JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 544–549
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.484

Substituent effects in solvolysis of 1,1-diphenylethyl *p*-nitrobenzoates. Symmetrically disubstituted and monosubstituted systems†

Mizue Fujio,* Md. Khabir Uddin, Hyun-Joong Kim and Yuho Tsuno

Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received 20 October 2001; revised 19 January 2002; accepted 24 January 2002

ABSTRACT: The rates of solvolysis of 1,1-diarylethyl *p*-nitrobenzoates and chlorides were determined conductimetrically at 25 °C in 80% (v/v) aqueous acetone. Applying the Yukawa–Tsuno (Y–T) equation, the symmetrical (X = Y) subseries gave a precise additivity relationship for the whole substituent range with a ρ_{sym} value of -3.78 and an r_{sym} value of 0.77. While any Y subsets gave statistically less reliable Y–T correlations, the apparent ρ value changed significantly depending on the fixed Y substituents; the ρ value decreases with the more electron-donating fixed substituents Y, which is compatible with the Hammond shift of the transition state coordinate. Nevertheless, the concave correlations of the More O'Ferrall non-linearity relationship for any Y subsets are not in line with what is expected from the reactivity–selectivity relationship suggesting an anti-Hammond shift of transition state. However, we found a precise extended Brønsted relationship between the $\mathrm{p}K_{\mathrm{R}^+}$ values of 1,1-diarylethylenes and solvolysis rate process with a constant slope of $\alpha = 1.03 \pm 0.03$. This is direct evidence indicating that there is no significant shift of the transition-state coordinate over the whole range of substituent change. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: α-methylbenzhydryl system; substituent effect; Yukawa–Tsuno equation; non-linearity and non-additivity; coordinate shifts of transition state; extended Brønsted relationship

INTRODUCTION

It is well known that the kinetic effects of two substituents on two equivalent aromatic rings are not additive.[1,2] The solvolysis of α,α-di(substituted-phenyl)ethyl *p*-nitrobenzoates also shows a complicated non-linear correlation of substituent effects. To scrutinize the non-linearity and non-additivity in the multiple-substituents effects in this system, the Yukawa–Tsuno (Y–T) equation has been used as a very effective tool in correlation analysis:[2,3]

$$\log(k/k_0) = \rho(\sigma^\circ + r\Delta\bar{\sigma}_{\mathrm{R}}^{+}) = \rho\bar{\sigma} \qquad (1)$$

where σ° is the normal substituent constant and $\Delta\bar{\sigma}_{\mathrm{R}}^{+}$ is the resonance substituent constant measuring the capability for π-delocalization of electron donor substituents and is defined by $\sigma^+ - \sigma^\circ$.[3b] Apparent Y–T σ values with an appropriate r are presented by $\bar{\sigma}$.

The non-additivity of ρ_{Y} in multiple-substituent effects was most simply dealt with using the equation[4]

$$\rho_{\mathrm{Y}} = \rho_{\mathrm{H}} + q\bar{\sigma}_{\mathrm{Y}} \qquad (2)$$

Dubois and co-workers, in their studies on the bromination of disubstituted diarylethylenes,[5] proposed the following equation,[1,5,6] which describes the non-additive effect in terms of different reaction constants for X and Y substituents:

$$\log(k_{\mathrm{XY}}/k_{\mathrm{HH}}) = \rho_{\mathrm{H}}(\bar{\sigma}_{\mathrm{X}} + \bar{\sigma}_{\mathrm{Y}}) + q\bar{\sigma}_{\mathrm{X}}\bar{\sigma}_{\mathrm{Y}} \qquad (3)$$

$$= \rho_{\mathrm{H}}\bar{\sigma}_{\mathrm{Y}} + (\rho_{\mathrm{H}} + q\bar{\sigma}_{\mathrm{Y}})\bar{\sigma}_{\mathrm{X}} \qquad (3a)$$

Non-additivity is therefore taken into account by the $q\bar{\sigma}_{\mathrm{Y}}$ term in Eqn. (3a).[1,5,6] The selectivity parameter ρ for a reaction series varies appreciably with the reactivities (or the stabilities of transition states) of the parent substrates.

However, the analysis has often suffered from significant non-linearity within a single (X) substituent effect correlation for the respective Y-fixed subset.[1,2,5]

The non-linearity in the correlations for respective Y subsets has been dealt with by the More O'Ferrall

---

**Correspondence to:* M. Fujio, Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.
E-mail: fujio@ms.ifoc.kyushu-u.ac.jp

† Presented at the 8th European Symposium on Organic Reactivity (ESOR-8), Cavtat (Dubrovnik), Croatia, September 2001.

equation:[7]

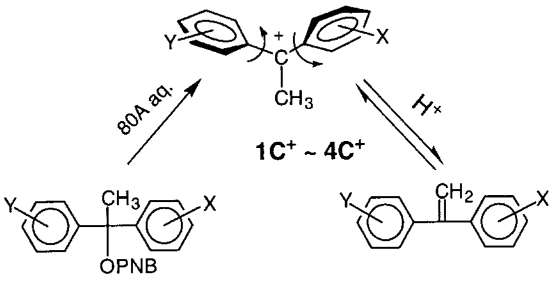
$$\log(k_X/k_H)_Y = (\rho_0)_Y\bar{\sigma}_X + (2m)_Y(\bar{\sigma}_X)^2 \qquad (4)$$

where $(\rho_0)_Y$ is the tangential ρ value at X = H of the Y subset, and the coefficient $(2m)_Y$ is a susceptibility parameter describing the degree of curvature of correlations of given Y subsets.

This behavior is often referred to as adherence to the reactivity–selectivity relationship (RSR).[5,6b,8] There is generally an inverse relationship between reactivity and selectivity insofar as both are related to shifts in the transition-state position.[9] The progress of the reaction at this transition state is usually obtained from coefficients α of Brønsted or of other rate–equilibrium relationships that compare substituent effects on kinetics and thermodynamics:[10]

$$\log(k_{XY}/k_{HH}) = \alpha(\Delta pK_R{}^+) \qquad (5)$$

We recently investigated[11] the non-linearity and non-additivity in the substituent effects on the solvolyses of α-CF$_3$-diarylmethyl system. While the simple precise additivity relationship was found to exist for the symmetrical (X = Y) subseries, for any unsymmetrical subsets (X ≠ Y) there were significant non-linearity and non-additivity of substituent effects for the two aryl rings. The non-linear and non-additive substituent effects in this α-CF$_3$ system were explained by the substituent-induced change in propeller conformation of two aromatic rings. Accordingly, our interest has been focused on exploring the scope of non-linearity and non-additivity behavior in the substituent effects in the α,α-diarylcarbocation systems. The same conformation effects should also be operative in the 1,1-diarylethyl system, so that we should take into account the non-additivity effect caused from substituent-induced change in conformation in addition to those caused from coordinate shifts of the transition state.



1C$^+$ ~ 4C$^+$

	variable	fixed
1	X	(Y = X)
2	X	(Y = H)
3	X	(Y = *p*-MeO)
4	X	(Y = *p*-Me)

1a ~ 4a

Scheme 1

We have extended our substituent-effect studies to the non-linearity and non-additivity behaviors in the solvolysis of 1,1-diarylethyl *p*-nitrobenzoates (Scheme 1). The solvolytic cation formation of this system should be connected mechanistically to the hydration[12] as a single reversible process, an E1 elimination process, with a common intermediate intervening. Both transition states should reflect any perturbations of the common intermediate, and the comparative studies will provide

Table 1. Rates of solvolysis of α,α-diarylethyl *p*-nitrobenzoates (OPNB) in 80% aqueous acetone at 25 °C

Monosubstituted OPNB		Disubstituted OPNB	
Substituent	$k_{OPNB} \times 10^5$ (s^{-1})	Substituent	$k_{OPNB} \times 10^5$ (s^{-1})
p-MeO	63.0	(*p*-MeS)$_2$	111.3
p-MeS	7.00	(*p*-Me)$_2$	7.39
p-MeO-*m*-Cl	2.61	(*p*-MeS-*m*-Cl)$_2$	0.808
p-Me	1.28	(*m*-Me)$_2$	0.2938
p-Et	1.00	(*p*-Cl)$_2$	5.28×10^{-3}
p-*t*-Bu	0.775	(*p*-Br)$_2$	4.85×10^{-3c}
p-SMe-*m*-Cl	0.354	(*m*-Cl)$_2$	6.50×10^{-5c}
m-Me	0.170	(*m*-CF$_3$)$_2$	1.23×10^{-5c}
H	0.103	*p*-MeO *p*-Br	26.4
	7.85×10^{-2a}	*m*-Cl	9.20
p-Cl	2.48×10^{-2}	*m*-CF$_3$	6.38
m-Cl	3.11×10^{-3b}	3,5-Cl$_2$	1.77
m-CF$_3$	1.42×10^{-3b}	3,5-(CF$_3$)$_2$	0.85
p-CF$_3$	8.61×10^{-4b}	*p*-Me *m*-Cl	7.76×10^{-2}
3,5-Cl$_2$	1.47×10^{-4c}	3,5-Cl$_2$	2.66×10^{-3c}
3,5-(CF$_3$)$_2$	2.88×10^{-5c}	3,5-(CF$_3$)$_2$	7.93×10^{-4c}

[a] Ref. 13.

[b] Estimated from the rates in 50% aqueous acetone; $\log k_{80A} = -1.037 + 1.142\log k_{50A}$.

[c] Estimated from the corresponding chloride reactivities based on the *p*-nitrobenzoate/chloride ratio = 1.034×10^{-5}.

Table 2. Correlation analysis of substituent effects using the Yukawa–Tsuno equation [Eqn. (1)]

No.	System	Substituent (X) range	n[a]	ρ	r	R	SD
1	**1**	p-MeS–m-CF_3	9	-3.78 ± 0.09	0.77 ± 0.04	0.9990	0.12
2	**2**	p-MeO–3,5-$(CF_3)_2$	14	-3.68 ± 0.08	0.88 ± 0.04	0.9988	0.10
3		s-ED[b]	4	-4.22 ± 0.10	(0.36 ± 0.4)[e]	0.9998	0.03
4	**3**	p-MeO–3,5-$(CF_3)_2$[c]	8	-1.97 ± 0.12	(1.33 ± 0.17)[e]	0.9978	0.10
5		H–3,5-$(CF_3)_2$	6	-1.91 ± 0.10	(0.87 ± 0.34)[e]	0.9967	0.07
6	**4**	p-MeO–3,5-$(CF_3)_2$[d]	6	-3.23 ± 0.18	(0.99 ± 0.15)[e]	0.9985	0.15
7	Y = m-Cl[f]	p-MeO–m-Cl	10	-4.61 ± 0.08	0.93 ± 0.03	0.9995	0.05
8	Y = 3,5-Cl_2[f]	p-MeO–H	9	-4.78 ± 0.26	1.09 ± 0.09	0.9976	0.11
9	Y = 3,5-$(CF_3)_2$[f]	p-MeO–H	11	-5.04 ± 0.18	1.14 ± 0.06	0.9984	0.09

[a] Number of substituents involved.
[b] Including p-MeO, p-MeS, p-MeO-m-Cl and p-MeS-m-Cl.
[c] The rate constant $k_{(p-\mathrm{MeO})2}$ was estimated by the Y–T correlation (entry 1) for the **1** (X = Y) subseries.
[d] The rate $k_{(p-\mathrm{MeO},p-\mathrm{Me})}$ is estimated by Eqn. (4) for the **3** (Y = p-MeO) subset.
[e] The r value should be statistically indefinite.
[f] Unpublished data.

important information concerning the behavior of transition states causing non-linearity and non-additivity.

RESULTS

Solvolysis rates

The rates of solvolysis of the p-nitrobenzoates and the corresponding chlorides were determined conductimetrically at 25 °C in 80% (v/v) aqueous acetone (80A) at initial concentrations of 10^{-5}–10^{-4} mol dm^{-3} of substrates. The rates for highly deactivating derivatives were only obtained from the chloride rates. The rates for the chlorides were converted into p-nitrobenzoate reactivities using the rate ratio of p-nitrobenzoate to chloride = 1.034×10^{-5}. The rates of solvolyses of the p-nitrobenzoates are summarized in Table 1.

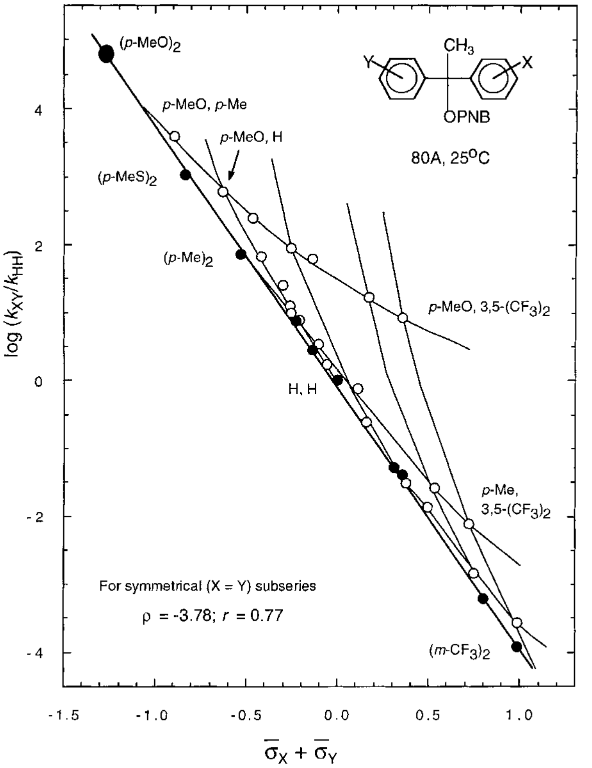


Figure 1. Plots of log (k_{XY}/k_{HH}) for the solvolysis of 1,1-diphenylethyl p-nitrobenzoates against $\bar{\sigma}_X + \bar{\sigma}_Y$ with $r = 0.77$; solid circles represent the symmetrical subseries **1** (X = Y)

Correlation analysis of substituent effects

The correlation analysis of substituent effects was carried out based on the Y–T equation [Eqn. (1)] as a routine procedure. The results are summarized in Table 2. The substituent effects on the solvolysis of symmetrical subseries **1** (X = Y) gave an excellent linear Y–T correlation for the whole range of substituents with a ρ value of -3.78 (for single $\bar{\sigma}_X$) and an r value of 0.77; correlation coefficient $R = 0.9990$ and SD = 0.12. For subset **2**, a precise Y–T correlation can be obtained with a ρ value -3.68 and $r = 0.88$. For the **3** (Y = p-MeO) subset a good Y–T correlation with a reduced ρ value was obtained, but the r value was not statistically definite. A similar correlation with a reduced ρ was obtained also for **4** (Y = p-Me). On the other hand, the subsets Y = m-Cl, 3,5-Cl_2 and 3,5-$(CF_3)_2$ were correlated linearly by Eqn. (1) with significantly higher ρ and r values. While the Y–T correlations for any subsets are statistically lightly less certain or sometimes indefinite, the apparent ρ_Y value for the Y–T correlations of variable X substituents changes significantly depending upon fixed Y substituents.

Non-linear correlation analysis

Figure 1 demonstrates a poor correlation of the $\log(k/k_0)_{\mathrm{OPNB}}$ values against $\bar{\sigma}_X + \bar{\sigma}_Y$ with the r scale

Table 3. Analysis of substituent effects by Eqn. (4)

Subset (Y)	n^a	$(\rho_0)_Y$	$(2m)_Y$	R	SD
(*m*-Cl)	6^b	-4.92 ± 0.16	0.53 ± 0.79	0.9984	0.09
2(H)	14	-4.08 ± 0.06	0.54 ± 0.11	0.9992	0.08
4(*p*-Me)	6	-3.62 ± 0.14	0.43 ± 0.22	0.9987	0.14
3(*p*-MeO)	8	-2.61 ± 0.04	0.69 ± 0.06	0.9995	0.05

[a] Number of substituents involved.
[b] Substituents range: *p*-Me–*m*-Cl.

of 0.77 identical with r_{sym} for the symmetrical subseries. The following simple additivity relationship against $\bar{\sigma}_X + \bar{\sigma}_Y$ instead of $2\bar{\sigma}_X$ does not hold as a whole but gives a widely spread pattern with branched correlations for the respective Y subsets:

$$\log\ (k/k_0)_{X,Y} = \rho_{sym}(\bar{\sigma}_X + \bar{\sigma}_Y) \qquad (6)$$

While the limited substrates where the two substituents X and Y are essentially kinetically equivalent are involved in Eqn. (6), we find a significant deviation when $\bar{\sigma}_X$ is entirely different from $\bar{\sigma}_Y$ of the fixed substituent Y. As seen in Fig. 1, all the Y subsets result in significant concave correlations, each of which contacts with the tangential correlation line defined by symmetrical subseries **1** at the point X = Y. A non-linear correlation analysis was carried out for respective Y subsets with the More O'Ferrall equation [Eqn. (4)][7] in terms of the same $\bar{\sigma}$ scale (at $r = 0.77$), and the results are summarized in Table 3.

The tangent $(\rho_0)_Y$ values are, to a good approximation, proportional to the corresponding ρ values of the Y–T correlations in Table 2, and both show the same dependence upon Y substituents; the $(\rho_0)_Y$ value becomes more negative as the Y substituent becomes more electron withdrawing. On the other hand, the $(2m)_Y$ coefficient remains constant at 0.5 for Y substituents; the coefficient with a constant value indicates the same shape of curvature for all the Y subset correlations, while the positive sign should constrain the shape of a significantly bent-back curvature for all subsets as seen in Fig. 1.

DISCUSSION

The correlation results in Table 2 indicate that the apparent ρ_Y values of the Y–T correlations for Y subsets with variable X substituents change significantly depending upon fixed Y substituents, and that there is a qualitative trend of a linear decrease in the ρ value as the fixed substituent Y for the respective subsets becomes more electron donating. The observed dependence of ρ_Y values on the second (fixed) Y substituents appears to accord with the changes caused by the early shift of the transition-state coordinate which would be expected from the Hammond–Leffler rate-equilibrium relationship (or extended Brønsted relationship).[10]

This elegant conclusion, however, relies heavily upon the validity of the Y–T correlations defined for the respective Y subsets. The Y–T correlation given for subset **3** (Y = *p*-MeO) should be that for the electron-withdrawing range of substituents and the *r* value should be almost meaningless. The situation should be the same in the case of **4** (Y = *p*-Me). In the case of electron-withdrawing Y subsets, on the other hand, the correlation was assigned only for the electron-donating range, and there is no evidence for the same ρ value applying to the other range of substituents.

Whereas the symmetrical subseries where X = Y gives an excellent linear correlation against $2\bar{\sigma}_X$ over the whole range of substituents, the simple additivity relationship in Eqn. (6) against $\bar{\sigma}_X + \bar{\sigma}_Y$ no longer holds and gives a wide dispersion pattern as in Fig. 1 when $\bar{\sigma}_X$ are entirely different from $\bar{\sigma}_Y$. This characteristic dispersion pattern of the additivity relationship has been generally observed for multiple substituent effects in typical α,α-diarylcarbenium ion formation processes, and presumably a 'concave plot' where both the head and the tail are bent back upwards from the reference line should be the best description of the shape of the correlation inherent in the substituent effect of the respective subsets.

The individual correlation of any Y subset appears to be a non-linear (concave) correlation, which may be delineated using the More O'Ferrall equation [Eqn. (4)].[7] The tangent $(\rho_0)_Y$ for the respective Y subset which has essentially the same physical significance as the apparent ρ_Y value in the Y–T correlation varies in the same way as the latter: The $(\rho_0)_Y$ becomes more negative as the Y substituent becomes more electron attracting. The variation of $(\rho_0)_Y$ will be related to the Hammond shift of the transition state if the variation can be ascribed to the coordinate shift of the transition state.[7,10]

A positive $(2m)_Y$ coefficient in Eqn. (4) implies an assignment of a 'concave correlation' for any Y subset: the shape of the plot should be related to the anti-Hammond shift of the transition state coordinate (or the late transition state) for accelerating substrates. This clearly conflicts with what has been deduced from the behaviors of other selectivity indices. Most seriously, it conflicts with the so-called saturation effect that would be generally expected from the More O'Ferrall theory.[7,10]

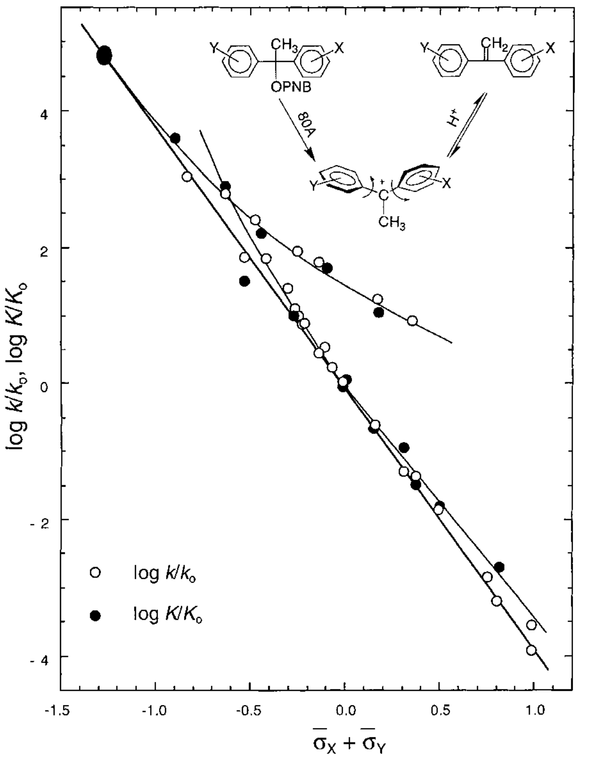


Figure 2. Plots of log k/k_0 for the solvolysis of 1,1-diphenylethyl *p*-nitrobenzoates and logK/K_0 values for the corresponding carbocations against $\bar{\sigma}_X + \bar{\sigma}_Y$ with $r = 0.77$; open circle represent solvolyses and solid circles equilibria

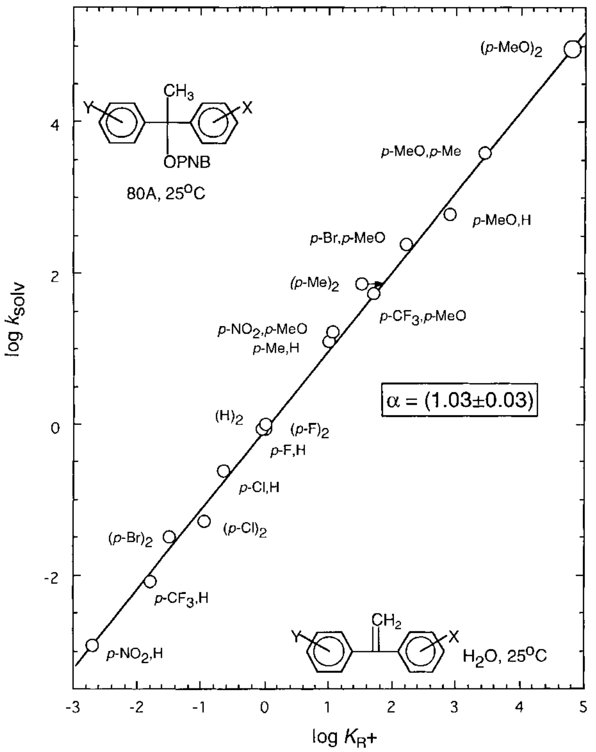


Figure 3. Linear relationship between log k_{solv} for the solvolysis of 1,1-diphenylethyl *p*-nitrobenzoates and the corresponding log K_{R^+} values; log $(k_{XY}/k_{HH})_{OPNB} = -(1.03 \pm 0.03)\Delta pK_{R^+}$

The characteristic dispersion of this non-additivity relationship appears to be general in many solvolysis processes of α,α-diarylcarbocation formation, among which the reaction of particular importance in the present study is the protonation equilibria of α,α-diarylethylenes.[12] Despite the wide dispersion pattern for the respective Y subsets of the additivity correlation against $\bar{\sigma}_X + \bar{\sigma}_Y$, we found that the scattered plots of the pK_{R^+} values against $\bar{\sigma}_X + \bar{\sigma}_Y$ of α,α-diarylethylenes, as a whole, can be superimposed precisely upon the corresponding plots of the non-additivity relationship of *p*-nitrobenzoates as in Fig. 2. This finding naturally points to the existence of a precise extended Brønsted relationship:[10]

$$\log\,(k_{XY}/k_{HH})_{OPNB} = -(1.03 \pm 0.03)\Delta pK_{R^+} \qquad (7)$$

which is demonstrated in Fig. 3 as a linear relationship between log $(k_{XY}/k_{HH})_{OPNB}$ for the solvolysis and ΔpK_{R^+} values with a constant slope. The exceptionally large deviation of the (*p*-Me)$_2$ substrate may presumably be attributed to experimental error. The observed value of the Brønsted coefficient α of close to unity may be coincidental, since the solvents are different between the solvolysis and the equilibrium.

While any Y subsets show different dependences upon X substituents (Fig. 2) for either the solvolysis or the pK_{R^+}, they all satisfy the rate–equilibrium relationship in Eqn. (7) with the same Brønsted coefficient α = 1.03; if any linear substituent effect correlation holds for an individual Y subset, Eqn. (8) should also be satisfied with the same α coefficient for the rate–equilibrium system:

$$(\rho^k)_Y = \alpha(\rho^t)_Y \qquad (8)$$

then,

$$\log\,(k/k_0)_Y = \alpha\log(K/K_0)_Y \qquad (8a)$$

The Brønsted relationship in Eqn. (8a) should include any constituent Y subsets, regardless of whether the Hammett-type correlations of the subsets are linear or not.

The constant α coefficient irrespective of the Y subsets should suffice as direct convincing evidence for the absence of coordinate shifts of transition states in this rate process. Changes in $(\rho^k)_Y$ with subsets should be independent of coordinate shifts of transition states in the present rate process. Whatever the cause of non-linearity and non-additivity behaviors of any selectivity parameters, $(\rho^k)_Y$, $(2m)_Y$, $(\rho_0)_Y$, etc., in the present solvolysis rate process, the constant α coefficient does not allow them to be ascribed to the substituent-induced coordinate shifts of the transition state.

For the hydration reaction of 1,1-diphenylethylenes where the intermediate carbenium ion is identical with that for the present solvolysis, we may expect a closely similar pattern of the kinetic substituent effect, without the effect associated with coordinate shifts of the transition state. The same expectation may be extended to the bromination of 1,1-diphenylethylenes, since a similar characteristic dispersion pattern of the additivity correlation was found for the bromination of diphenylethylenes. Nevertheless, Dubois and co-workers concluded[6] that the non-additivity in the bromination reaction arose not only from changes in the stability of the cationic intermediate but also significantly from coordinate shifts of the transition state.[1]

The characteristic dispersion pattern of this non-additivity relationship has been observed also in the α-CF_3-diarylmethyl system;[11] the observed variation of the ρ value within any given Y subset just displayed the dependence of the selectivity (ρ) on the deviation from the symmetrical propeller conformation of diaryl carbocations (or of the corresponding transition states). Thus the significant non-linearity and non-additivity were concluded to be caused by a conformational change of the transition state with varying substituents, and not caused by coordinate shifts of the transition state.

Although are not prepared at this time to speculate about the cause of significant non-linearity and non-additivity, evidently the coordinate shift of the transition state is not the main cause of the significant scattering behavior in this system. The non-linear Y–T correlations in the present system is most probably caused by varying conformations of the transition state. Further studies are in progress in order to clarify the conformational dependence of the selectivity ρ and r parameters on second substituents Y.

REFERENCES

1. Ruasse MF. *Adv. Phys. Org. Chem.* 1993; **28**: 207–291.
2. Tsuno Y, Fujio M. *Adv. Phys. Org. Chem.* 1999; **32**: 267–385.
3. (a) Yukawa Y, Tsuno Y. *Bull. Chem. Soc. Jpn.* 1959; **32**: 971–981; (b) Yukawa Y, Tsuno Y, Sawada M. *Bull. Chem. Soc. Jpn.* 1966; **39**: 2274–2286; (c) Tsuno Y, Fujio M. *Chem. Soc. Rev.* 1996; **25**: 129–139.
4. (a) Nishida S. *J. Org. Chem.* 1967; **32**: 2692–2701; (b) Fox JR, Kohnstam G. *Proc. Chem. Soc.* 1964; 115–116.
5. (a) Dubois JE, Hegarty AF, Bergmann ED. *J. Org. Chem.* 1972; **37**: 2218–2222; (b) Hegarty AF, Lomas JS, Wright WV, Bergmann ED, Dubois JE. *J. Org. Chem.* 1972; **37**: 2222–2228.
6. (a) Dubois JE, Ruasse MF, Argile A. *J. Am. Chem. Soc.* 1984; **106**: 4840–4845; (b) Ruasse MF, Argile A, Dubois JE. *J. Am. Chem. Soc.* 1984; **106**: 4846–4849.
7. O'Brien M, More O'Ferrall RA. *J. Chem. Soc., Perkin Trans. 2* 1978; 1045–1053.
8. (a) Johnson CD. *Tetrahedron* 1980; **36**: 3461–3480; (b) Giese B. *Angew. Chem., Int. Ed. Engl.* 1977; **16**: 125–136; (c) Formosinho SJ. *J. Chem. Soc., Perkin Trans. 2* 1988; 839–846; (d) Exner O. *J. Chem. Soc., Perkin Trans. 2* 1993; 973–979.
9. McLennan DJ. *Tetrahedron* 1978; **34**: 2331–2341.
10. (a) Hammond, GS. *J. Am. Chem. Soc.* 1955; **77**: 334–338. (b) Leffler JE, Grunwald E. *Rates and Equilibria of Organic Reactions*. Wiley: New York, 1963; (c) Lewis ES, Shen CC, More O'Ferrall RA. *J. Chem. Soc., Perkin Trans. 2* 1981; 1084–1088.
11. (a) Fujio M, Morimoto H, Kim HJ, Tsuno Y. *Bull. Chem. Soc. Jpn.* 1997; **70**: 1403–1411; (b) Fujio M, Morimoto H, Kim HJ, Tsuno Y. *Bull. Chem. Soc. Jpn.* 1997; **70**: 3081–3090; (c) Fujio M, Kim HJ, Morimoto H, Yoh SD, Tsuno Y. *J. Phys. Org. Chem.* 1999; **12**: 843–857.
12. Goethals G, Membrey F, Ancian B, Doucet JP. *J. Org. Chem.* 1978; **43**: 4944–4947.
13. Brown HC, Ravindranathan M, Peters EN. *J. Org. Chem.* 1977; **42**: 1073–1076.