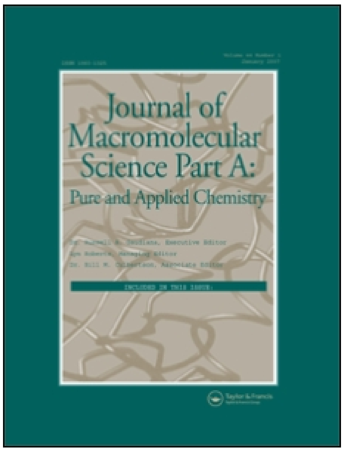

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Substituent Effects in the Reaction between Acetophenones and Polymethyl Methacrylate Radicals

Lalit N. Patnam[a]; Narayan C. Saul[a]; Manjushree Senapati[a]; Swoyam P. Rout[a]; Ranu Mishra[a]; Mahendra K. Rout[a]
[a] Department of Chemistry, Ravenshaw College, Cuttack, India

To cite this Article Patnam, Lalit N. , Saul, Narayan C. , Senapati, Manjushree , Rout, Swoyam P. , Mishra, Ranu and Rout, Mahendra K.(1983) 'Substituent Effects in the Reaction between Acetophenones and Polymethyl Methacrylate Radicals', Journal of Macromolecular Science, Part A, 19: 7, 1061 — 1067

To link to this Article: DOI: 10.1080/00222338308081085

URL: http://dx.doi.org/10.1080/00222338308081085

J. MACROMOL. SCI.–CHEM., A19(7), pp. 1061-1067 (1983)

Substituent Effects in the Reaction between Acetophenones and Polymethyl Methacrylate Radicals

LALIT N. PATNAIK, NARAYAN C. SAMAL, MANJUSHREE SENAPATI, SWOYAM P. ROUT, RANU MISHRA, and MAHENDRA K. ROUT

Department of Chemistry
Ravenshaw College
Cuttack 753003, India

ABSTRACT

The substituent effects in the reaction between acetophenones and the polymethyl methacrylate radical have been correlated with Swain and Lupton's Field (F) and Resonance (R) parameters including Williams and Norrington's unique positional weighting factors (SLWN) and also in terms of a conventional Hammett type equation with σ^+. Excellent correlations have been obtained with both models. Attempts have also been made to ascertain the nature and characteristics of the transition state from the sign and magnitude of the reaction parameters.

INTRODUCTION

The correlation of the composite rate constants with a multiparameter equation containing Hammett's [1] substituent constant σ and related parameters has been expressed as a linear combination of two principal components F and R. F and R, representing the field and resonance components, respectively, have been developed

0022-233X/83/1907-1061$3.50/0

and calculated by Swain and Lupton [2] from Hammett's σ_m and σ_p values by assuming that any set of substituent constants σ_m and σ_p, etc. may be expressed as fF + rR where f and r are the positional weighting factors suggested by Williams and Norrington [3]. By carrying out a statistical analysis of the reaction series, the values of the positional weighting factors of meta and para positions (as in the present case) are:

$f_m = 1.002$ $f_p = 1.000$

$r_m = 0.424$ $r_p = 1.000$

These values help in the study of correlation between the physicochemical properties of the side chain and the substituent parameters of mixed or multiple substituted derivatives of benzonoid compounds.

The original Hammett equation

$$P_i = \rho_i \sigma_k + P_i^0 \tag{1}$$

(where P_i's are some free energy related property, P_i^0 is for a standard reference state for the i-th reaction set) can now be restated in terms of the Swain-Lupton [2] and the Williams-Norrington [3] modifications

$$P_i = \alpha_i f_j F_k + \beta_i r_j R_k + P_i^0 \tag{2}$$

The final form of the (SLWN) equation (Swain-Lupton, Williams-Norrington) is achieved by adding an error term e_i to make allowance for uncertainties in the data, assumed to be normally distributed and independent of the position and nature of the substituent:

$$P_i = \alpha_i f_j F_k + \beta_i r_j R_k + e_i + P_i^0 \tag{3}$$

The present paper deals with the study of the substituent effects on the kinetics of AIBN-initiated polymerization of methyl methacrylate, retarded by substituted acetophenones by two methods: 1) in terms of Tudo's kinetic parameter β and 2) with the aid of K [5], the slope of the plot of [monomer]/R_p vs [retarder].

REACTION SCHEMES AND KINETIC PARAMETERS

<u>Simonyi, Tüdös, and Pospisil</u> [4]

Initiation $\longrightarrow R^{\cdot}$ (R_i)

Propagation:

$$R^{\cdot} + M \longrightarrow R^{\cdot} \qquad (k_2)$$

Termination:

$$R^{\cdot} + R^{\cdot} \longrightarrow \text{polymer} \qquad (k_4)$$

$$R^{\cdot} + ZH \longrightarrow \text{polymer} \qquad (k_5)$$

where M = monomer molecule, R = chain carrier, and ZH = retarder.

$$\beta = \frac{\mu k_5 \sqrt{x}}{2R_i k_4} = \frac{\phi\sqrt{x}}{[ZH]} \tag{4}$$

$$\phi = \frac{1}{2}\left(\frac{1}{R_p^{\,rel}} - R_p^{\,rel}\right), \qquad R_p^{\,rel} = R_p/R_p^{\,o} \tag{5}$$

where μ is the stoichiometry of the hydrogen abstraction reaction, x is the concentration of the initiator, R_p is the rate of polymerization in the presence of retarder, and $R_p^{\,o}$ is that in the absence of retarder.

<u>Our Scheme</u> [5]

Initiation:

$$M + I^{\cdot} \longrightarrow M^{\cdot} \qquad (R_i)$$

Propagation:

$$M^{\cdot} + M \sim\!\sim\!\sim \longrightarrow M_n^{\cdot} + M \longrightarrow P \qquad (k_2)$$

Termination:

$$M_n^{\bullet} + ZH \longrightarrow M_nH + Z^{\bullet} \qquad (k_3)$$

$$M_n^{\bullet} + M_n^{\bullet} \longrightarrow M_n - M_n \qquad (k_4)$$

$$M_n^{\bullet} + Z^{\bullet} \longrightarrow M_n + Z \qquad (k_5)$$

The following relationship is obtained:

$$[M]/R_p = k_3[ZH]/k_2R_i + 1/k_2\sqrt{k_4/R_i} \qquad (6)$$

or

$$[M]/R_p = K[ZH] + C \qquad (7)$$

Thus $[M]/R_p$ is linearly related to retarder concentration ZH. The results of this regression with substituted acetophenones are described in Table 1, indicating the validity of Eq. (7). The slope of the regression, K, is proportional to k_3, i.e., the rate of the hydrogen abstraction process, and it can therefore be used as a parameter for the retardation kinetics.

F and R Correlations

The applicability of the SLWN equation (Eq. 3) has been examined in a number of cases in studies of the substituent effects in radical reaction. In continuation of earlier work, we report on the present

TABLE 1. Results of the Regression[a]

Substituent	K	C	S	r
p-NO_2	18.25	0.0325	0.0412	0.9651
m-NO_2	6.1389	0.1644	0.0300	0.985
p-Cl	0.6944	0.0576	0.0007	0.9997
p-OH	52.12	0.0555	0.5439	0.845
p-OCH_3	1.75	0.0447	0.0060	0.9895

[a] S = standard deviation, r = correlation coefficient.

reaction system using the kinetic parameters β and K for the correlation of the reactivity of substituted acetophenones with polymethyl methacrylate radicals and the substituent parameters with the aid of Eq. (3).

Equivalence of β and K.

The following relationship has been obtained from Eqs. (4) and (6) at constant initiator concentration:

$$\beta = C_1 k \qquad (8)$$

and

$$K = C_2 k \qquad (9)$$

where k is used for the hydrogen abstraction process. It is seen from Eqs. (8) and (9) that there should be linearity between log β and log K. When a regression line is drawn between log β and log K at 0.01 mol/L concentration of AIBN, the average scatter points in the ordinate (s) is 0.1335 and correlation coefficient r is 0.9801. Hence the relationship is

$$\log \beta = 0.6146 \log K + 0.0873 \qquad (10)$$

Hammett Correlation

The rate data were correlated with the Brown-Okamoto [6] substituent constant σ^+ by the Hammett equation

$$\log (k/k^0) = \rho\sigma^+ + C \qquad (11)$$

In order to avoid giving infinite weight to the unsubstituted compound, an intercept term C is used in the equation.

Hammett correlation results are presented in Table 2 for both β and K.

The equation is well fitted to the proposed reaction scheme with a low standard deviation (S) and high correlation coefficient (r).

The substituent parameters and the rate data and the correlation results are described in Tables 3 and 4.

The low standard deviation (S) and the high correlation coefficient (r) justify the applicability of Eq. (3) to the proposed reaction scheme. Although the numerical values of the reaction parameters α_i and β_i are different for β and K, they have the same sign.

TABLE 2

Correlation with	ρ	C	S	r
β	0.4284	0.4143	0.115	0.9626
K	0.4572	0.6039	0.1813	0.9265

TABLE 3. Substituent Parameters and Rate Data. [AIBN] = 0.01 mol/L

Substituent	σ^{+a}	fF^{b}	rR^{b}	log β	log K
H	0	0	0	0.249	0
p-NO_2	0.79	1.109	0.155	0.8212	1.0705
m-NO_2	0.67	1.1112	0.0657	0.6891	0.8564
p-CH_3	-0.31	-0.052	-0.141	0.3646	0.6478
p-OCH_3	-0.78	0.413	-0.5	0.1059	0.234

[a] Data collected from Ref. 7.
[b] Data collected from Refs. 2 and 3.

TABLE 4. Correlation Results. [AIBN] = 0.01 mol/L

Correlation with	α_i	β_i	e	S	r
β	0.368	0.5872	0.2843	0.1854	0.9610
K	0.3905	1.0818	0.3396	0.2409	0.9552

Sign and Magnitude of ρ, α_i, and β_i

As reported [8], the characteristics of ρ are generally reflected in the signs of α_i and β_i which determine the contribution of the structure (polar and nonpolar) to the transition state of the process of hydrogen abstraction from a substrate (ZH) by a radical ($R^{\bullet}$) which can be described by

$$R^{\bullet} + ZH \longrightarrow [\underset{I}{R\ldots H\ldots Z} \longleftarrow \underset{II}{\bar{R}:\dot{H}Z^{+}} \longleftarrow \overset{+}{R}\dot{H}:\bar{Z}] \longrightarrow \underset{III}{RH + Z^{\bullet}}$$

The relative contribution of the nonpolar structure I or the polar structures II or III to the transition state has been the subject of some controversy. However, Pryor et al. [9] have critically discussed and reported that with regard to reaction parameter ρ, it is only the sign, and not the magnitude, which has mechanistic significance. In the present case a positive ρ as well as positive α_i and β_i are obtained which suggests a predominant contribution of Structure III to the transition state. It is therefore suggested that Structure III plays a significant role in the transition state of the hydrogen abstraction reaction under discussion, i.e., reactivity of polymethyl methacrylate radicals toward acetophenones.

ACKNOWLEDGMENTS

The authors are grateful to the U.G.C., New Delhi, India, for providing teacher fellowships to R.M. and N.C.S., and to the government of Orissa for sanctioning a study leave to M.S.

REFERENCES

[1] L. P. Hammett, Chem. Rev., 17, 125 (1935).
[2] C. G. Swain and E. C. Lupton, J. Am. Chem. Soc., 90, 4328 (1968).
[3] S. G. Williams and F. E. Norrington, Ibid., 98, 508 (1976).
[4] M. Simonyi, F. Tüdős, and J. Pospisil, Eur. Polym. J., 3, 101 (1967).
[5] L. N. Patnaik, R. K. Satapathy, S. N. Patnaik, B. K. Mishra, and M. K. Rout, Ibid., 16, 117 (1980).
[6] H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80, 4979 (1958).
[7] J. March, Advances in Organic Chemistry, McGraw-Hill, New York, 1968, p. 241.
[8] L. N. Patnaik, M. K. Rout, S. P. Rout, and A. Rout, Eur. Polym. J., 15, 509 (1979).
[9] W. A. Pryor, W. H. Davis, and J. P. Stanley, J. Am. Chem. Soc., 95, 4754 (1973).

Accepted by editor October 5, 1982
Received for publication November 5, 1982