Substituent Effects in the Kinetics of Polymerization of Acrylonitrile Retarded by Substituted Chalcones

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ABSTRACT

Substituent effects in the kinetics of polymerization of acrylonitrile retarded by substituted chalcones are studied in terms of Hammett-type correlations with sigma-plus and also in terms of the field and resonance components of the substituents. With the modified sigma-plus values for halogen substituents, both the correlations are found to give excellent results. The significance of the values of the observed reaction constants and the relative merits of the two types of correlations are discussed.

We have earlier reported [1] the kinetics of the Ce(IV)-initiated polymerization of acrylonitrile by chalcone, in which it was proposed that the polymerization of acrylonitrile by Ce(IV) is retarded by a radical produced by the interaction of chalcone with Ce(IV). The following reaction scheme, which satisfactorily accounted for all the observed kinetic results, was proposed.

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(1) $Ce(IV) + M \xrightarrow{k_i} M^{\bullet} + Ce(III)$

(2) $M^{\bullet} \xrightarrow{k_p} M_n^{\bullet}$

(3) $AH + Ce(IV) \rightleftharpoons complex \xrightarrow{k} A^{\bullet} + Ce(III) + H^+$

(4) $A^{\bullet} + M_n^{\bullet} \xrightarrow{k_t} M_nA$

(5) $A^{\bullet} + Ce(IV) + H_2O \xrightarrow{k_0} oxidation\ products$
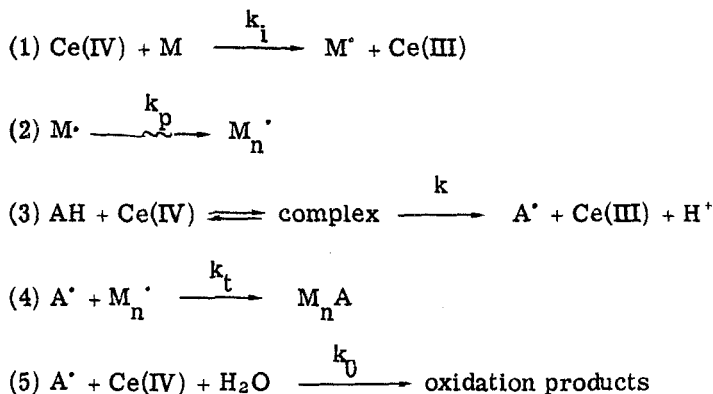
where M is the monomer and AH is the chalcone.

Applying steady-state kinetics, the following expression for the rate of polymerization R_p is obtained:

$$R_p = \frac{k_p k_0 k_i [M]^2 [Ce(IV)]}{kk_t [AH] - k_i k_t [M]} \tag{1}$$

This expression, on rearrangement, gives

$$\frac{[M]}{R_p} = \frac{kk_t [AH]}{k_p k_0 k_i [Ce(IV)][M]} - \frac{k_t}{k_p k_0 [Ce(IV)]} \tag{2}$$

It follows from Eq. (2) that at constant Ce(IV) and chalcone concentrations, a plot of $[M]/R_p$ should be linear with $1/[M]$.

The present communication deals with the influence of the substituents on the kinetics of Ce(IV)-initiated polymerization of acrylonitrile retarded by substituted chalcones (I) in terms of the usual Hammett-type correlations [2] and also in terms of their field

$$\underset{R}{\langle\!\langle\rangle\!\rangle} - \overset{O}{\underset{\|}{C}} - CH = CH - \langle\!\langle\rangle\!\rangle$$

(I)
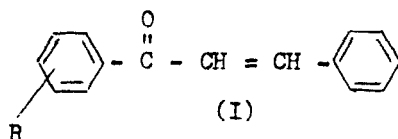
and resonance components [3]. The kinetic parameter which we used is obtained from the slope of the above plot for various chalcones:

$$\text{Slope} \times \frac{[Ce(IV)]}{[AH]} = \frac{kk_t}{k_p k_0 k_i} = K \tag{3}$$

Oxidation of the radical A· and the recombination of the radicals A· and M_n· may be considered to be too fast to have any substituent effect. The parameter K is, therefore, proportional to the rate constants of the hydrogen abstraction reactions (k) in which the substituents may have any influence on the kinetics. Various substituent parameters and the rate data are given in Table 1.

Hammett Correlation

The rate data were correlated with the Brown-Okamoto substituent constants [4] (σ^+) by the following Hammett equation:

$$\log (K/K_0) = \rho\sigma^+ + C \tag{4}$$

An intercept term C was used to avoid giving infinite weight to the unsubstituted compounds. The results of the correlation are

$\rho = 0.7674;$ $C = -0.0441$

where the standard deviation (S) is 0.0562 and the correlation coefficient (r) is 0.9954.

The p-Cl derivative showed maximum deviation in the above correlation. Deviations of halogen substituents from Hammett correlations were also observed by Simonyi, Tüdös, and Pospisil [5] in the reaction of polyvinyl acetate radicals with substituted phenols. After considering various possible causes for such deviations, these authors attributed it to the inapplicability of the conventional Brown-Okamoto σ^+ values for halogens and have suggested a modified set of σ^+ values (-0.10 for p-Cl). We also found that use of the modified σ^+ values for the p-Cl derivative markedly improves the correlation. With the modified σ^+ values for p-Cl:

$\rho = 0.7864;$ $C = -0.0096$

$S = 0.028;$ $r = 0.9994$

F and R Correlations

A study of substituent effects in terms of their field and resonance components was first proposed by Swain and Lupton [3]. They

TABLE 1. Substituent Parameters and Rate Data at 20°C

Substituent	σ^{+a}	fF^b	rR^b	$\log(K/K_H)$
m-NO₂	0.67	1.1112	0.0657	0.5051
p-Cl	0.11 (-0.10)^c	0.6900	-0.1610	-0.0450
m-CH₃	-0.07	-0.0521	-0.0598	-0.0728
p-CH₃	-0.31	-0.0520	-0.1410	-0.2660
p-OCH₃	-0.78	0.4130	-0.5000	-0.6332

^{a}Data from Advanced Organic Chemistry, J. March, McGraw-Hill, New York, 1978, p. 241.
^{b}F and R data from Ref. 3.
^{c}Modified value suggested by Tüdös et al.

suggested that the Hammett-substituent constant σ for any substituent k may be expressed as a linear combination of its two, viz., the field (F_k) and the resonance (R_k) components,

$$\sigma_k = aF_k + bR_k \tag{5}$$

where a and b are the appropriate weighting factors.
Substitution of Eq. (5) in the Hammett equation

$$\log \frac{k_i}{k_0} = \rho_i \sigma_k \tag{6}$$

gives:

$$\log \frac{k_i}{k_0} = \rho_i(aF_k + bR_k)$$
$$= \rho_i aF_k + \rho_i bR_k \tag{7}$$

Swain and Lupton considered the weighting factors a and b as set dependent. Williams and Norrington [6], who subsequently extended the scope of Swain and Lupton's work, suggested unique positional weighting factors f_j and r_j which depend only on the substituent position j and are independent of the reaction set. Thus a and b of Eq. (5) can

be split up into two components α_i' and β_i' which are reaction dependent and f_j and r_j which depend only on the substituent position. Equation (7) can now be written as

$$\log k/k_0 = \rho_i(\alpha_i'f_jF_k + \beta_i'r_j\bar{F}_k)$$

$$= \rho_i\alpha_i'f_jF_k + \rho_i\beta_i'r_jR_k$$

$$= \alpha f_jF_k + \beta r_jR_k \tag{8}$$

Williams and Norrington introduced a normally distributed error term e_i into Eq. (8) and finally proposed the following equation [6]:

$$\log k/k_0 = \alpha_if_jF_k + \beta_ir_jR_k + e_i \tag{9}$$

By a statistical analysis of a large number of reactions they suggested the following unique values for f_j and r_j for a mixed data set of p- and m-derivatives:

$$f_m = 1.002; \quad r_m = 0.424; \quad f_p = 1.000, \quad r_p = 1.000 \tag{10}$$

The correlation results are

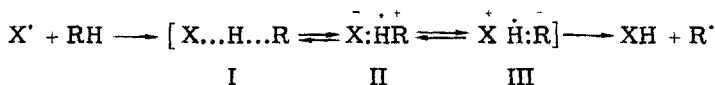$$e = 0.0081; \quad \alpha = 0.3409; \quad \beta = 1.5977$$

where the standard deviation (S) is 0.0415 and the correlation coefficient (r) is 0.9987. They indicate the applicability of Eq. (9) to the present reaction series (low standard deviation and high correlation coefficient).

On the Sign and Magnitude of ρ, α, and β:

It can be seen from the derivation of Eq. (9) that α and β are related to the reaction parameter ρ. It is therefore expected that the qualitative characteristics of ρ in terms of sign are reflected in α and β. Although it does not follow automatically, it is seen from the examination of a number of radical reactions [7] that a negative sign for both α and β may perhaps be taken as indicative of a negative ρ and a positive sign for both α and β indicates a positive ρ.
A study of the hydrogen abstraction reactions from substituted

phenols by polyvinyl acetate radicals and those from substituted thiols by polymethyl methacrylate radicals give a negative Hammett reaction parameter [8] (ρ) and also negative α and β [7]. It was concluded [7] that in these reactions the transition state could be described by Structure II:

$$X^{\cdot} + RH \longrightarrow [X...H...R \rightleftharpoons \overset{-}{X}:\overset{\cdot}{H}\overset{+}{R} \rightleftharpoons \overset{+}{X}\,\overset{\cdot}{H}:\overset{-}{R}] \longrightarrow XH + R^{\cdot}$$
$$\quad\quad\quad\quad\quad\quad I \quad\quad\quad\quad\quad II \quad\quad\quad\quad III$$

The reaction of m- and p-substituted nitrobenzenes with polyvinyl acetate radicals, however, gave a positive ρ [9] as well as positive α and β [7]. Following the same line of reasoning as Pryor et al. [9], it is suggested that for this reaction, structure III makes a greater contribution to the transition state.

As has already been stated, the reaction parameter used in the present correlation studies relates to the substituent effects on Reaction (3) of the proposed reaction scheme, which is a hydrogen abstraction process by Ce(IV) from chalcone. In the present study we also find a positive ρ as well as positive α and β. This might perhaps mean that in this reaction the transition state of Type III is more important than the other two.

Finally, we wish to make brief comments on the relative merits of the correlation Eqs. (4) and (9). Although equally good results are obtained in both the cases, Eq. (9) has certain advantages over Eq. (4). The substituent constants F and R are of a more generalized nature than either σ or σ^{+}. Besides, Eq. (9) also enables one to determine the susceptibility of the reaction to the inductive and resonance effects separately; for example a value of 4.6867 for the β/α ratio suggests that 82% of the total substituent effect is contributed by the mesomeric effect and the rest by the inductive effect.

REFERENCES

[1] R. K. Satapathy, S. N. Patnaik, B. K. Misra, S. P. Rout, and M. K. Rout, J. Macromol. Sci.–Chem., A13(2), 273 (1979).

[2] L. P. Hammett, Chem. Rev., 17, 125 (1935).

[3] C. G. Swain and E. C. Lupton, J. Am. Chem. Soc., 90, 4328 (1968).

[4] H. C. Brown and Y. Okamoto, Ibid., 80, 4979 (1958).

[5] M. Simonyi, F. Tüdös and J. Pospisil, Eur. Polym. J., 3, 101 (1967).

[6] S. G. Williams and F. E. Norrington, J. Am. Chem. Soc., 98, 508 (1976).

[7] L. N. Patnaik, M. K. Rout, S. P. Rout, and A. Rout, Eur. Polym. J., 15, 509 (1979).

[8] References to Hammett correlations in hydrogen abstraction reactions are given in Ref. 7.

[9] W. A. Pryor, W. H. Davis, and J. P. Stanley, J. Am. Chem. Soc., 95, 4754 (1973).