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## Ortho Effect and Additivity of Substituent Parameters in the Reaction between Phenols and Poly(vinyl Acetate) Radicals

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### ABSTRACT

The ortho effect and the additivity of substituent parameters in the reaction between phenols and poly(vinyl acetate) radicals have been investigated in the light of theories postulated by Swain and Lupton on substituent constants  $F_k$  and  $R_k$  and that of Williams and Norrington on the unique positional weighting factors  $f_j$  and  $r_j$ . The present correlation studies show that while Charton's theory that the ortho-substituent effect is primarily electrical is true for most of the substituents, some steric considerations have to be invoked while dealing with groups like *o*-tert-butyl. The additivity of  $f_j F_k$  and  $r_j R_k$  is much less satisfactory than that of Hammett's  $\sigma$  or Brown-Okamoto's electrophilic  $\sigma^+$  substituent constants.

Swain and Lupton [1] have proposed that the Hammett [2] substituent constants  $\sigma_k$  can be expressed as a linear combination of their

two components: the field ( $F_k$ ) and resonance ( $R_k$ ) effects, i. e.,

$$\sigma_k = aF_k + bR_k \quad (1)$$

where  $a$  and  $b$  are the empirical sensitivities or weighting factors independent of the substituents but different for each set of substituent constants ( $\sigma_m$ ,  $\sigma_p$ ,  $\sigma_p^+$  etc.).

Swain and Luptons' work was subsequently refined and given a more generalized character by Williams and Norrington [3], who proposed unique positional weighting factors  $f$  and  $r$  in place of Swain and Luptons' empirical sensitivities  $a$  and  $b$  which can be applied to ortho, meta, and para positions of the benzene ring simultaneously. The suggested values are,

$$f_o = 1.248, f_m = 0.980, f_p = 1.000$$

$$r_o = 0.863, r_m = 0.347, r_p = 1.000$$

For a data set consisting of only meta and para derivatives, the values suggested are:

$$f_m = 1.002, f_p = 1.000$$

$$r_m = 0.424, r_p = 1.000$$

These values yielded good correlation between various free energy related properties of the side chain and substituent parameters of mixed or multiply substituted benzene derivatives.

The original Hammett equation,

$$P_i = \rho_i \sigma_k + P_i^o \quad (2)$$

(where  $P_i$ 's are some free energy-related property,  $P_i^o$  being that for a standard reference state for the  $i$ -th reaction set), now becomes, in terms of Swain-Lupton and Williams-Norrington's modifications,

$$P_i = \alpha_i f_j F_k + \beta_i r_j R_k + P_i^o \quad (3)$$

where  $f_j$  and  $r_j$  are the Williams-Norrington positional weighting factors for the position  $j$ ,  $F_k$  and  $R_k$  are the field and resonance components of the substituent  $k$  (Swain-Lupton). In the final form of the Swain-Lupton-Williams-Norrington (SLWN) equation, a normally distributed error term  $e_i$ , independent of the position and nature of the substituent, was added [3] to Eq. (3):

$$P_i = \alpha_i f_j F_k + \beta_i r_j R_k + e_i + P_i^0 \quad (4)$$

By analogy with the additivity of the original polar substituent constants due to Hammett over a polysubstituted aromatic system, it was suggested [3] that the substituent parameters  $f_j F_k$  and  $r_j R_k$  are also additive, so that for polysubstituted benzenoid derivatives, Eq. (4) can be written:

$$P_i = \alpha_i \sum f_j F_k + \beta_i \sum r_j R_k + P_i^0 + e_i \quad (5)$$

The validity of this additivity hypothesis was tested by considering the  $pK_a$  values of three series: benzoic acids, phenols, and anilines.

The present communication deals with the application of Eqs. (4) and (5) to the rate data of the reaction of substituted phenols with poly(vinyl acetate) radicals [4]. The object is to study the ortho-effect and to test the additivity of  $f_j F_k$  and  $r_j R_k$  in polymerization reactions. The reaction dependent parameters  $\alpha_i$  and  $\beta_i$  and the error term  $e_i$  were determined by the method of multiple regression. The statistical parameters, i. e., standard deviation  $S$ , correlation coefficient  $C$ , the  $F$ -distribution  $F$ , and the significance levels were calculated by the method suggested by Shorter [5].

## ORTHO EFFECT

The rate data and the substituent parameters ( $F_k$  and  $R_k$ ) are described in Table 1. The regression coefficients  $\alpha, \beta$  and  $e$  and the statistical parameters are given in Table 2.

There seem to be conflicting opinions about the effect of ortho substituents on chemical reactivity. While Charton [6, 7] maintains that such effects are not primarily steric but are essentially electrical

TABLE 1. Rate Data and Substituent Parameters<sup>a</sup>

Substituent	F <sub>k</sub>	R <sub>k</sub>	log k <sub>x</sub> /k <sub>H</sub> (≡ P <sub>i</sub> - P <sub>i</sub> <sup>o</sup> ) (log k <sub>H</sub> = 0.36) <sup>b</sup>
p-CH <sub>3</sub>	0.052	-0.141	0.36
m-CH <sub>3</sub>	0.052	-0.141	0.26
o-CH <sub>3</sub>	0.052	-0.141	0.24
p-Cl	0.690	-0.161	+0.05
m-Cl	0.690	-0.161	-0.32
o-Cl	0.690	-0.161	0.12
p-Br	0.727	-0.176	0.13
p-OH	0.487	-0.643	0.23
m-OH	0.487	-0.643	0.01
o-OH	0.487	-0.643	1.44
p-OEt	0.363	-0.444	1.12
p-CHO	0.667	-0.156	-0.66
p-F	0.708	-0.336	0.13
o-tert-Bu	-0.104	-0.138	1.43

<sup>a</sup>Data of Simonyi et al. [4].

<sup>b</sup>The rate parameters k refer to the transfer constants.

in origin, others like Taft [8, 9] point to a definite steric influence of the ortho substituents. Simonyi, Tüdös, and Pospisil [4], from whose work the present data are taken, have accounted for their observed data by considering a steric effect, particularly, when both the ortho positions are substituted, although they are not very explicit with regard to the effect of a single ortho substituent. In order to test these theories, the correlation data obtained with only meta and para substituents were first compared with those of the data including ortho-substituted compounds. As a further check, an additional calculation was undertaken first with the exclusion of some bulky ortho groups like tert-butyl as well as groups which are likely to have other complicating influence like hydrogen bonding (o-OH, o-Cl and o-F). Since the last set of data leaves only one ortho substituent

TABLE 2

Set	Nature of rate data (number of data points)	e	$\alpha$	$\beta$	S	C ( $C^2$ )	F	Significance level (%)
(i)	Only m- and p-substituents (10)	-0.0061	-0.8595	-2.659	0.272	0.923 (0.852)	11.48	99
(ii)	o-, m- and p-substituents [15]	0.1764	-0.98	-2.7285	0.377	0.848 (0.718)	9.36	99
(iii)	Set (iii) excluding o-tert-butyl [14]	0.0804	-0.6395	-2.8479	0.291	0.899 (0.807)	13.98	99.9
(iv)	Set (iii) excluding o-tert-butyl, o-OH, o-F, and o-Cl (11)	-0.034	-0.8018	-2.6902	0.254	0.921 (0.849)	13.09	99

TABLE 3

No.	Substituent in phenol	log c $\beta$				
		$\Sigma fF$	$\Sigma rR$	Calcd by Eq. (6)	Observed	
1	3,5-Di-OH	0.9546	-0.4462	0.818	1.197	0.30
2	3,5-Di-Me	-0.1020	-0.0978	0.903	0.623	0.49
3	2,6-Di-Me	-0.1298	-0.2434	1.328	1.065	1.42
4	2,4-Di-Me	-0.1169	-0.2627	1.308	1.103	1.28
5	2,3-Di-OH	1.0851	-0.7780	1.596	1.801	3.02
6	2,4-Di-Cl	1.5511	-0.2999	-0.165	0.142	0.59
7	2,6-Di-Cl	1.7222	-0.2778	-0.393	-0.031	0.58
8	2-OH, 3-Br	1.3203	-0.6160	0.923	1.19	1.70
9	2-tert-Bu-5-Me	-0.1808	-0.1680	0.923	1.19	1.70
10	2-Me-6-tert-Bu	-0.1947	-0.2408	1.384	-	1.23
11	2,6-Di-tert-Bu	-0.2596	-0.2382	1.441	-	0.40
12	2,4,6-Tri-Me	-0.1818	-0.3844	1.763	1.491	1.89
13	2,3,5-Tri-Me	-0.1669	-0.2195	1.3	1.01	0.90
14	2,6-Di-Me	0.3572	-0.8864	2.605	2.576	2.53
15	2,5-Di-Cl-4-OH	2.0243	-0.8378	0.839	1.371	1.50
16	2,4,6-Tri-Cl	2.4122	-0.4388	-0.630	-0.014	0.89

17	2,4,6-Tri-Br	2.5416	-0.4798	-0.645	0.0207	1.04
18	2,5-Di-tert-Bu-4-OH	0.2533	-0.8100	2.496	-	2.35
19	2,6-Di-tert-Bu,4-Me	-0.3116	-0.3792	1.876	-	0.74
20	2,4,6-Tri-tert-Bu	-0.3636	-0.3762	1.919	-	0.61
21	2,3,5,6-Tetra-Me-4-OH	0.2552	-0.9842	2.972	2.919	2.81
22	2-OH,3,4,5,6-Tetra-Cl	3.5113	-0.9666	-0.267	0.787	1.34
23	2,3,4,5,6-Penta-Cl	3.7646	-0.5506	-1.65	-0.56	0.57
24	2-OH,3,4,5,6-Tetra-Br	3.6671	-1.0050	-0.315	0.797	1.90



( $o\text{-CH}_3$ ) in the data set, it may have less credibility, but the results could be suggestive. The results are described in Table 2.

It is difficult to account for the significant improvement of the correlation set (iii) without invoking some sort of steric effect exerted by the  $o$ -tert-butyl group. We are inclined to avoid an extreme position. While it may be true that with most of the ortho substituents, the steric effect plays a minor role, it will not be correct to make it a general rule. In dealing with groups like  $o$ -tert-butyl, the spatial geometry of the substituent should be considered to exert a steric effect.

### ADDITIVITY OF $f_j F_k$ AND $r_j R_k$

The Hammett substituent constants  $\sigma$  were found to be additive for polysubstituted aromatic systems and could be used to accurately predict the  $pK_a$  values of benzoic acids or phenols [10] and anilines [11]. The present set of rate data were also subjected to a similar treatment with the use of  $\sigma^+$  values by the original workers [4] and satisfactory correlations were obtained.

In the present investigation, the additivity of the  $f_j F_k$  and  $r_j R_k$  values have been tested by using the regression coefficients of set (ii) [Eq. (6)] and set (iii) [Eq. (7)].

$$\log c\beta = 0.5364 - 0.98 \sum fF - 2.7285 \sum rR \quad (6)$$

$$\log c\beta = 0.2796 - 0.6395 \sum fF - 2.8479 \sum rR \quad (7)$$

The results are described in Table 3.

The correspondence with the experimental values is far from satisfactory, and the behavior is rather erratic. Although there is a slight improvement with Eq. (7), it is clear that either the additivity rule for  $f_j F_k$  and  $r_j R_k$  does not hold or the ortho substituents markedly change the transfer constants ( $c\beta$ ) by some additional mechanism as has been suggested in case of the  $pK_a$  values of phenols [10].

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