

Dual Substituent Parameter Treatment in the Aromatic Series using 'Universal' Inductive and Resonance Constants: the Superfluity of Different Scales of Resonance Substituent Constants

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For the analysis of the effects of *para*- and *meta*-substituents in aromatic compounds, the two-parameter equation $x_i - x_o - \rho^* \sigma^* + r^* \sigma^r + B$ was proposed. It was shown that the application of this equation does not require the use of special sets of resonance substituent constants for various classes of aromatic compounds and leads to a more accurate separation of polar and resonance substituent effects. Introduction of a free term B , which appears to show the ability of a functional group or of a fixed substituent to polarize the π -electronic system, significantly increases the precision of the correlations.

Recently, various two-parameter correlations such as the Taft,¹ Swain-Lupton,² and Yukawa-Tsuno³ equations which permit the division of substituent effects into inductive (polar) and resonance components have been developed. The Swain-Lupton equation contains one set of inductive substituent constants (F) and one set of resonance substituent constants (R) for all the correlations used, the Yukawa-Tsuno equation contains one set of inductive constants (σ_i) and two sets of resonance constants (σ_R^+ values for electron-donating substituents $-R$ and σ_R^- values for electron-withdrawing ones $+R$), and the Taft equation contains one set of inductive constants (σ_i) and four sets of resonance constants $\sigma_R(\text{BA})$, σ_R^+ , σ_R^- , and σ_R^0 for different classes of aromatic compounds.

Taft and his co-workers¹ obtained the most precise correlations, but the necessity of using four sets of resonance substituent constants which have uncertain regions of application can hardly be considered as a merit of the method. Further investigations led to 'erosion' of the resonance constants sets. Thus, Taagepera *et al.*⁴ concluded that only the $-R$ substituents manifest resonance effects on the acidities of pyridinium ions, the σ_R^+ values of the $+R$ substituents in this case being close to zero. The σ_R^- scale was criticized⁵ on the ground that the substituent effects on the phenol acidities in water (which were used for calculation of σ_R^- values) are distorted by solvation effects. It was also shown⁶ that σ_R^0 values are not invariant parameters but depend on the ability of a given substituent to polarize the π -electrons of the aromatic system.

These facts diminish the value of the two-parameter correlation equations. Moreover, there is another reason for criticism. Indeed, Taft and his co-workers¹ found that $\rho_I \geq \rho_R$ in most cases for *para*-substituted compounds (for example ρ_I 0.997 and ρ_R 1.003 for series 1, Table 2). But these results are paradoxical as it is difficult to understand how the inductive mechanism for the transfer of the effects of *para*-substituents through an aromatic ring can be more important than the resonance transfer mechanism.

One can therefore suppose that the shortcomings of the two-parameter correlation equations can be explained by erroneous separation of inductive and resonance substituent effects in these equations and not by the impossibility of the creation of a universal scale of resonance substituent constants. It has been already pointed out² that the erroneous separation might be the consequence of equating inductive substituent effects in the *para*- and *meta*-positions.

Earlier we proposed^{7,8} a different method for the separation of polar (inductive) and resonance substituent effects in aromatic compounds based on the Taft polar substituent

constants (σ^*) and our resonance substituent constants (σ^r) of the XCH_2 groups.* In this case no preliminary assumptions about the ratio of inductive and resonance contributions are required, and therefore one can hope to obtain a more correct separation of these effects.

We showed⁹ that the correlations of the *para*-substituent ¹³C n.m.r. chemical shifts of aromatic compounds with σ^* and σ^r constants have practically the same precision as the correlations with σ_I and σ_R^0 constants.^{6,10} We also found that the ρ^* values are identical for all the disubstituted benzenes $p\text{-XC}_6\text{H}_4\text{Y}$ with a different fixed substituent Y ($\rho_{av}^* -1.3 \pm 0.3$). Thus, a previously noted shortcoming of the Taft equation which gives greater ρ_I values for both the electron-donating Y = SiMe₃ and the electron-withdrawing Y = Br¹¹ in comparison with a ρ_I value for C₆H₅X is eliminated. This seems to indicate that a more correct separation of polar and resonance effects can be achieved with σ^* and σ^r constants.

In this work a two-parameter equation with σ^* and σ^r was applied to all basic classes of aromatic compounds.

Results and Discussion

The σ^* and σ^r values are given in Table 1. With the exception of the σ^* and σ^r values for the CO₂R substituent and the σ^* value for the NO₂ substituent, all values are taken from previous work.⁹ The σ^* value of CO₂R was corrected by taking into account the statistical factor 2 omitted in the original work.¹² The σ^r value of CO₂R was determined as previously⁹ on the basis of the value of the *para*-substituent ¹³C n.m.r. chemical shift of C₆H₅CO₂R and a new value of $\sigma^{\text{CO}_2\text{R}*}$, 0.75.

Earlier we calculated^{7,8} the values of $\sigma_{\text{NO}_2}^*$ (0.40) and of $\sigma_{\text{NO}_2}^r$ (0.89) using the values of the rate constant of the methyl radical reacting with nitromethane and of the proton coupling constant for the free radical Me₂CNO₂. This value of $\sigma_{\text{NO}_2}^*$ is much smaller than the Taft value, 1.40,¹² but the necessity of introducing the new $\sigma_{\text{NO}_2}^*$ value was confirmed by the fact that the sum of $\sigma_{\text{NO}_2}^*$ and $\sigma_{\text{NO}_2}^r$ calculated from kinetic data was 1.29.

The new $\sigma_{\text{NO}_2}^*$ and $\sigma_{\text{NO}_2}^r$ values were successfully applied by us to series of *para*-substituted compounds.⁷⁻⁹ However, the data obtained confirm the correctness of the accepted value of $\sigma_{\text{NO}_2}^r$ but not of $\sigma_{\text{NO}_2}^*$, since the resultant effect of *para*-substituents is basically the resonance one (see below). In this

* σ^r Values were originally calculated on the basis of the spin densities of aliphatic free radicals CH₃CHX and later were partly modified by using the *para*-substituent ¹³C n.m.r. chemical shifts of substituted benzenes.^{8,9}

Table 1. The polar (σ^*) and resonance (σ^r) substituent constants for aromatic compounds

Substituent	σ^*	σ^r
NMe ₂	0.82	-1.41
NH ₂	0.48	-1.29
MeO	0.52	-0.94
HO	0.555	-0.92
PhO	0.85	-0.57
F	1.10	-0.42
Cl	1.05	0.00
Br	1.00	0.00
Me	-0.10	-0.42
H	0.00	0.00
CCl ₃	0.946	0.39
CF ₃	0.92	0.61
CONH ₂	0.61	0.55
MeCO	0.60	0.69
CO ₂ R	0.75 ^a	0.70 ^a
CN	1.30	0.72
SO ₂ Me	1.32	0.88
NO ₂	1.40 ^b	0.89

^a This work; previous values σ^* 1.05, σ^r 0.76.⁹ ^b This work; previous σ^* value 0.40.^{7,8}

work we found that the inclusion of the NO₂ substituent in the correlations for *meta*-substituted compounds can be made only with using the increased value of $\sigma_{\text{NO}_2}^*$.

Another reason for rejecting the value of $\sigma_{\text{NO}_2}^* = 0.40$ is the large effect of the NO₂ substituent in phenylbicyclo-[2.2.2]octanes^{13,14} where the substituents manifest mainly inductive effects. The correlations of the *para*-substituent ¹³C and ¹⁹F n.m.r. chemical shifts of these compounds with σ^* values are not very precise, but nonetheless they give $\sigma_{\text{NO}_2}^*$ 1.40–1.60. Therefore, in this work we used the old Taft value of $\sigma_{\text{NO}_2}^* = 1.40$ in all correlations. The reason for the decreased polar effect of the NO₂ substituent in radical reactions of aliphatic compounds remains obscure.

The physicochemical data of substituted aromatic compounds used in this work are given in Table 2. For calculation, equation (1) was used where x_i and x_0 are the physical or

$$x_i - x_0 = \rho^* \sigma^* + r^* \sigma^r + B \quad (1)$$

chemical data for substituted and unsubstituted aromatic compounds (log k , log K_{eq} , chemical shifts, etc.). Equation (1) differs from the two-parameter equation which has been used by us earlier⁷⁻⁹ by the introduction of a free term B . The importance of such a modification is shown below. The results of the calculations for *para*- and *meta*-substituted compounds are given in Tables 3 and 4, respectively. It is obvious that σ^* and σ^r values are indeed 'universal' substituent constants as reliable correlations were obtained for all classes of aromatic compounds. Furthermore, equation (1) permits us to obtain a more precise separation of polar (inductive) and resonance substituent effects. Indeed, for all series of experimental data corresponding to all four sets of the Taft resonance substituent constants, the resonance contribution to the total effect of *para*-substituents is predominant: $R = 100A^r/r^* : (A^*|\rho^*| + A^r/r^*) = 70-92\%$.^{*} Thus in these correlations, a basic shortcoming of the previous correlation equations which overestimated the inductive effect of *para*-substituents is absent.

* $A^{*(r)} = \left[\frac{1}{n} \sum (\sigma^{*(r)} - \bar{\sigma}^{*(r)})^2 \right]^{\frac{1}{2}}$. I thank a referee who pointed out the necessity of taking into account the $A^{*(r)}$ terms.

Table 2. Physicochemical series used in the correlation analysis

No.	Series
1a	pK_a values of XC ₆ H ₄ CO ₂ H, H ₂ O, 25 °C ^a
1b	The same ^b
2	pK_a values of XC ₆ H ₄ CO ₂ H, gas phase, 25 °C ^c
3	pK_a values of XC ₆ H ₄ CO ₂ H, 50% EtOH, 25 °C ^b
4	pK_a values of α -naphthoic acids, H ₂ O, 25 °C ^d
5	pK_a values of β -naphthoic acids, H ₂ O, 25 °C ^d
6	Rate constants for the hydrolysis of XC ₂ H ₄ CO ₂ Et, 60% acetone, 25 °C ^b
7	Rate constants for the solvolysis of XC ₆ H ₄ CM ₂ Cl, 90% EtOH, 25 °C ^e
8	Rate constants for the solvolysis of XC ₆ H ₄ CHPhCl, EtOH, 25 °C ^f
9	Rate constants for the reaction of galvinoxyl with phenols, CCl ₄ , 25 °C ^g
10	Rate constants for the thermolysis of <i>t</i> -butyl peroxybenzoates, 120 °C ^h
11	Rate constants for the methoxymercuration of substituted styrenes, MeOH, 25 °C ⁱ
12	pK_a values of pyridinium ions, H ₂ O, 25 °C ^j
13	pK_a values of pyridinium ions, gas phase, 25 °C ^j
14	Rate constants for the reaction of substituted pyridines with ethyl iodide, CH ₂ Cl ₂ , 25 °C ^k
15	pK_a values of pyridine <i>N</i> -oxides, H ₂ O, 25 °C ^l
16	pK_a values of anilinium ions, H ₂ O, 25 °C ^j
17	pK_a values of phenols, H ₂ O, 25 °C ^m
18	pK_a values of phenols, gas phase, 25 °C ^m
19	<i>para</i> -Substituent ¹ H chemical shifts of the phenol hydroxyl, DMSO ⁿ
20	<i>para</i> -Substituent ¹³ C chemical shifts of C ₆ H ₅ X, cyclo-C ₆ H ₁₂ ^o
21	<i>para</i> -Substituent ¹³ C chemical shifts of XC ₆ H ₄ NO ₂ , CDCl ₃ ^p
22	<i>para</i> -Substituent ¹⁹ F chemical shifts of XC ₆ H ₄ F, MeOH ^q

^a T. Matsu, H. C. Ko, and L. G. Hepler, *Can. J. Chem.*, 1974, **52**, 2906.

^b Ref. 1. ^c R. Yamdagni, T. B. McMahon, and P. Kebarle, *J. Am. Chem. Soc.*, 1974, **96**, 4035. ^d P. R. Wells, S. Ehrenson, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1968, **6**, 147. ^e L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35. ^f S. Nishida, *J. Org. Chem.*, 1967, **32**, 2692. ^g N. Nishimura, K. Okahashi, T. Yukutomi, A. Fujiwara, and S. Kobo, *Aust. J. Chem.*, 1978, **31**, 1201. ^h C. Fillatre, B. Maillard, and J. J. Villenave, *Thermochim. Acta*, 1980, **39**, 195. ⁱ A. Lewis and J. Azoro, *J. Org. Chem.*, 1981, **46**, 1764. ^j Ref. 4. ^k C. D. Johnson, I. Roberts, and P. G. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1981, 409. ^l M. Sawada, Y. Yukawa, T. Hanafusa, and Y. Tsuno, *Tetrahedron Lett.*, 1980, **21**, 4013. ^m Ref. 5. ⁿ M. T. Tribble and J. G. Traynham, *J. Am. Chem. Soc.*, 1969, **91**, 379. ^o Ref. 10. ^p Ref. 6. ^q R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, 1963, **85**, 3146.

For all series involved, the ratio $\rho_{\text{meta}}^* : \rho_{\text{para}}^* > 1$. Thus the suggestion that inductive effects of *para*- and *meta*-substituents are equal may be replaced by the more obvious one that the inductive effect of *meta*-substituents is greater than that of *para*-substituents.

In comparison with the Taft treatment,¹ equation (1) indicates a greater resonance contribution in the resultant effect of *meta*-substituents (Table 4).

We now consider the significance of the correlations obtained. In Tables 3 and 4 the significance of the correlations is characterized by the parameter f which is equal to the ratio of the root mean square deviation of the fitted set to the root mean square of experimental data.¹⁵ Taft and his co-workers¹ proposed that a correlation is 'good' if $f \leq 0.1$. In many cases they obtained very precise correlations with f 0.06–0.10¹ and even 0.01–0.05^{6,10} when four sets of resonance substituent constants or their modifications were used. But it was shown in recent work of these authors^{4,5} that such great precision does not guarantee the correctness of separation of inductive and resonance substituent effects or even the choice of the resonance constant set.

Table 3. Application of equation (1) to the series of *para*-substituted compounds

No.	ρ^*	r^*	B	s^a	f	$P(\%)$	$R(\%)$	$\frac{ B }{ r^* }$	n^b	c
1a	0.123 ± 0.109	0.578 ± 0.075	0.124 ± 0.096	0.088	0.12	14.0	86.0	0.21	6	
1b	0.124 ± 0.076	0.596 ± 0.037	0.052 ± 0.071	0.094	0.16	10.0	90.0		14	$\sigma_R(\text{BA})$
2	2.64 ± 0.57	3.50 ± 0.38	1.14 ± 0.56	0.53	0.089	33.5	66.5	0.33	7	
3	0.253 ± 0.119	0.786 ± 0.059	0.100 ± 0.106	0.14	0.15	12.5	87.5		12	$\sigma_R(\text{BA})$
4	0.175 ± 0.116	1.02 ± 0.08	0.208 ± 0.115	0.11	0.11	10.0	90.0	0.20	9	
5	0.111 ± 0.044	0.429 ± 0.027	0.130 ± 0.045	0.046	0.097	12.0	88.0	0.30	8	
6	0.339 ± 0.154	1.41 ± 0.08	0.260 ± 0.158	0.16	0.11	11.6	88.4	0.18	11	$\sigma_R(\text{BA})$
7	-0.739 ± 0.417	-3.30 ± 0.30	0.214 ± 0.377	0.43	0.15	13.7	86.3		9	
8	-0.845 ± 0.185	-2.48 ± 0.18	0.266 ± 0.178	0.16	0.065	22.2	77.8	0.11	6	
9	-0.246 ± 0.534	-2.47 ± 0.042	0.356 ± 0.512	0.48	0.19				6	
10	-0.097 ± 0.054	-0.210 ± 0.037	-0.029 ± 0.047	0.063	0.24	24.1	75.9		10	
11	-0.738 ± 0.180	-1.62 ± 0.13	0.152 ± 0.155	0.20	0.11	24.4	75.6		8	
12	0.870 ± 0.690	2.94 ± 0.34	-0.080 ± 0.684	0.79	0.25	12.7	87.3		11	σ_R^+
13	4.16 ± 2.17	6.19 ± 1.17	-2.38 ± 1.98	2.59	0.35	26.4	73.5		10	
14	-0.363 ± 0.203	-0.911 ± 0.095	0.135 ± 0.169	0.22	0.18	15.7	84.3		8	
15	0.172 ± 0.362	2.07 ± 0.18	0.036 ± 0.316	0.41	0.18				9	
16	0.577 ± 0.364	1.90 ± 0.21	0.489 ± 0.318	0.42	0.19	14.9	85.1	0.26	11	σ_R^-
17	0.643 ± 0.314	1.05 ± 0.15	0.417 ± 0.286	0.39	0.24	22.9	77.1	0.39	13	
18	3.77 ± 1.14	6.04 ± 0.55	2.40 ± 1.04	1.40	0.15	23.2	76.8	0.40	13	
19	0.346 ± 0.111	0.917 ± 0.053	0.154 ± 0.102	0.14	0.14	15.4	84.6	0.17	15	σ_R^-
20	-1.23 ± 0.29	7.25 ± 0.14	-0.163 ± 0.268	0.36	0.055	7.7	92.3		13	σ_R^0
21	-1.57 ± 0.50	6.01 ± 0.25	-0.403 ± 0.457	0.61	0.11	11.5	88.5		12	σ_R^0
22	-0.42 ± 1.04	-11.3 ± 0.5	1.09 ± 0.93	1.35	0.13				16	σ_R^0

^a Standard deviation. ^b Number of points in the set. ^c Type of resonance substituent constants in the Taft treatment.^{1,6,10}

Table 4. Application of equation (1) to the series of *meta*-substituted compounds

No.	ρ^*	r^*	B	s	f	$P(\%)$	$R(\%)$	$\frac{ B }{ r^* }$	n
1a	0.333 ± 0.049	0.178 ± 0.038	0.074 ± 0.049	0.045	0.090	40.4	59.6	0.42	7
1b	0.299 ± 0.058	0.224 ± 0.029	0.049 ± 0.054	0.072	0.16	39.6	60.4		14
2	2.76 ± 0.54	2.52 ± 0.36	0.916 ± 0.534	0.50	0.094	42.3	57.7	0.36	7
3	0.476 ± 0.105	0.307 ± 0.051	0.022 ± 0.092	0.12	0.18	43.2	56.8		11
4	0.422 ± 0.071	0.291 ± 0.058	0.091 ± 0.064	0.056	0.066	54.3	45.7	0.31	6
5	0.404 ± 0.067	0.315 ± 0.043	0.047 ± 0.063	0.057	0.092	44.8	55.2		8
6	0.657 ± 0.119	0.628 ± 0.066	0.179 ± 0.122	0.12	0.11	36.5	63.5	0.29	10
7	-1.58 ± 0.16	-0.736 ± 0.116	-0.154 ± 0.148	0.17	0.072	60.3	39.7		9
8	-1.46 ± 0.12	-0.728 ± 0.097	-0.091 ± 0.118	0.11	0.048	61.6	38.4		6
12	2.05 ± 0.40	1.46 ± 0.20	0.091 ± 0.367	0.49	0.18	41.1	58.9		12
13	5.33 ± 1.97	4.28 ± 1.06	-1.81 ± 1.79	2.35	0.34	40.1	59.9		10
14	-0.790 ± 0.139	-0.393 ± 0.080	0.053 ± 0.100	0.13	0.13	56.3	43.7		7
16	1.07 ± 0.11	0.445 ± 0.064	0.081 ± 0.098	0.13	0.092	58.2	41.8		11
17	0.791 ± 0.086	0.348 ± 0.043	0.114 ± 0.079	0.10	0.095	53.1	46.9	0.33	13
18	4.58 ± 0.89	3.08 ± 0.44	0.48 ± 0.82	1.09	0.16	42.5	57.5		12

As can be seen from Tables 3 and 4, in this work f is as a rule 0.05–0.2. For *para*-substituted compounds, it is of interest to compare the results obtained with equation (1) with those obtained with (2). As mentioned, *para*-substituent effects are

$$x_i - x_0 = r^* \sigma^r + b \quad (2)$$

basically the resonance ones. Therefore, it can be suggested that for *para*-substituted compounds the precision of equation (2) may be close to that of (1). The results obtained with equation (2) are given in Table 5. It is evident that the f values for equation (2) are only *ca.* 0.03 greater than the corresponding values for equation (1).

At the same time, the precision of equation (2) can be easily compared with that of the classical Hammett equation. For the latter, the Jaffé estimate¹⁶ is generally accepted, according to which a correlation is satisfactory if the correlation coefficient $r \geq 0.95$. As seen in Table 5, 18 correlations with $f \leq 0.23$ have $r \geq 0.960$ –0.996. Even for f 0.27–0.29, r is 0.91–0.96 (correlations 10, 11, 17) *i.e.* the fits are fair.¹⁶ And only for f 0.43

does the correlation coefficient become smaller than 0.90 (correlation 13). Comparison of equations (1) and (2) also shows that $b = \rho^* \bar{\sigma}^* + B$ (where $\bar{\sigma}^*$ is the mean value of the σ^* s used). As seen in Table 5, this equality is fulfilled in all cases.

From comparison of the precision of equations (1) and (2), we can conclude that the two-parameter correlations with f 0.1–0.2 are reasonably reliable. And what is more, we believe that the precision of the correlations with $f < 0.05$ exceeded as a rule that of the experimental data used and probably the possible precision of quantitative separation of polar and resonance substituent effects (*i.e.* the possibility of neglecting steric effects, medium effects, *etc.*).

It is generally accepted that the necessity for various sets of resonance constants is due to the ability of different substituents to change their resonance effect in different ways from one reaction (interaction) type to another.* For example it was

* It is important, as a referee pointed out, that the various σ_R scales are not, in detail, collinear.

Table 5. Application of equation (2) to the series of *para*-substituted compounds

No.	r^*	b	s	f	r^a	$ b : r^* $	$\rho^*\sigma^* + B$
1a	0.617 ± 0.046	0.210 ± 0.031	0.07	0.15	0.989	0.34	0.209
1b	0.622 ± 0.036	0.157 ± 0.028	0.10	0.18	0.981	0.25	0.160
2	4.75 ± 0.61	3.57 ± 0.47	1.20	0.23	0.962	0.75	3.51
3	0.857 ± 0.057	0.310 ± 0.047	0.16	0.19	0.979	0.36	0.311
4	1.10 ± 0.06	0.372 ± 0.042	0.12	0.13	0.991	0.34	0.362
5	0.469 ± 0.031	0.236 ± 0.023	0.06	0.13	0.987	0.50	0.235
6	1.53 ± 0.07	0.589 ± 0.061	0.19	0.14	0.990	0.38	0.577
7	-3.61 ± 0.27	-0.398 ± 0.169	0.50	0.18	0.980	0.11	-0.412
8	-3.03 ± 0.32	-0.472 ± 0.169	0.40	0.18	0.978	0.16	-0.484
9	-2.61 ± 0.27	0.138 ± 0.175	0.43	0.20	0.979		0.139
10	-0.240 ± 0.038	-0.104 ± 0.024	0.07	0.29	0.914	0.43	-0.107
11	-1.88 ± 0.21	-0.413 ± 0.138	0.38	0.23	0.963	0.22	-0.443
12	3.16 ± 0.30	0.620 ± 0.246	0.81	0.27	0.962	0.20	0.618
13	7.09 ± 1.24	1.06 ± 0.95	3.00	0.43	0.897	0.15	1.07
14	-0.995 ± 0.097	-0.135 ± 0.090	0.25	0.23	0.973	0.14	-0.124
15	2.11 ± 0.15	-0.171 ± 0.129	0.38	0.18	0.984	0.34	-0.172
16	2.08 ± 0.23	0.952 ± 0.136	0.56	0.22	0.964	0.46	0.952
17	1.22 ± 0.15	0.959 ± 0.122	0.44	0.29	0.930	0.79	0.958
18	7.04 ± 0.64	5.58 ± 0.54	1.93	0.22	0.958	0.79	5.59
19	0.999 ± 0.059	0.449 ± 0.047	0.18	0.19	0.978	0.45	0.454
20	6.93 ± 0.16	-1.24 ± 0.16	0.56	0.089	0.996	0.18	-1.22
21	5.61 ± 0.30	-1.74 ± 0.24	0.84	0.15	0.986	0.31	-1.73
22	-11.3 ± 0.42	0.780 ± 0.332	1.32	0.14	0.990	0.07	0.736

^a Correlation coefficient.

suggested¹⁷ that the resonance effects of the $-R$ substituents increase the solvolysis of cumyl chlorides, and those of the $+R$ substituents increase the dissociation of phenols. However, as seen in Table 3, our results do not coincide with this point of view. Indeed, the differences between series of different types are not essential. It might be noted that the free term B is small in comparison with the resonance term for the σ_R^+ and σ_R^0 series, whereas for the $\sigma_R(\text{BA})$ and σ_R^- series the $|B|:|r^*|$ ratio is much greater (0.2–0.4). In addition to the type of interactions (reactions), the ratio of polar and resonance contributions for *para*-substituents are also influenced by the phase conditions. As in the Taft treatment,⁴ the polar and resonance constants of proportionality (ρ^* and r^*) are greater in the gas phase than in the liquid phase. However, it seems to be more important that polar (inductive) contributions to the resultant *para*-substituent effects become greater in the gas phase (compare series 1 and 2 or 12 and 13). It is of interest that earlier we obtained similar results for reactions of the hydroxyl radical with aliphatic compounds.¹⁸ In both cases the medium effect appears to be due to the expansion of the transition state in the gas phase by comparison with the liquid phase.¹⁸

As mentioned above, unlike the equation used in previous work,^{7–9} equation (1) contains the free term, B , which decreases considerably the f values of the correlations. We believe that the introduction of this term not only gives more precise correlations, but that it has a definite physical meaning: it shows the ability of a functional group or a fixed substituent to polarize the aromatic π -electron system. In accordance with this, the $|B|:|r^*|$ ratio has the largest values for ionization of aromatic acids and phenols and for hydrolysis of esters (series 1–6, 17 and 18, Table 3), where the π -electron system of *para*-substituted compounds is polarized by the groups CO_2H , CO_2R , and OH . Solvolysis of cumyl chlorides and diphenylmethyl chlorides (series 7 and 8) and thermolysis of *t*-butyl perbenzoates (series 10) proceed with the formation of intermediates (carbocations and free radicals) which do not have polar functional groups, and therefore for these reactions the $|B|:|r^*|$ ratio is about zero.

The parameter B is bound up with the Taft parameter ϵ

(electron demand)⁶ in the dual parameter treatment of the ¹³C chemical shifts of *para*-substituted benzenes. However, unlike equation (1), equation (3) cannot be applied to reaction series.⁶

$$\delta = \rho_I \sigma_I + \rho_R \sigma_R^0 (1 - \epsilon \sigma_R^0) \quad (3)$$

In addition, the practical application of equation (3) is more difficult, owing to the necessity of primary calculation of the ϵ values for all series investigated. In conclusion, it should be noted that in our opinion equation (1) can be successfully used for quantitative separation of polar (inductive) and resonance effects of *para*- and *meta*-substituents of aromatic compounds.

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