

# RATE PARAMETERS FOR TRANSFER REACTIONS OF SOME POLYMER RADICALS: IN TERMS OF SWAIN AND LUPTON'S $F$ AND $R$ AND THE UNIQUE POSITIONAL WEIGHTING FACTORS OF WILLIAMS AND NORRINGTON

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**Abstract**—Rate parameters of the reaction of phenols, deuterated phenols and nitrobenzenes with polyvinylacetate radicals and of aromatic thiols with polymethylmethacrylate radicals have been correlated with Swain and Lupton's substituent constants ( $F_k$  and  $R_k$ ) and Williams and Norrington's unique positional weighting factors ( $f_j$  and  $r_j$ ) by the following equation:

$$P_i = \alpha_i f_j F_k + \beta_i r_j R_k + e_i + P_i^0$$

where  $P_i$ 's are the rate parameters,  $P_i^0$  being that for a standard reference state. The correlations were found to be quite satisfactory. The sign and magnitude, and the ratio of the reaction dependent parameters  $\alpha_i$  and  $\beta_i$  throw light on the nature of the transition state and the relative contributions of the mesomeric and inductive effects. The present studies also show that the mesomeric effect of meta-substituents is significantly greater than reported by earlier workers.

There have been many attempts to modify the Hammett [1] equation to fit the experimental data for newly studied systems. One approach was to develop new substituent parameters based upon new model systems, inevitably resulting in a proliferation of substituent constants. The use of a Hammett type equation became increasingly complex, and to some extent subjective, because of such a wide choice of substituent parameters.

The second and a more fundamental approach towards the modification of Hammett's  $\rho - \sigma$  relationship has been to express substituent constants as linear combinations of fundamental components of substituent constants, meant to measure exclusively and separately the resonance and inductive effects of the substituents. Significant work in this area has been reported by Taft and Lewis [2], Charton [3] and Swain and Lupton [4].

Swain and Lupton's approach towards correlation between structure and activity has been to express Hammett's substituent constants  $\sigma$  and related parameters as linear combinations of their two principal components, viz., the field ( $F$ ) and resonance ( $R$ ) effects of the substituents without regard to position in the molecule. These constants,  $F$  and  $R$ , have been calculated by Swain and Lupton from Hammett's  $\sigma_m$  and  $\sigma_p$  values by assuming that any set of substituent constants  $\sigma_m$ ,  $\sigma_p$ , etc. may be expressed as:

$$\sigma = aF + bR \quad (1)$$

where  $a$  and  $b$  are the empirical sensitivities or weighting factors independent of substituent but different for each set of substituent constants ( $\sigma_m$ ,  $\sigma_p$ , etc.). The constants  $F$  and  $R$  have been claimed as better defined and physically more significant substituent parameters for correlating or predicting substituent

effects, on a variety of free energy dependent processes, than any other pair  $\sigma_m$ ,  $\sigma_p$ ,  $\sigma_p^+$ , etc.

The scope and significance of Swain and Lupton's work were greatly enhanced and refined by Williams and Norrington [5] who proposed unique values for the positional weighting factors  $f$  and  $r$ , in place of Swain and Lupton's empirical sensitivities  $a$  and  $b$ , applicable to the *ortho*-, *meta*- and *para*-positions of the benzene ring simultaneously. The values suggested are:

$$\begin{array}{ll} f_{ortho} = 1.248 & r_{ortho} = 0.863 \\ f_{meta} = 0.980 & r_{meta} = 0.347 \\ f_{para} = 1.000 & r_{para} = 1.000 \end{array}$$

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

$$\begin{array}{ll} f_{meta} = 1.002 & r_{meta} = 0.424 \\ f_{para} = 1.000 & r_{para} = 1.000 \end{array}$$

These values give good correlation between physico-chemical properties of the side-chain and substituent parameters of mixed or multiple-substituted benzenoid compounds.

Incorporation of these modifications and suggestions of Swain and Lupton [4] and Williams and Norrington [5], the original Hammett equation

$$P_i = P_i\sigma + P_i^0 \quad (2)$$

(where  $P_i$ 's are some free energy related property,  $P_i^0$  being that for some standard reference state for the  $i$ th reaction set) becomes

$$P_i = \alpha_i f_j F_k + \beta_i r_j R_k + P_i^0 \quad (3)$$

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 (Swain and Lupton) of the substituent  $k$ . As a further refinement, Williams and Norrington [5] introduced a normally distributed error term  $e_i$  independent of the nature and position of the substituent in Eqn (3) so that the final form of the Swain-Lupton-Williams-Norrington (SLWN) equation becomes:

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

Attempts at evaluation and application of substituent parameters for radical reactions have been made by various workers. Reactivity ratios of monomers in binary copolymerization were related to two fundamental parameters for a given monomer and its corresponding radical in the well known  $Q - e$  equation of Alfrey and Price [6]. Bamford and Jenkins [7] proposed a general expression for the rate constant of a reaction between a radical and a substrate in terms of polar and nonpolar factors,

$$\log k = \log k_{3,T} + \alpha\sigma + \beta \quad (5)$$

where  $k$  is the velocity coefficient for the reaction between the given radical and any substrate,  $k_{3,T}$  is the rate constant of a given radical in a transfer reaction with toluene at 60°, taken as a measure of the general or nonpolar reactivity. The polar contributions to the transition state are supposed to be expressed by the Hammett  $\sigma$  functions of the substituents in the free radical.  $\alpha$  and  $\beta$  are considered to be characteristic of the substrate. Timberlake *et al.* [8] have reported that no single substituent parameter like  $\sigma$ ,  $\sigma^+$  etc. can give the desired linear Hammett plot for radical reactions. They suggested that multiparameter equations may perhaps be an answer to this problem. Use of multiparameter equations for radical reactions was suggested earlier by Yamamoto and Otsu [9], and Streitwieser and Perrin [10] in the light of similar equations proposed for ionic reactions by Yukawa and Tsuno [11] and Ryan and Humfrey [12]. Afanasev [13] has suggested a method

for the calculation of resonance substituent constants of the two-parameter, Taft equation, based on the relationship between the spin density in free radicals and the rate constants of radical substitution reactions of  $\text{CH}_3$ . A new approach for the evaluation of radical substituent parameters, based on the equations of Yamamoto and Otsu [9] and Streitwieser and Perrin [10], has been developed by us and will be reported elsewhere.

The present communication deals with the application of the SLWN Eqn (4) to the rate parameters of some polymerizations induced by initiators such as  $\alpha, \alpha'$ -azobisisobutyronitrile (AIBN). Applicability of Eqn (4), as far as the authors are aware, has not so far been investigated for polymerization reactions. Accepting the general validity of Eqn (4), an assumption based on the satisfactory correlation of parameters that have been obtained (*vide infra*), it can be seen that the treatment can be used to investigate the mechanistic details of the reactions, either to confirm or question proposed schemes.

The following reaction series have been used for the present study:

- Reactivities of phenols towards polyvinylacetate radicals [14].
- Reactivities of nitrobenzenes towards polyvinylacetate radicals [15].
- The effect of aromatic thiols on the polymerization of methyl methacrylate [16].
- The effect of phenols and deuterated phenols on the polymerization of vinyl acetate [17].

The rate data are summarized in Table 1.

The values of the reaction dependent parameters  $\alpha_i$  and  $\beta_i$  and the error term  $e_i$  of Eqn (4) were determined by the method of multiple regression. The statistical parameter-standard deviation ( $S$ ), correlation coefficient ( $C$ ), the  $F$ -distribution ( $F$ ) and the significance levels were calculated by the method suggested by Shorter [18].

Table 1. Rate data for the reactions

Substituent $\log k_H$	$\log k_x/k_H (\equiv P_i - P_i^0)$				
	Series-a = 0.36	Series-b = 12.09	Series-c = 4.7	Series-d = 0.019	Series-d (with $\text{C}_6\text{H}_5\text{OD}$ ) = 0.002
<i>p</i> -CH <sub>3</sub>	0.36	-0.218	0.1971	0.5725	0.8751
<i>m</i> -CH <sub>3</sub>	0.26	-0.130	0.00	0.3840	0.7782
<i>p</i> -Cl	0.05	0.156	-0.0093	0.3840	0.6990
<i>m</i> -Cl	-0.32	0.386	-0.128	0.1526	0.5440
<i>p</i> -Br	0.13	—	0.0761	—	—
<i>m</i> -Br	—	—	-0.0923	—	—
<i>p</i> -COCH <sub>3</sub>	—	—	-0.2571	—	—
<i>m</i> -COCH <sub>3</sub>	—	—	-0.0488	0.9254	1.8354
<i>p</i> -OH	1.23	—	—	—	—
<i>m</i> -OH	0.01	—	—	—	—
<i>p</i> -OCH <sub>3</sub>	—	-0.376	—	—	—
<i>m</i> -OCH <sub>3</sub>	—	0.062	—	—	—
<i>p</i> -NH <sub>2</sub>	—	-0.499	—	—	—
<i>m</i> -NH <sub>2</sub>	—	-0.110	—	—	—
<i>m</i> -CN	—	—	—	0.5601	1.5250
<i>p</i> -OEt	1.12	—	—	—	—
<i>p</i> -CHO	-0.66	—	—	—	—
<i>p</i> -F	0.24	—	—	—	—
<i>p</i> -NO <sub>2</sub>	—	0.806	—	—	—
<i>m</i> -NO <sub>2</sub>	—	0.654	—	—	—

Table 2.

Type of rate data (number of data points <i>n</i> )	<i>e</i>	$\alpha$	$\beta$	<i>S</i>	<i>C</i>	<i>F</i>	Significance level
(i) All <i>m</i> - and <i>p</i> -substituents [10]	-0.0061	-0.8596	-2.695	0.272	0.923	11.48	>99%
(ii) All <i>m</i> - and <i>p</i> -substituents excluding halogens [6]	-0.0972	-1.6488	-3.5170	0.186	0.986	23.51	96%

(a) *Reactivities of phenols towards polyvinyl acetate radicals* [14]

The correlation data are described in Table 2.

Simonyi, Tüdös and Pospisil [14] have found a satisfactory correlation of their rate data with the electrophilic substituent constant  $\sigma^+$  for all but the halogenated phenols. The deviation for halogenated phenols could be attributed to either a change in the mechanism involving processes like (i) addition to the aromatic ring as side-chain, (ii) splitting of carbon-halogen bonds, (iii) a change in the stoichiometry or (iv) halogen-hydroxyl interaction (formation of hydrogen bond) or alternatively the inapplicability of the reported  $\sigma^+$  values. After considering several explanations, they maintain that the latter cause is responsible for the observed discrepancy with the halogen substituents and have suggested a set of modified  $\sigma^+$  values for these substituents.

The present studies can clearly be used to test the validity of their proposition, at least in so far as the suggestion that the anomalous behaviour of *meta*- and *para*-substituted phenols is not due to any change in the reaction mechanism. This point is at once obvious from Table 2. The apparent increase in the correlation coefficient with the data set (ii) (not containing halogenated phenols) is more than compensated by a fall in the significance level.

The relative magnitude of  $\alpha$  and  $\beta$  indicate that the substituent effect is predominantly governed by the mesomeric effect.

(b) *Reactivities of nitrobenzenes towards polyvinyl acetate radicals* [15]

With ten data points involving *meta*- and *para*-substituted nitrobenzenes, the following correlation parameters are obtained:

$$e = 0.0061, \quad \alpha = 0.5428, \quad \beta = 0.9081$$

$$S = 0.0999, \quad C = 0.982, \quad F = 53.56$$

Significance level >99.9%.

By invoking the Taft-Lewis concept [2] of separability of the substituent effect into inductive and resonance components, i.e.

$$\sigma_p = \lambda\sigma_I + \sigma_R \quad \text{and} \quad \sigma_m = \sigma_I + a\sigma_R$$

and the consequent linear relationship between

$$\frac{\log \frac{k_m}{k_0}}{\sigma_I} \quad \text{and} \quad \frac{\log \frac{k_p}{k_0}}{\sigma_I}$$

Foldes-Bereznykh, Tüdös and Szkacs [15] have found from the slope that *a* is 0.26; this result con-

trasts with the more widely accepted value of 0.333 (Taft and Lewis, *loc. cit.*) and has been justified on the grounds that *a* is not independent of the reaction type as assumed by Taft and Lewis and others. The excellent correlation, obtained in the present study with *r* = 0.424 (which is closely analogous to *a*), shows that the mesomeric effect exerted by the *m*-substituents is much stronger than that envisaged in earlier works. The positive values of both  $\alpha$  and  $\beta$  indicate operation of a mechanism different from that for the reaction between phenols and polyvinyl acetate radical (series-a).

(c) *Effect of aromatic thiols on the polymerization of methyl methacrylate* [16]

The relevant data are described in Table 3.

It can be seen that the data set (ii), with the exclusion of only *meta*-methyl thiol, has the best correlation. The improvement in the correlation coefficient with sets (iii) and (iv) is nullified by the decrease in the *F*-values and the significance levels. Exclusion of *meta*-methyl can be rationalized in view of apparent uncertainty in the rate data. Since there is a visible influence, though not large, of all other *meta*-substituents on the rate, it is difficult to see why this should not be so also with the methyl substituent.

Thus taking (ii) as the final regression, it can be seen that the inductive effect (reflected in  $\alpha$ ) is not of only minor importance as proposed by the authors. The value of the  $\beta/\alpha$  (= 2.3) ratio suggests that nearly one-third of the total substituent effect comes from the inductive influence.

(d) *Effect of phenols and deuterated phenols on the polymerization of vinyl acetate* [17]

The regression coefficients and statistical parameters are described in Table 4.

The unexpectedly poor correlation with the phenols points to a possibility that perhaps the same mechanism is not operative with all the substituents, as rather vaguely suggested by Bird and Russell [17]. There is however no reason why it should be so, particularly in view of the excellent correlation obtained with the mixed data of a very similar reaction (series-a). Moreover, exclusion of the acetyl and cyano-derivatives, the only two substituents in the set which are likely to behave differently, does not in any way improve the correlation. There is unexpected improvement in the correlation with the deuterated phenols and the present study also confirms the earlier observation [17] with regard to a very minor role played by the inductive effect ( $\beta/\alpha \sim 40$ ).

An attempt will be made now to find out what generalizations, if any, can be drawn from the sign

Table 3.

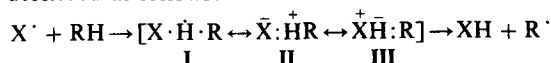
	Type of rate data (number of data points)	<i>e</i>	$\alpha$	$\beta$	<i>S</i>	<i>C</i>	<i>F</i>	Significance level (%)
(i)	All <i>m</i> - and <i>p</i> - substituents [8]	0.0251	-0.1902	-0.6613	0.078	0.902	5.79	
(ii)	Set (i) excluding <i>m</i> -methyl [7]	0.0887	-0.2867	-0.6661	0.068	0.944	8.14	93
(iii)	Set (i) excluding <i>m</i> - and <i>p</i> -acetyl [6]	0.0044	-0.1981	-0.8206	0.074	0.917	3.53	
(iv)	Set (i) excluding <i>m</i> - and <i>p</i> -acetyl and <i>m</i> -methyl [5]	0.1381	-0.2961	0.2864	0.096	0.931	2.15	

Table 4.

System (number of data points)	<i>e</i>	$\alpha$	$\beta$	<i>S</i>	<i>C</i>	<i>F</i>
<i>m</i> - and <i>p</i> -substituted phenols [6]	0.6722	-0.2211	1.7509	0.253	0.788	1.09
<i>m</i> - and <i>p</i> -substituted deuterated phenols [6]	1.2854	-0.1093	4.3726	0.332	0.913	3.32

and magnitudes of the regression parameters  $\alpha$  and  $\beta$ . Taking the best correlations of all the series, the data can be summarized as in (Table 5).

Reactions 1 to 3 have been reported as essentially hydrogen abstractions. The process of hydrogen abstraction by a radical  $X^\cdot$  from substrates has been described as follows:



where RH is a generalized hydrogen donor (phenol in this case). Significance of the contributions of dipolar structure, such as II or III, to the transition state is demonstrated by the correlation of these radical reactions with a Hammett type equation. This implies that  $\rho$  is a function of both electrophilicity of the abstracting radical and of the extent of bond breaking in the transition state [19]. Depending on whether structure II or III stabilizes the transition state, the reaction parameter  $\rho$  will be either negative or positive [20]. Since  $\rho$  is related to the parameters  $\alpha$  and  $\beta$ , its qualitative characteristics in terms of sign

should be reflected by  $\alpha$  and  $\beta$ . Though it does not follow automatically, a negative sign for both  $\alpha$  and  $\beta$  may perhaps indicate a negative  $\rho$  and a positive sign for both  $\alpha$  and  $\beta$  indicates a positive  $\rho$ .

To confirm the validity of the generalization, correlations of other hydrogen abstraction reactions with Eqn (4) known to exhibit negative  $\rho$  values were also undertaken; the results confirm the above view (Table 6).

One may, therefore, conclude that reactions 1 and 3, which exhibit negative  $\alpha$  and  $\beta$  values, may be characterized by a polar transition state of the type described by structure II.

A positive value of both  $\alpha$  and  $\beta$  is here suggested to imply the operation of a different mechanism. This is, of course, obvious with the particular reaction here (reaction 4) which exhibits this behaviour. Reaction of the polyvinyl acetate radical with nitrobenzene has been reported not to involve any abstraction process [15]. Hammett correlation gave a positive  $\rho$  value. Following the same line of reasoning as Pryor *et al.* [20], this suggests contribution of structure III to the

Table 5.

Reaction	<i>e</i>	$\alpha$	$\beta$	$\beta/\alpha$	<i>S</i>	<i>C</i>
1. <i>m</i> - and <i>p</i> -subst. phenols + polyvinyl acetate radicals [6]	-0.006	-0.8596	-2.659	3.093	0.272	0.923
2. <i>m</i> - and <i>p</i> -subst. C <sub>6</sub> H <sub>5</sub> OD + polyvinyl acetate radical [9]	1.285	-0.109	4.373	4.119	0.332	0.913
3. <i>m</i> - and <i>p</i> -subst. thiols + methyl methacrylate radical [8]	0.089	-0.287	-0.666	2.321	0.068	0.944
4. <i>m</i> - and <i>p</i> -subst. nitrobenzenes + polyvinylacetate radicals [7]	0.006	0.543	0.908	1.672	0.099	0.982

Table 6.

Sl. no.	Substrate	Attacking radical	$\alpha$	$\beta$	C	Reference on rate data on which basis the present calculations of $\alpha$ , $\beta$ , C were made
(i)	Phenols	RO <sub>2</sub> <sup>·</sup>	-0.7446	-2.8492	0.967	Howard <i>et al.</i> [21]
(ii)	Toluene	HOOC CH <sub>2</sub> <sup>·</sup>	-0.4935	-1.3409	0.951	Koehl <i>et al.</i> [22]
(iii)	Toluene	Cl <sub>3</sub> C <sup>·</sup>	-0.9642	-3.2075	0.983	Huyser [23]
(iv)	Toluene	Cl <sup>·</sup>	-0.4396	-0.8233	0.983	Russell <i>et al.</i> [19]
(v)	Toluene	Br <sup>·</sup>	-0.8176	-2.2436	0.983	Martin <i>et al.</i> [24]
(vi)	Toluene	t-BUO <sup>·</sup>	-0.3290	-1.2743	0.993	Gilliom <i>et al.</i> [25]

transition state. It may be seen that the  $\beta/\alpha$  ratio, which conveys the relative contributions of the inductive and resonance effects to the total polar effect of the reaction, is in the expected direction for reactions 1, 3 and 4.

An interesting case is presented by reaction 3.  $\alpha$  and  $\beta$  have opposite signs and  $\beta/\alpha$  is unusually large, suggesting that the reaction is almost exclusively controlled by a mesomeric effect. From the arguments of Zavitsas and Pinto [26], this might mean that the differences in the reactivities of substituted deuterated phenols towards the polyvinyl acetate radicals are, perhaps, due to the differences in the bond dissociation energies of the O—D bond and this will depend on the electron donating or withdrawing characteristics of the substituents. This may imply that structures II and III are unimportant, having little or no contribution to the transition state. The reaction of deuterated phenols with polyvinyl acetate radicals may, therefore, be considered to involve predominantly a nonpolar transition state.

The following conclusions emerge from the above studies and discussions:

1. The same sign of the regression parameters  $\alpha$  and  $\beta$  indicates contribution of polar structures to the transition state. A negative sign for both  $\alpha$  and  $\beta$  indicates contribution of structures of type II and a positive sign indicates that structures of type III are important in the transition state. When  $\alpha$  and  $\beta$  have opposite signs, there is weak contribution of polar structures to the transition state, which may be written as structure I.

2. The ratio  $\beta/\alpha$  reflect the contribution of the mesomeric and inductive effects to the total substituent effect.

(3) The excellent correlation obtained with most of the data in the present studies shows that the mesomeric effect of the *meta*-substituents ( $r_m = 0.424$  with no *ortho*-data and  $r_m = 0.34$  with *ortho*-data included) is significantly more than that reported by earlier workers (0.333).

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