Pergamon

Tetrahedron Vol. 50, No. 25, pp. 7503-7512, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)E0363-X

Can the Spin-Delocalization Effect Express Itself at the Transition State of the Hydrogen-Atom Abstraction Reaction? Correlation Analysis of Relative Rates Measured by a Rigorous Methodology for Eleven p-Y-Substituted Isopropylbenzenes

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Abstract: A rigorous procedure has been developed for measuring the relative rates, i.e., $k_T(Y) = k_Y/k_H$, of hydrogen-abstraction from eleven substituted iso-propylbenzenes (1-Y, with Y = NO_2, CN, F, Cl, Br, CO_2Me, Me, *t*Bu, COMe, OMe and SMe) by bromine atoms. The reaction was run in cyclohexane in the presence of HBr, O_2 and dibutyl peroxyoxalate at 50°C. It has been demonstrated that the H-atom abstraction step shown by eq 4 is the measured step, and all products are derived from the intermediate benzylic radical 4. Correlation analysis of these rate data seems to suggest that a spin effect is also operating at the transition state of H-atom abstraction reaction, even though the polar effect predominates. Among various combinations of σ^X and $\sigma^\bullet$ for the dual-parameter eq 1, the $(\sigma_p+\sigma^\bullet_{JJ})$ combination yields the best correlation.

INTRODUCTION

In recent years, polar (including resonance polar) and spin-delocalization effects of substituents have been demonstrated to be independent of each other.[1,2] 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 1, where σ^x is the polar substituent constant and $\sigma^\bullet$ is the spin-delocalization substituent constant, rather than by the single-parameter

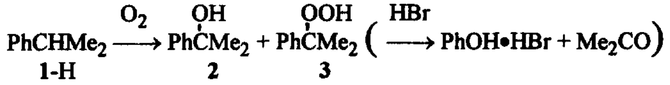
$$\log k_Y / k_H = \rho^X\sigma^X + \rho^\bullet\sigma^\bullet \qquad (1)$$

$$\log k_Y / k_H = \rho^X\sigma^X \qquad (2)$$

eq 2. Furthermore, if the σ^X scales are normalized or comparable in magnitude[1d] and the same set of $\sigma^\bullet$ scale is used, then the relative magnitude of the $|\rho^X/\rho^\bullet|$ ratio of a certain set of reactions might be a rough but useful indicator of the relative importance of polar and spin-delocalization effects for that particular set of reactions.[1a-c,2b] In fact, this $|\rho^X/\rho^\bullet|$ ratio has been found to be 0.30 for the radical dimerization of substituted α,β,β-trifluoro styrenes,[1c] 0.42 for the $^\bullet CCl_3$ radical addition to styrenes,[1b] and 0.37 for bromine atom addition to α-methylstyrenes.[1a] Particularly noteworthy is the fact that the single-parameter eq 2 has been definitely shown to be inapplicable to the rigorously measured rate data of the aforesaid three reactions.

Therefore, we were puzzled by the fact that many sets of reactions, especially hydrogen-atom abstractions,[3] have been claimed to be correlatable by the single-parameter eq 2. We have also postulated[1a,b] that one or more of the following factors might have affected the accuracy of some of the previous results: (1) the kinetic method used might not be the most rigorous, e.g., measurements were not performed and cross-checked over a wide range of the extent of reaction;[4,5] (2) the reaction studied was not clean enough (cf. Arnold's comment in ref. 6 on Jackson's approach); and (3) the number of well distributed para-substituents used was not large enough. We have also speculated[1a] that at the transition state (TS) of some reactions, e.g., H-atom abstractions, the spin effect is almost completely overshadowed by the polar effect. Under these circumstances, it will be possible to obtain good or even excellent correlations by the single-parameter eq 2, and it will be exceedingly difficult to establish the necessity of using the dual-parameter eq 1. Obviously, veracity of the above statement can only be established by the existence of a set of rate data derived from a truly rigorous kinetic methodology. We have proposed that this methodology should fulfill the following requirements:[1a,b] (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 φ_Y / ln φ_H ratios, where φ represents the mole fraction of unreacted substrate at a particular time t (cf. eq 7), without worrying about the relative amounts of the products; (3) a rigorous procedure should be followed, for example, several (e.g. 5-8) 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 5-8 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. Regrettably, although many fine works have been done on H-atom abstraction (cf. Fisher's work in ref. 7) or other radical reactions, to our knowledge there exist no previous data which are derived from a methodology that fulfills all the above-mentioned requirements. The present work, therefore, aims to address this problem.

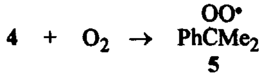
Two of the most important previous works on H-atom abstraction by bromine atoms are those of Fisher[7] and Martin.[3d] They both used Y-substituted toluenes and a conventional kinetic methodology, i.e., their k_Y/k_H values were not cross-checked at different time intervals or degrees of conversion (cf. requirement-3 mentioned above). We reckoned that one possible complication or drawback of using Y-substituted toluenes might be the reactivity of C-H bonds in the substituents, i.e., reactivity of the C-H bond of the CH_3 group in the toluenes may not be very much larger than those of the C-H bonds in the substituents, when Y = CH_3, OCH_3, $COCH_3$, SCH_3, etc. We therefore decided to use para Y-substituted cumenes, abbreviated as **1-Y**'s, for our study because the benzylic C-H bond of the isopropyl group of cumene is well known for its exceptionally high reactivity.[8] By far the most difficult part of our work was, of course, to find the reaction and methodology which satisfy all our requirements previously proposed. We finally found that the HBr-catalyzed O_2 oxidation reaction of cumenes at 50°C in cyclohexane is a reaction very well suited for our task.[1a,9] As eq 3 shows, from cumene (**1-H**) it yields only 2-phenyl-2-propanol (**2**) and products directly derived from 2-phenyl-2-propanol hydroperoxide (**3**). In the presence of HBr, **3** is converted into acetone and a complex of phenol and HBr:



$$\underset{\textbf{1-H}}{\mathrm{PhCHMe_2}} \xrightarrow{O_2} \underset{\textbf{2}}{\mathrm{Ph\overset{OH}{C}Me_2}} + \underset{\textbf{3}}{\mathrm{Ph\overset{OOH}{C}Me_2}} \left(\xrightarrow{HBr} \mathrm{PhOH{\bullet}HBr} + \mathrm{Me_2CO} \right) \qquad (3)$$

Compounds **2** and **3** are formed from chain reactions involving eq 4 to eq 6:

$$\textbf{1-H} + Br^{\bullet} \rightarrow \underset{\textbf{4}}{Ph\dot{C}Me_2} + HBr \qquad (4)$$



$$\textbf{4} + O_2 \rightarrow \underset{\textbf{5}}{\overset{OO^{\bullet}}{PhCMe_2}} \qquad (5)$$

$$\textbf{5} + HBr \rightarrow \textbf{3} + Br^{\bullet} \qquad (6)$$

Eq 4 represents the rate-determining step ($k_4 = 4 \times 10^6$ $M^{-1}s^{-1}$, cf. ref. 8) which cannot be reversed because it is immediately intercepted by an extremely fast step shown by eq 5 ($k_5 \sim 5 \times 10^9$ $M^{-1}s^{-1}$, cf. ref. 10). The rate constant for eq 6 is roughly comparable (estimated to be $10^{5\text{-}6}M^{-1}s^{-1}$, cf. ref. 11) to that of eq 4. Incidentally, even in the absence of the O_2 interception, the α-H-atom abstraction reaction (eq 4) can hardly reverse itself because of its high exothermicity [cf. BDE(H-Br) = 366 kj mol^{-1}, BDE($PhCH_2$-H) = 353 kj mol^{-1} >> BDE($PhCMe_2$-H)].[12] In short, our chosen reaction is a very clean (chain) reaction, and all products formed therefrom are derived from the same measured step (eq 4). Therefore, for the measurement of the relative rate $k_r(Y)$ for each **1-Y**, eq 7[1,13] applies and is used in the present work to assess the relative importance of polar and spin-delocalization effects at the TS of a H-atom abstraction reaction.

$$k_r(Y) = \frac{k_Y}{k_H} = \frac{\log\{[\mathbf{1\text{-}Y}]_t / [\mathbf{1\text{-}Y}]_0\}}{\log\{[\mathbf{1\text{-}H}]_t / [\mathbf{1\text{-}H}]_0\}} = \frac{\log \varphi_Y}{\log \varphi_H} \qquad (7)$$

EXPERIMENTAL SECTION

^1H NMR spectra were obtained at 60 MHz on a Varian EM-360A spectrometer with TMS as the external standard. Mass spectrometry (MS) was carried out using a Finnigen-Mat 4510 GC-MS system. IR spectra were recorded on a Shimadzu IR-440 spectrometer. GC analysis were performed on a model 103G gas chromatograph equipped with an HP 3390A integrator. An SE-30 capillary column (40 m × 0.2 mm i.d.) was used with a flame ionization detector and with nitrogen as the carrier gas.

Commercial cyclohexane, cumene (**1-H**) and p-methyl cumene (**1-Me**) were dried with CaH_2 and distilled prior to use. Gaseous HBr was generated by the reaction of Br_2 with tetralin and purified as previously described.[1a] Dibutylperoxyoxalate (DBPO) was used in the form of a 0.2 M hexane solution at -20°C.[14]

Para-Y-substituted cumenes, i.e., **1**-Y's with Y = NO_2, CN, CO_2Me, COMe, F, Cl, Br, *t*Bu, SMe, and OMe are known compounds and were prepared by previously reported methods.[15] They were further identified by ^1H NMR and IR. Boiling points of **1**-Y's prepared in our lab were as follows: **1**-NO_2, 134-136°C/15 torr (lit.[15a] 126°C/13 torr); **1**-CN, 135-137°C/60 torr (lit.[15b] 110-110.5°C/24 torr); **1**-CO_2Me, 118°C/12 torr (lit.[15c] 117-119°C/11 torr); **1**-COMe, 140-142°C/30 torr (lit.[15d] 133°C/20 torr); **1**-Cl, 114-116°C/30 torr (lit.[15b] 192-194°C); **1**-F, 152-154°C (lit.[15e] 153-155°C); **1**-Br, 116-118°C/30 torr (lit.[15c] 123.5°C/53 torr); **1**-*t*Bu, 130-132°C / 50 torr (lit.[15b] 125.5°C / 44 torr); **1**-OMe, 110-114°C / 32 torr (lit.[15f] 103 °C/20 torr); **1**-SMe,[15g,h] 128-130°C/30 torr.

Reaction of 1-H in the HBr-cyclohexane-O_2-DBPO system

In a round bottomed flask (100 ml), a mixture of cyclohexane (20 ml), **1-H** (10 mmol), internal GC standards (100 μl), 0.2 M DBPO hexane solution (1 ml, 2 mol%) was added. The flask was immersed in a thermostated bath (50°C) and vigorously stirred. A stream of O_2 (40 ml/min) carrying gaseous HBr (generated by 10 mmol Br_2 slowly added into 10 mmol tetralin in about 30 min) was passed through the solution. The conversion of **1-H** was monitored by GC. It was observed that the conversion of **1-H** was 35%, 50% and 63% at t = 5 min, 15 min and 1 h respectively. During this time, a purple sticky mass slowly formed. In order to stop the reaction, the crude mixture was treated with hydroquinone (*ca.* 5 mol%), and triethylamine (*ca.* 1 equivalent). GC/MS analysis showed that the reacted crude solution (t = 1 h) contained the following compounds, with yields calculated on the basis of the total initial amount of **1-H** used (10 mmol): unreacted **1-H**, 37%; α-methylstyrene, the dehydration (350°C for GC analysis) product of **2**, 5%; the hydroperoxide **3** [m/z: 153 $(M+H)^+$, 95 $(PhOH_2)^+$, 58 $(Me_2CO)^+$], 10%; acetone, which was continuously carried away by the stream of O_2, *ca.* 10%; free phenol, 3%. However, if the crude mixture was not treated with triethylamine but was concentrated under reduced pressure (50°C/20 torr), the sticky mass thus obtained was dissolved in acetone-D_6, ^1H NMR showed that it contained 55% of the phenol complex [PhOH•HBr: δ 6.8-7.3 (5H, m, H on benzene ring), 9.0(2H, s, O-H and Br-H)] derived from the hydroperoxide **3** and HBr, 5% of the compound **2**,[16a] and no other detectable byproducts. When treated with $NaHCO_3$ powder, it released free phenol (identification by ^1H NMR).[16b] In short, at least 97% of the reacted 1-H was initially transformed into the two products **2** and **3**.

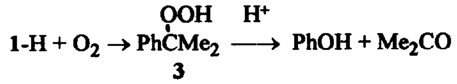
Kinetic competition procedure.

In a round bottomed flask (100 ml), a solution of **1-Y** (4-5 mmol), **1-H** (5 mmol), internal GC standards (100 μl each), 0.2 M DBPO hexane solution (1 ml, 2 mol%) was added and vigorously stirred at 50±0.5°C. A stream of O_2 (40 ml/min) carrying gaseous HBr was passed through the solution. Half or one hour later, the degree of conversion of **1-H** or **1-Y** could reach 20% (φ = 0.8) to 90% (φ = 0.1). During this time, fifteen to twenty samples (about 0.1 ml each) were taken, usually at t = 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3, 4, 5, 6, 8, 10, 12, 15, 20, 25, 30, 40, 50, 60 min, and immediately injected into cooled tubes containing 20 μl triethylammine saturated with hydroquinone, they were sealed and about half of these samples were analyzed by GC. Typical GC conditions were: oven temperature 350°C, column temperature increased from 80 to 220°C at 10°C/min, and carrier gas flow-rate 3 ml/min.

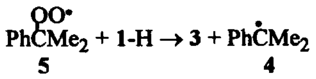
GC internal standards were chosen according to the requirements of convenient retention times and no interference with the integration of substrate and product GC peak. The internal standards used were decane for **1-H**, **1-Me** and **1-F**, undecane for **1-Br** and **1-OMe**, dodecane for **1-CN**, **1-Cl**, **1-COMe**, **1-*t*Bu** and **1-SMe**, tridecane for **1-NO_2**, tetradecane for **1-CO_2Me**. As the GC peaks of **1-F** and **1-H** overlap with each other, the k_r(F) cannot be measured by direct competition between **1-F** and **1-H**, it was calculated by the equation $k_F/k_H = (k_F/k_{Br}) \times (k_{Br}/k_H)$.

RESULTS AND DISCUSSION

Our chosen reaction can claim a background which is related to a commercial process, i.e., the autooxidation of cumene.[18] Eq 8 also shows that the unstable hydroperoxide intermediate **3** is completely converted by an acid to the product phenol. The intermediate **3** can be formed from two chain steps, namely,



$$1\text{-H} + O_2 \rightarrow \underset{\mathbf{3}}{Ph\overset{OOH}{C}Me_2} \xrightarrow{H^+} PhOH + Me_2CO \qquad (8)$$



$$\underset{\mathbf{5}}{Ph\overset{OO^\bullet}{C}Me_2} + 1\text{-H} \rightarrow \mathbf{3} + \underset{\mathbf{4}}{Ph\overset{\bullet}{C}Me_2} \qquad (9)$$

eq 6 and eq 9, but the latter is a very slow step with $k_9 = 0.3\ M^{-1}s^{-1}$ at 50°C.[8] In the presence of HBr, the autooxidation of cumene may proceed 10^{3-4} times faster.[9c] This is a natural consequence of the fact that a very slow step (eq 9) is replaced by two fast steps shown previously by eq 4 and eq 6. Therefore, veracity of the mechanism described in our introduction not only is based on the fact that phenol, acetone, and compounds **2** and **3** are the only detectable products, but also is supported by all literature reports.[17,9c]

The above-mentioned facts are not sufficient, however, to establish the trustworthiness of our methodology, a more rigorous test is required. We proposed to make the constancy (within experimental uncertainty) of the five to ten $k_r(Y)$ values measured over a wide range of the extent of reaction to be the test. In other words, for the eleven 1-Y's, plots of ln φ_Y against ln φ_H (vide supra) should yield eleven good straight lines. Evidently, one great advantage of this methodology is that further reactions of products do not affect the measurement of the $k_r(Y)$ values. Furthermore, the following facts also contribute to the cleanness of our measured reaction step. (1) The H-atom abstraction by the peroxy radical **5** can be neglected because the relative reactivity of $Br^\bullet/ROO^\bullet$ is about 10^7 at 50°C.[8] At a **1**-H concentration of about 0.1 M and at a controlled HBr concentration larger than 10^{-6} M, the actual ratio of H-atom abstraction by $Br^\bullet$ and $ROO^\bullet$ should be > 100. (2) The β-H-atom abstraction by $Br^\bullet$ from the isopropyl group of **1**-H is negligible because the α-H/β-H reactivity ratio is about 60000.[8] (3) The H-atom abstraction by $Br^\bullet$ on C-H bonds of the Y substituents has been shown to be negligible, i.e., we have actually measured the relative rates (Y/*i*Pr) of H-atom abstraction from Y and from the *i*Pr group for five p-Y-substituted bromobenzenes (chosen for convenience in GC analysis), with Y = *t*Bu, COMe, Me, OMe and SMe, the corresponding Y/*i*Pr values are <0.001, 0.01, 0.012, 0.008 and 0.033 respectively.

Finally, the reliability of our methodology has been cross-checked by measuring the $k_r(Me)$ values at three different molar ratios of **1**-Me/**1**-H, i.e., at roughly 1:1, 2:1 and 1:2, as shown by the first three entries of Table 1. The data show that within experimental uncertainty the $k_r(Me)$ values are not affected by the reactant molar ratios. Table 2 is a sample of a set of φ_Y versus φ_H data, with Y = Me. Eight samples taken at eight 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 $r = 0.9996$ ($n = 8$), as shown by Figure 1. Twelve (two for Y = Me, 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 1 are indicators of the reliability of our kinetic procedure. The $k_r(Y)$ values summarized in Table 1 are the averaged $k_r(Y)$ values obtained from regression analysis of the 5-10 independently measured k_r values at 5-10 consecutive time intervals. They are almost the same as the $k_r(Y)$ values obtained by simply averaging the n independently measured k_r's.

In substituent-effect studies, we can define the "rate-span (R-S)" as the ratio of the largest rate-constant (k_w for substituent w) to the smallest rate-constant (k_z for substituent z), i.e., R-S = k_w / k_z. Although the R-S values for many free radical reactions are relatively small, this has not discouraged radical chemists from carrying out meaningful correlation analysis of important radical reactions, as long as their experimental uncertainties or standard deviations of their rate constants are much smaller than their R-S values.[3-5] For

Table 1. Relative Rates [k_r(Y)] of H-Atom Abstraction from p-Y-Substituted Cumenes by Br•

Y_1/Y_2	Ratio	$k_r(Y) \pm \Delta k_r$	$\Delta k_r / k_r$	S[b]	D[c]	*n*	*r*
Me/H	1:1	1.622±0.019	1.2 %	0.005		8	0.9996
Me/H	2:1	1.678±0.016	1.0 %	0.004	0.07	8	0.9997
Me/H	1:2	1.640±0.014	0.9 %	0.004		7	0.9998
NO_2/H	1:1	0.234±0.007	3.0 %	0.013	0.08	10	0.9954
CN/H	1:1	0.291±0.012	4.0 %	0.017	0.05	7	0.9955
CO_2Me/H	1:1	0.483±0.006	1.2 %	0.005	0.00	8	0.9995
COMe/H	1:1	0.654±0.010	1.5 %	0.006	0.16	7	0.9994
Br/H	1:1	0.777±0.014	1.8 %	0.008	0.03	7	0.9992
Cl/H	1:1	0.779±0.024	3.1 %	0.013	0.00	7	0.9980
F/Br	1:1	1.048±0.017	1.6 %			6	0.9994
F/H[a]		0.814±0.030		0.007	0.09		
*t*Bu/H	1:1	1.63 ±0.02	1.2 %	0.005	0.09	6	0.9997
SMe/H	1:1	1.93 ±0.08	4.0 %	0.017	0.06	5	0.9985
OMe/H	1:1	2.51 ±0.11	4.4 %	0.019	0.08	6	0.9979

a) $k_F/k_H = (k_F/k_{Br}) \times (k_{Br}/k_H)$. b) S stands for the experimental uncertainties of log k_r values as defined in the text. c) D stands for the deviation of the log k_r values from the regression line of Figure 2.

Table 2. φ Values of the Reaction of **1**-Me and **1**-H in Competition for the Bromine Atoms at 8 Successive Time Intervals

t (min)	φ_H	$- \ln \varphi_H$	φ_{Me}	$- \ln \varphi_{Me}$
0	1.00	0	1.00	0
1	0.989	0.011	0.968	0.033
2	0.791	0.235	0.680	0.385
3	0.727	0.319	0.579	0.547
5	0.630	0.462	0.471	0.753
10	0.563	0.574	0.384	0.956
20	0.496	0.702	0.313	1.160
50	0.463	0.770	0.290	1.239

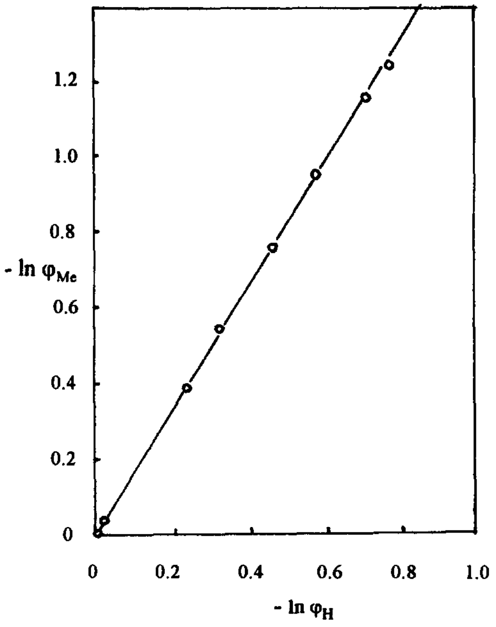


Figure 1. Plot of $- \ln \varphi_{Me}$ vs. $-\ln \varphi_H$

Table 3. Values of ρ^X and $\rho^\bullet$ of Eq 1 and Eq 2, and Corresponding Values of the Correlation Coefficient *R*, Ψ and *F*-test for Correlation of $k_r(Y)$ Values of *n* 1-Y's with σ^X and $\sigma^\bullet$.[a]

σ^X or $\sigma^X + \sigma^\bullet$	ρ^X	$\rho^\bullet$	*n*	*R*	Ψ	F^b
σ^+	-0.626±0.048	/	11	0.974	0.25	163
σ_n	-0.901±0.073	/	11	0.967	0.28	128
σ_{mb}	-0.603±0.070	/	11	0.934	0.39	62
$\sigma^+ + \sigma^\bullet_{JJ}$	-0.632±0.049	0.088±0.019	11	0.975	0.26	76
$\sigma_n + \sigma^\bullet_{JJ}$	-0.995±0.019	0.494±0.018	11	0.997	0.09	729
$\sigma_{mb} + \sigma^\bullet_{JJ}$	-0.699±0.037	0.613±0.090	11	0.980	0.23	97
$\sigma_n + \sigma^\bullet_\alpha$	-1.032±0.034	4.05 ±0.41	9	0.995	0.12	300
$\sigma_{mb} + \sigma^\bullet_\alpha$	-0.671±0.065	4.25 ±1.12	9	0.962	0.34	37
$\sigma_n + \sigma^\bullet_C$	-1.062±0.050	0.474±0.09	9	0.992	0.15	197
$\sigma_{mb} + \sigma^\bullet_C$	-0.691±0.055	0.456±0.148	9	0.957	0.36	32
$\sigma^+ + \sigma^\bullet_F$	-0.769±0.065	0.397±0.135	8	0.989	0.21	114
$\sigma_n + \sigma^\bullet_F$	-1.073±0.052	0.413±0.078	8	0.993	0.13	336
$\sigma_{mb} + \sigma^\bullet_F$	-0.808±0.056	0.690±0.135	8	0.991	0.15	155
σ_n + RRS	-1.033±0.035	0.021±0.003	11	0.993	0.14	267
σ_{mb} + RRS	-0.700±0.052	0.021±0.007	11	0.960	0.33	47

a) When *n* = 11, Y = NO_2, CN, F, Cl, Br, CO_2Me, Me, *t*Bu, COMe, OMe and SMe; *n* = 9, for $\sigma^\bullet_\alpha$, Y = CN, F, Cl, CO_2Me, Me, *t*Bu, COMe, OMe and SMe; for $\sigma^\bullet_C$, Y = CN, F, Cl, Br, CO_2Me, Me, *t*Bu, OMe and SMe; for $\sigma^\bullet_F$, Y = NO_2, CN, F, Cl, Br, Me, COMe and OMe. b) Critical *F* values: $F_{0.001}(1,9) = 22.9$, $F_{0.01}(1,9) = 10.6$, $F_{0.001}(2,8) = 18.5$, $F_{0.01}(2,8) = 8.7$, $F_{0.001}(2,6) = 27.0$, $F_{0.01}(2,6) = 10.9$, $F_{0.001}(2,5) = 37.1$, $F_{0.01}(2,5) = 13.3$.

illustration, the R-S values of some H-atom abstraction reactions are: for $Br^\bullet$ + Y-C_6H_4-CH_2-H, 27 - 53;[3c] for $ROO^\bullet$ + Y-C_6H_4-CH_2-H, 5.6;[15c] for $ROO^\bullet$ + Y-C_6H_4-CMe_2-H, 2.4.[15c] In the present work, our R-S values is 10.7, and the usual experimental uncertainty (Δk_r / k_r) is <±3% (the maximum is ±4.4%, see Table 1). In other words, we have good precision in our measured values. This data, together with our rigorous methodology and the fact that a good number of well-distributed substituents has been used, should make it possible for us to obtain reliable and meaningful structure-reactivity correlation results.

Correlation of our data with both eq 1 and eq 2 are summarized in Table 3, in which *R*, Ψ, *F*, ρ^X, $\rho^\bullet$ values are listed. All possible combinations of ($\sigma^X + \sigma^\bullet$) had been tried, with $\sigma^X = \sigma_p$, σ^+ and σ_{mb}, and $\sigma^\bullet = \sigma^\bullet_{JJ}$, $\sigma^\bullet_\alpha$, $\sigma^\bullet_C$, $\sigma^\bullet_F$ and RRS. Unlike the previous three cases involving radical additions to styrenes,[1a-1c] the σ_{mb} scale[1d] is no longer a "tailor-made" polar substituent scale for the H-atom abstraction reaction. Thus the σ_{mb} or ($\sigma_{mb}+\sigma^\bullet$) combinations are not expected to yield the best correlation results among other σ^X's or ($\sigma^X+\sigma^\bullet$) combinations. Only meaningful correlations are summarized in Table 3. Values of $\sigma^\bullet$ and σ^X are from the following sources: $\sigma^\bullet_{JJ}$, Ref. 1c; $\sigma^\bullet_\alpha$, Ref. 6; $\sigma^\bullet_C$, Ref. 4c; $\sigma^\bullet_F$, Ref. 7; RRS, Ref. 2; σ_p and σ^+, Ref. 18; σ_{mb}, Ref. 1d.

The *R* and Ψ values (0.974 and 0.25 for σ^+; 0.967 and 0.28 for σ_p; 0.934 and 0.39 for σ_{mb}) calculated for the single-parameter eq 2 indicate that reasonably good correlations can be obtained by application of the single-parameter equation. But the scatter of points in the plot of these log k_r values versus σ^+ (the best among the three σ^X's) in Figure 2 indicates that some substituents (COMe, F, OMe and *t*Bu) deviate too much from

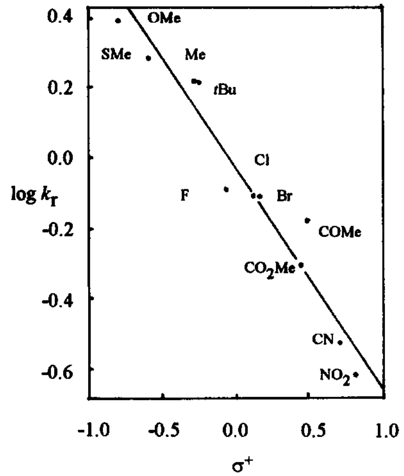


Figure 2. Plot of log k_r vs σ^+

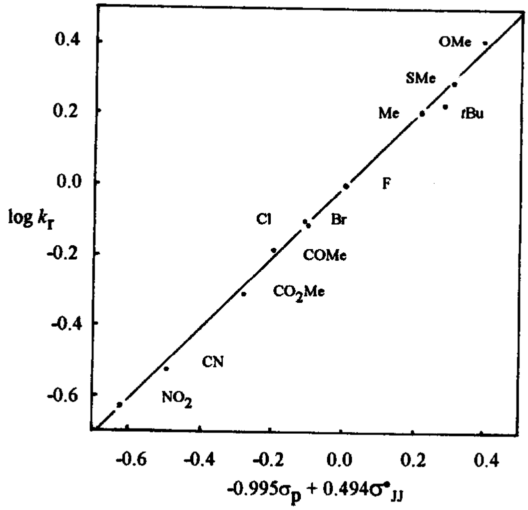
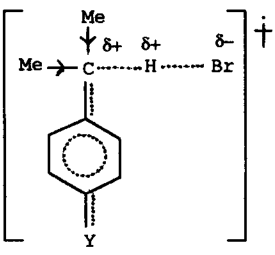


Figure 3. Plot of experimental log k_r vs values calculated by $-0.995\sigma_p + 0.494\sigma^\bullet_{JJ}$

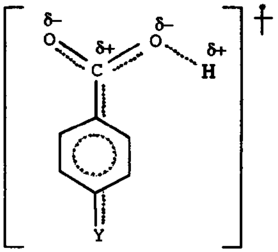
the regression line. This is clearly indicated by comparison of the D and S values listed in Table 1, and by direct inspection of Figure 2. D stands for the deviation of the log k_r values from the regression line in Figure 2 and the S values are the experimental uncertainties of log k_r values calculated by the equation: S = [log (k_r + Δ k_r) - log k_r] or S = [log (k_r - Δ k_r) - log k_r]. It is noteworthy that the D values of COMe, F, OMe and *t*Bu are much larger than their S values (< 0.02, cf. Table 1). We propose that, in performing a reliable correlation, these deviations should not be ignored, 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 1, as summarized in Table 3, shows that the correlation with n = 11 were not improved with $\sigma^x = \sigma_{mb}$ or σ^+, e.g., the $(\sigma^+ + \sigma^\bullet_{JJ})$ combination yields a correlation with r = 0.975, $\Psi = 0.26$ and $F = 76$, and the scatter of points in the plot of log k_r versus $0.632\sigma^+ + 0.088\sigma^\bullet_{JJ}$ indicates that the substituents COMe, OMe and *t*Bu still deviate too much from the regression line. However, with $\sigma^x = \sigma_p$, the three dual-parameter correlations lead to observable improvements, e.g., for the $(\sigma_p + \sigma^\bullet_{JJ})$ combination, $R = 0.997$, $\Psi = 0.09$ and $F = 729$. As Figure 3 clearly shows, for the dual-parameter correlation with $(\sigma_p + \sigma^\bullet_{JJ})$, all points fall on the regression line within experimental uncertainty. This result shows that among all the σ^x scales› the σ_p scale best reflects the polar effect of the reaction, and this seems to suggest that the residual δ^+ (the δ sign is not related to the exact magnitude of the charge) on the α-carbon of **6** at the TS of our H-atom abstraction reaction bears a certain degree of resemblance to the δ^+ on the α-carbon at the TS 7 of ionizing benzoic acids. In other words, polar effects of Y in **6** may quite well parallel those of Y in 7.

On the basis of these considerations, we are inclined to visualize the TS of a H-atom abstraction as a TS dominated by polar effects but also affected to a small degree by spin-delocalization effect. In other words, in vivid contrast to radical additions to π-bonds of Y-substituted styrenes,[1a,b] for reactions such as H-atom abstraction, the spin effect is barely detectable. This state of affairs could be a consequence of the fact that the



6



7

π-bond of styrenes are already fully conjugated with the substituents Y before they interact with the attacking radical, whereas the C-H σ-bonds (of Y-substituted cumenes) are not spatially oriented for full conjugation. Notably, the $|\rho^{X}/\rho^{\bullet}|$ ratio (vide supra) of 2.0 for the (σ_p+$\sigma^{\bullet}_{JJ}$) combination is in accord with our above-mentioned views. It is much larger than the $|\rho^{X}/\rho^{\bullet}|$ ratios (0.30 to 0.40) for the radical additions (vide supra). It is particularly noteworthy that when Fisher put a m-CN group on his p-Y-substituted toluenes, so that the polar effects of the p-Y-substituents became less pronounced, and the $|\rho^{X}/\rho^{\bullet}|$ ratio based on the equation $\log k_r = -1.21\sigma^{+} + 0.80\,\sigma^{\bullet}_{JJ}$ is 1.5 ($R = 0.984$, $\Psi = 0.22$, $F = 108$, $n = 9$), smaller than our 2.0 value. This observation is also in harmony with the proposition that a spin effect is also operating at the TS of H-atom abstraction reactions, even though it is overshadowed by the polar effect.

ACKNOWLEDGEMENT

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

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(*Received in China* 12 *January* 1994; *accepted* 8 *April* 1994)