, both of the following two observations from the present work are in accord with our expectation that α-positioned substituents on the benzylic carbon with moderate spin-delocalization ability, *e.g.* an alkoxy group, may stabilize the transition state for the H-atom abstraction reactions from the benzylic C–H bond. The two observations are: (1) the reactivity of the C–H bond of α,α-ethylenedioxytoluene toward bromine is much greater than that of cumene. (2) The $|\rho^x/\rho_{JJ}^{\bullet}|$ ratio in the bromination reaction of **1**-Y is smaller than that of cumenes. Furthermore, H-atom abstraction reactions from **1**-Y and cumenes by bromine seem to belong to the second of the following four possible circumstances for correlation analysis in radical chemistry.[3e,f] The four categories are: (1) when both polar and spin effect are of comparable importance, the $|\rho^x/\rho_{JJ}^{\bullet}|$ values might fall in the range of (very) roughly 0.2 to 0.8, and the dual-parameter equation (variable = $\rho^x\sigma^x + \rho^{\bullet}\sigma^{\bullet} + C$) must be used for achieving a good correlation. (2) When the polar effect predominates, this ratio might be around or greater than unity, and a good correlation can be obtained by using the single-parameter equation (variable = $\rho^x\sigma^x + C$) with polar substituent constants σ^x, but spin-delocalization effects may still be revealed by considerations of the deviations of some individual substituents from the regression lines. (3) When the spin-delocalization effect predominates, the $|\rho^x/\rho_{JJ}^{\bullet}|$ values might fall below (roughly) 0.1 ~ 0.2, and a good correlation can be obtained by using the single-parameter equation (variable = $\rho^{\bullet}\sigma^{\bullet} + C$) with spin-delocalization substituent constants $\sigma^{\bullet}$. (4) When there are other complicating and interacting factors or effects, no reasonable correlation can be achieved.

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