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Substituent Effects in the 1,1-Diphenylcarbenium Systems: Hydration and Bromination of 1,1-Diphenylethylenes

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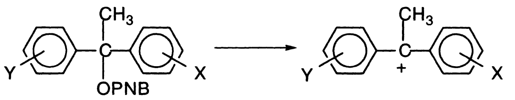
Substituent effects log $(k_{XY}/k_{HH})_{\mathbf{Br}}$ on the bromination of 1,1-diarylethylenes were analyzed in comparison with those log $(k_{XY}/k_{HH})_{\mathbf{OPNB}}$ in the solvolysis of 1,1-diarylethyl *p*-nitrobenzoates. The non-linearity and non-additivity were significant in both cases. While an extended Brønsted relationship against ΔpK_{BH^+} for diarylethylenes holds in the latter process, of particular importance is the finding of a precise linear correlation between the bromination and solvolysis for the whole substituents; log $(k_{XY}/k_{HH})_{\mathbf{OPNB}} = 1.07$ log $(k_{XY}/k_{HH})_{\mathbf{Br}} - 0.83\ \Delta\bar{\sigma}_R^+$, where the $\Delta\bar{\sigma}_R^+$ is the Yukawa–Tsuno resonance parameter. This relationship can be rewritten in the form of an *extended Brønsted correlation*: log $(k_{XY}/k_{HH})_{\mathbf{Br}} = \alpha$ [log $K_{XY}/K_{HH}]_{\mathbf{Br}}$, where [log $K_{XY}/K_{HH}]_{\mathbf{Br}} = -\Delta pK_{BH^+} + 0.81\ \Delta\bar{\sigma}_R^+$, for the thermodynamic stabilities of the intermediate in the bromination. The constant α coefficient should suffice as convincing evidence for the absence of a coordinate shift of the transition state that is induced by varying substituents in the bromination process. The additional contribution of 0.81 $\Delta\bar{\sigma}_R^+$ should be ascribed to the differential cationic charge at the benzylic position in the bromination transition state; a constant coefficient indicates a fixed position of the bromination transition state, irrespective of the fixed-Y subset.

Recently the Yukawa–Tsuno (Y–T) equation (Eq. 1)[1,2] has been applied to scrutinize the non-linearity and non-additivity in the effects of multiple substituents in α,α-diarylcarbenium ion systems.

$$\log(k/k_o) = \rho(\sigma^o + r\Delta\bar{\sigma}_R^+) = \rho\bar{\sigma} \tag{1}$$

Here σ^0 is the normal substituent constant, and $\Delta\bar{\sigma}_R^+ = \sigma^+ - \sigma^0$ is the resonance substituent constant measuring the π-delocalization ability of electron donor substituents.[1b] The parameter r is characteristic of a given reaction, measuring the resonance demand, i.e., the degree of resonance interaction between the aryl group and the reaction site in the transition state.[1,2] Apparent Y-T σ values with an appropriate r are abbreviated as $\bar{\sigma}$.

In a preceding paper,[3] we have reported the results of preliminary examinations of substituent effect in the solvolysis of 1,1-diarylethyl *p*-nitrobenzoates.



(2)

Where substituents X are variable ones and substituents Y are fixed ones. The subsets with a fixed Y-substituent in the solvolysis are abbreviated as in first column; the subsets in the corresponding bromination are similarly abbreviated as in the second column in Table 1.

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. In contrast, a simple additivity relationship of the log $(k/k_0)_{\text{OPNB}}$ values for the whole set against $\bar{\sigma}_X + \bar{\sigma}_Y$ instead of $2\bar{\sigma}_X$, Eq. 3, gives a widely spread pattern for the whole set with partial correlations for different fixed-Y-subsets,

Table 1. Abbreviations

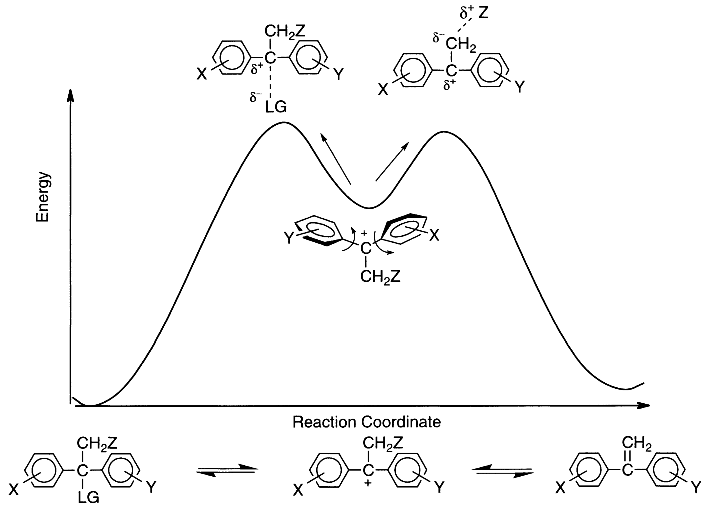
Subsets	Solvolysis	Bromination
Y = X	**1**	**1-Br**
Y = H	**2**	**2-Br**
Y = *p*-MeO	**3**	**3-Br**
Y = *p*-Me	**4**	**4-Br**
Y = *m*-Me	**5**	**5-Br**
Y = *p*-Br	**5a**	**5a-Br**
Y = *m*-Cl	**6**	**6-Br**
Y = *m*-NO_2	**6x**	**6x-Br**

$$\log(k/k_o)_{X,Y} = \rho_{\text{sym}}(\bar{\sigma}_X + \bar{\sigma}_Y). \tag{3}$$

All these Y subsets display significant concave correlations, each of which contacts the tangential correlation line defined by symmetrical subseries at the point X = Y. The concave plot, where both extremes are bent back upward from the reference line, appears to be typical of any subset with a fixed-Y substituent in the α,α-diaryl system.[2–4]

This characteristic dispersion pattern of additivity relationship (Eq. 3) has been generally observed for multiple substituent effects in many typical α,α-diarylcarbenium ion formation processes.[2–8]

The change in the selectivity parameter ρ for a reaction series with the change in the parent substrate is often referred to as adherence to the Reactivity–Selectivity Relationship



Scheme 1.

(RSR),[9–12] in the sense that there is an inverse relationship between reactivity and selectivity insofar as both are related to shifts in the transition state position.[13,14]

Despite the wide dispersion pattern with segments of Y-subsets correlations, we found a precise extended Brønsted relationship between the solvolytic $\log(k_{XY})$ and ΔpK_{BH^+} values[7] for the protonation equilibrium of 1,1-diarylethylenes (Eq. 4).[3,4]

$$\log(k_{XY}/k_{HH})_{solv} = -(1.03 \pm 0.03)\Delta pK_{BH^+} \quad (4)$$

Whereas any Y-subset shows a characteristic $\bar{\sigma}_X$-correlation with a significantly different $(\rho_X)_Y$ value in either the rates or the pK_{BH^+}, this Brønsted relationship should embrace all fixed-Y subsets, regardless of whether the $\bar{\sigma}_X$-correlations are linear or not. Whatever the reason of the non-linearity and non-additivity behavior, the constant α coefficient of 1.03 serves as convincing evidence for the absence of a coordinate-shift of the transition state in the rate process.

The solvolytic carbocation formation can be connected mechanistically to the electrophilic addition–elimination of water (hydration) which is its reversal, both processes having a common carbocation intermediate. The energy profiles for both rate-equilibrium processes are schematically shown in Scheme 1, where Z = H refers to the overall solvolytic elimination process and Z = Br to the overall bromination-elimination process.

When Z = H, the hydration step of 1,1-diphenylethylenes leads to the same carbenium ion intermediate formed in the solvolysis first step.[3,4] We may then expect a close pattern of the kinetic substituent effects, unless the effect is associated with coordinate-shifts of the transition state.

The overall bromination process (Z = Br) is mechanistically very close to the overall hydration process (Z = H) except that the intermediate is somewhat different, and hence a similar expectation for the substituent effect behavior may apply to both processes. Dubois and co-workers found[8] in the bromination of 1,1-diarylethylenes significant changes in the $(\rho_X)_Y$ value with the fixed substituents Y subsets, in a way consistent with the RSR[9–12] and the Hammond postulate,[14] and concluded[9,10] that the non-additivity in the bromination reaction does not arise from changes in the thermodynamic stability of the carbocation intermediate but from a coordinate-shift of the transition state. However, this conclusion is in sharp contrast to what was deduced from the substituent effect behavior in the rate-equilibrium process of the 1,1-diarylethyl cation system.[3,4] These reactions are particularly attractive for a detailed study of the origin of reactivity-selectivity effects, if the substituent effects arise from changes both in the stability of the cation intermediate and from transition-state vs reaction coordinate shifts.[9,10] Accordingly, we have carried out a comparative study of the two reactions in order to clarify the major cause of this characteristic non-additivity pattern.

Results

Reactivity Data Sets. All the kinetic data of the bromination of 1,1-diarylethylenes are taken from the literature data reported by Dubois and co-workers.[8] A wide set of the solvolysis rate data of 1,1-diarylethyl *p*-nitrobenzoates are available from relevant studies in our laboratory.[3,4,15] In Table 2, only relevant rates of the *p*-nitrobenzoates solvolysis required for the comparison with the bromination data are included. Rate constants of several substituents whose data are not available are estimated from the data of close-neighbor substituents, by using linear or non-linear substituent effect relationships.

Substituent Effects. The substituent effects in the solvolyses of 1,1-diphenylethyl *p*-nitrobenzoates were analyzed in detail in previous studies[3,4] based on the Y–T equation (Eq. 1),[1] as well as by using the More O'Ferrall equation (Eq. 5).[13]

The substituent effects on the bromination of 1,1-diarylethylenes were similarly analyzed by using the Y–T equation (Eq. 1). The results are summarized in Table 3. The symmetrical olefins, subseries **1-Br** (X = Y), gave an excellent linear Y–T correlation for the whole range of substituents. For the monosubstituted subset **2-Br** (Y = H), quite a precise Y–T correlation is obtained with a slightly higher $|(\rho_X)_Y|$ value and a higher *r* than for **1-Br**. For the **3-Br** (Y = *p*-MeO) and **4-Br** (Y = *p*-Me) subsets, good Y–T correlations with reduced $|(\rho_X)_Y|$ values were obtained, though the *r* value might not be very reliable statistically. Subsets with electron-withdrawing fixed-Y

Table 2. Rates of Solvolysis of 1,1-Diarylethyl *p*-Nitrobenzoates (OPNB) and Bromination of 1,1-Diarylethylenes

Subsets	Y	X	$k_{\mathrm{OPNB}} \times 10^5/\mathrm{s}^{-1}$	$k_{\mathrm{Br}}/l\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$ a)
			80% aq acetone at 25 °C	MeOH at 25 °C
1	(X = Y)			
	(p-MeO)$_2$		5.8×10^3 b)	3.47×10^6
	(p-MeS)$_2$		111.3	
	(p-Me)$_2$		7.39	9.83×10^4
	(m-Me)$_2$		0.294	6.45×10^3
	(m-MeO)$_2$			1.31×10^3
	(p-F)$_2$		0.137	1.23×10^3
	(p-Cl)$_2$		5.28×10^{-3}	1.27×10^2
	(p-Br)$_2$		4.85×10^{-3}	1.03×10^2
	(m-Cl)$_2$		6.50×10^{-5}	2.87
	(m-CF$_3$)$_2$		1.23×10^{-5}	
2	(Y = H)	p-MeO	63.0	3.76×10^5
		p-Me	1.28	1.56×10^4
		m-Me	0.170	3.28×10^3
		H	0.103	1.67×10^3
		m-MeO		1.64×10^3
		p-F	0.106	1.33×10^3
		p-Cl	2.48×10^{-2}	4.73×10^2
		p-Br	1.92×10^{-2}	3.61×10^2
		m-F	4.3×10^{-3} c)	9.00×10
		m-Cl	3.11×10^{-3}	7.30×10
		m-CF$_3$	1.42×10^{-3}	
		p-CF$_3$	8.61×10^{-4}	
		m-NO$_2$	2.41×10^{-4} c)	7.00
		3,5-Cl$_2$	1.47×10^{-4}	
		3,5-(CF$_3$)$_2$	2.88×10^{-5}	
3	(Y = p-MeO)	p-Me	3.8×10^2 c)	9.73×10^5
		m-Me	130 c)	5.57×10^5
		p-Br	26.4	1.07×10^5
		m-Cl	9.20	5.03×10^4
		m-Br	8.4 c)	5.02×10^4
		m-CF$_3$	6.38	
		m-NO$_2$	2.32 c)	8.13×10^3
		p-NO$_2$	1.58 c)	7.31×10^3
		3,5-Cl$_2$	1.77	
		3,5-(CF$_3$)$_2$	0.852	
4	(Y = p-Me)	m-Me	1.85	2.70×10^4
		p-F	1.18	9.93×10^3
		p-Br	0.294	4.12×10^3
		m-Cl	7.76×10^{-2}	7.20×10^2
		m-Br	4.88×10^{-2}	8.80×10^2
		m-NO$_2$	5.3×10^{-3} c)	1.28×10^2
		3,5-Cl$_2$	2.66×10^{-3}	
		3,5-(CF$_3$)$_2$	7.93×10^{-4}	
5	(Y = m-Me)	m-F	7.1×10^{-3} c)	1.83×10^2
		m-Cl	5.19×10^{-3}	

a) Data taken from Ref. 8. b) Estimated from the Y–T correlation (Eq. 1) in the symmetric subseries; log $(k/k_0) = -7.56\,\bar{\sigma}_{\mathrm{sym}}$ ($r = 0.77$). c) Estimated from the More O'Ferrall nonlinear correlation (Eq. 5) in the respective fixed-Y subsets.[4]

(Y = m-Cl and m-NO$_2$) correlate linearly by Eq. 1 with higher $|(\rho_X)_Y|$ and r values. Whereas all the Y–T correlations for any fixed Y subsets are highly precise, we cast doubt on the reliability of most of these correlations, especially on the validity of r values. This is because those subsets don't involve a sufficient number of data points and none of them satisfy the basic requirement of proper substituents for dual parameter regression analysis. Nevertheless, the r values obtained are in good agreement with the results given by Dubois' analysis. Apparently no single ρ value is applicable throughout the series, but various ρ values with good precision are obtained for each fixed Y-substituent subset.

Table 3. Correlation Analysis of Substituent Effects on the Bromination of 1,1-Diarylethylenes Using the Yukawa–Tsuno Equation

No.	Subsets	Substituents range	n[a]	ρ	r	R	SD
1	**1-Br** (Y = X)	p-MeO–m-Cl	9	-3.40 ± 0.13	0.54 ± 0.05	0.9978	0.12
2	**2-Br** (Y = H)	p-MeO–m-NO_2	11	-3.56 ± 0.12	0.76 ± 0.07	0.9979	0.08
3	**1-Br** + **2-Br**	equivalent class[b]	17	-3.45 ± 0.10	0.55 ± 0.04	0.9967	0.12
4	**3-Br** (Y = p-MeO)	p-MeO–p-NO_2	9	-2.20 ± 0.07	0.49 ± 0.07	0.9984	0.06
5	**4-Br** (Y = p-Me)	p-MeO–m-NO_2	9	-3.08 ± 0.14	0.69 ± 0.09	0.9973	0.10
6	**5-Br** (Y = m-Me)	p-MeO–m-NO_2	5	-3.58 ± 0.10	0.74 ± 0.04	0.9998	0.04
7	**5a-Br** (Y = p-Br)	p-MeO–p-Br	4	-3.50 ± 0.12	(0.85 ± 0.05)[c]	0.9997	0.04
8	**6-Br** (Y = m-Cl)	p-MeO–m-Cl	4	-3.55 ± 0.26	(1.02 ± 0.13)[c]	0.9996	0.09
9	**6x-Br** (Y = m-NO_2)	p-MeO–H	3	-4.56	(0.82)[c]		

a) Number of substituents involved. b) Equivalent class comprises all X = Y in **1-Br**, and X = p-Me, m-Me, m-MeO, p-F, p-Cl, p-Br, m-F, and m-Cl in **2-Br** (Y = H). c) The r value is not statistically definite.

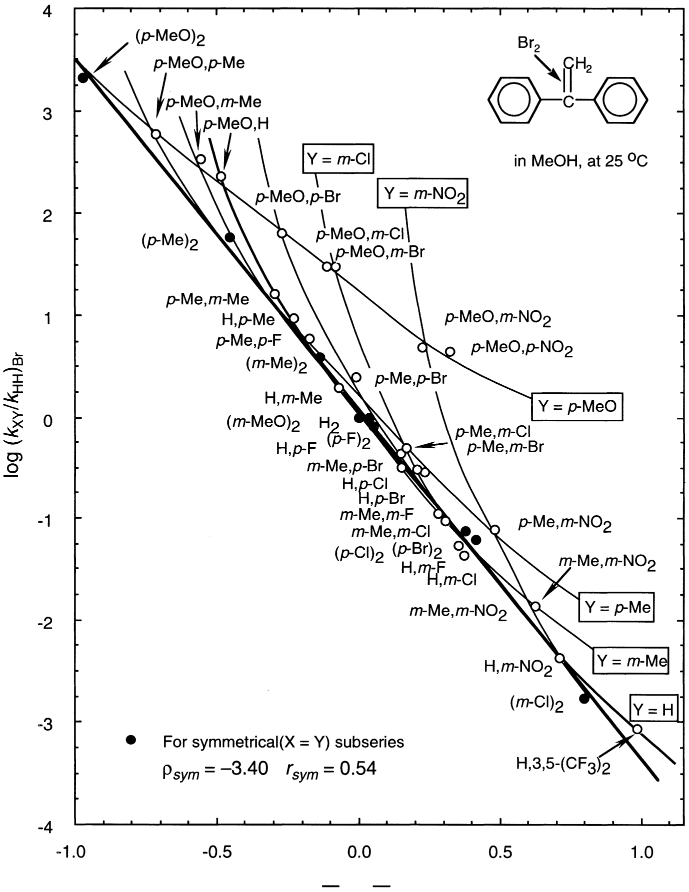


Fig. 1. Plots of log (k_{XY}/k_{HH}) for the bromination of 1,1-diphenylethylenes against $\bar{\sigma}_X + \bar{\sigma}_Y$ with $r_{sym} = 0.54$.

The symmetrical **1-Br** (X = Y) gave a linear Y–T correlation for the whole range of substituents with the selectivity parameters, $\rho_{sym} = -3.40$ and $r_{sym} = 0.54$ (Entry 1 in Table 3), characteristic of the symmetrical substituent subseries. In contrast, the correlation of the log $(k/k_o)_{Br}$ values for the whole set against $\bar{\sigma}_X + \bar{\sigma}_Y$ with $r = 0.54$ is poor, as demonstrated in Fig. 1. The simple additivity relationship, Eq. 3, against $\bar{\sigma}_X + \bar{\sigma}_Y$, gives a widely spread pattern for the whole set with partial correlations for different fixed-Y subsets. The resulting concave plot, where both extremes are bent back upward from the reference line, appears to be typical of any subset with a variable-X and a fixed Y substituent in the α,α-diaryl system.[2–6]

The non-linearity in the correlations for the fixed-Y subsets has been dealt with by the More O'Ferrall equation (Eq. 5),[13]

$$\log (k_X / k_H)_Y = (\rho_o)_Y \bar{\sigma}_X + (2m)_Y (\bar{\sigma}_X)^2 \qquad (5)$$

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

Table 4. Correlation Analysis of Substituent Effects on the Bromination of 1,1-Diarylethylenes by the More O'Ferrall Equation (Eq. 5)

No.	Subset	n[a)]	$(\rho_0)_Y$	$(2m)_Y$	R	SD
1	**6x-Br** (Y = m-NO$_2$)[b)]	4	−4.92 ± 0.62	2.83 ± 1.28	0.9986	0.08
2	**6-Br** (Y = m-Cl)[b)]	5	−4.60 ± 0.19	2.77 ± 0.60	0.9986	0.11
3	**5a-Br** (Y = p-Br)	4	−3.52 ± 0.22	3.21 ± 0.67	0.9995	0.07
4	**2-Br** (Y = H)	11	−4.11 ± 0.10	0.90 ± 0.21	0.9980	0.09
5	**5-Br** (Y = m-Me)	5	−3.99 ± 0.06	1.35 ± 0.20	0.9998	0.04
6	**4-Br** (Y = p-Me)	9	−3.42 ± 0.09	0.63 ± 0.20	0.9982	0.08
7	**3-Br** (Y = p-MeO)	9	−2.13 ± 0.07	−0.04 ± 0.14	0.9981	0.06

a) Number of substituents involved. b) X = m-Me for Y = m-Cl and Y = m-NO$_2$ substituents were estimated by Eq. 5 in the fixed subset **5-Br** (Y = m-Me).

The tangent $(\rho_o)_Y$ values (Table 4) change widely from subset to subset. They are to a good approximation proportional to the $(\rho_X)_Y$ values for the corresponding Y–T correlations in Table 3. Both selectivity parameters show the same dependence upon Y; the more electron-withdrawing Y is, the more negative the $(\rho_o)_Y$ value is. The $(2m)_Y$ coefficients increase as the fixed-Y substituent becomes more electron-withdrawing, indicating changes in the degree of curvature with the fixed substituent Y. Importantly, these values are largely positive, but zero for Y = p-MeO, implying the shape of a bent-back curvature for any subset, as seen in Fig. 1.

Discussion

The correlation results for the bromination of 1,1-diarylethylenes (X-Ar)(Y-Ar)C=CH$_2$ in Table 3 indicate that the respective fixed Y subsets provide significantly precise Y–T correlations and the apparent $(\rho_X)_Y$ value for Y–T correlations of variable X-substituents changes significantly for fixed-Y substituents. The results are in good accordance with those reported by Dubois and co-workers.[8] A qualitative linear trend, where $(\rho_X)_Y$ tends to be more negative as Y becomes more electron-withdrawing, is apparent (Table 3).

Such behavior is referred to as adherence to the RSR.[9–12] The small |ρ| value could be attributed to an early transition state, as required by the highly stabilized intermediate.[9,10] In addition to its kinetic effect (transition-state shift), the enhancement of the intermediate stability has a thermodynamic effect on the ρ parameter.[10] Thus, the authors concluded that the selectivities in the electrophilic additions are not directly related to the reactivities but to the position of the transition state.[10] However, all the mechanistic conclusions for the bromination contrast sharply with our conclusions for the mechanism of the solvolysis of 1,1-diarylethyl p-nitrobenzoates.

For the hydration reaction of 1,1-diphenylethylenes, we may expect the same pattern of the kinetic substituent effect as that in the solvolysis, in either case without the effect associated with coordinate-shifts of the transition state. The same expectation may be extended to the bromination of 1,1-diarylethylenes. The pattern of the additivity correlation for the bromination in Fig. 1 resembles that of the solvolysis of 1,1-diarylethyl-OPNBs. However, this expectation is inconsistent with the suggested mechanism in which the non-additivity in the bromination should be mainly caused by coordinate-shifts of the transition state, but not significantly by changes in the thermodynamic stability of the cationic intermediate.

Of particular importance is the precise linear correlation (Eq. 6) for the whole range of substituents between the bromination and the present solvolysis in Fig. 2 (R = 0.998, SD = ±0.12, n = 31).

$$\log (k_{XY} / k_{HH})_{\mathbf{OPNB}} = 1.07 \log (k_{XY} / k_{HH})_{\mathbf{Br}} - 0.83\Delta\bar{\sigma}_R^+ \tag{6}$$

Combining with Eq. 4, Eq. 6 is converted into Eq. 6a:

$$\log (k_{XY} / k_{HH})_{\mathbf{Br}} = -0.96\,(\Delta pK_{BH^+} - 0.81\Delta\bar{\sigma}_R^+). \tag{6a}$$

A brief comment will suffice to explain why this simple linear relationship holds. If the thermodynamic stabilities [log $K_{XY}/K_{HH}]_{\mathbf{Br}}$ of the intermediate for the bromination reaction can be given by Eq. 6b,

$$[\log K_{XY} / K_{HH}]_{\mathbf{Br}} = -\Delta pK_{BH^+} + 0.81\Delta\bar{\sigma}_R^+ \tag{6b}$$

Eq. 6a can be rewritten in the form (Eq. 7), which is regarded as an *extended Brønsted correlation* for the bromination process,

$$\log (k_{XY}/k_{HH})_{\mathbf{Br}} = \alpha\,[\log K_{XY}/K_{HH}]_{\mathbf{Br}} \tag{7}$$

We emphasize that the constant α coefficient serves as evidence for the absence of a coordinate shift of the transition state that is induced by varying substituents. Thus, the precise linear relationship (Eq. 6) is the key to the non-linearity and non-additivity in the bromination process.

While any fixed-Y subset shows a different dependence upon the changing X in either the rates or the equilibria, the rate-equilibrium relationship (Eq. 7a) holds for all the Y-subsets with the same α-coefficient; i.e., it should embrace any Y subset, regardless of whether their Hammett-type correlations are linear or not.

$$\log (k/k_o)_{\mathbf{Y}} = \alpha \log (K/K_o)_{\mathbf{Y}} \tag{7a}$$

When a linear correlation holds for any individual Y subset (superscripts k and t designate kinetics and thermodynamics, respectively),

$$(\rho^k)_{\mathbf{Y}} = \alpha(\rho^t)_{\mathbf{Y}} \tag{7b}$$

it implies that the significant changes in $(\rho^k)_{\mathbf{Y}}$ with the fixed-Y

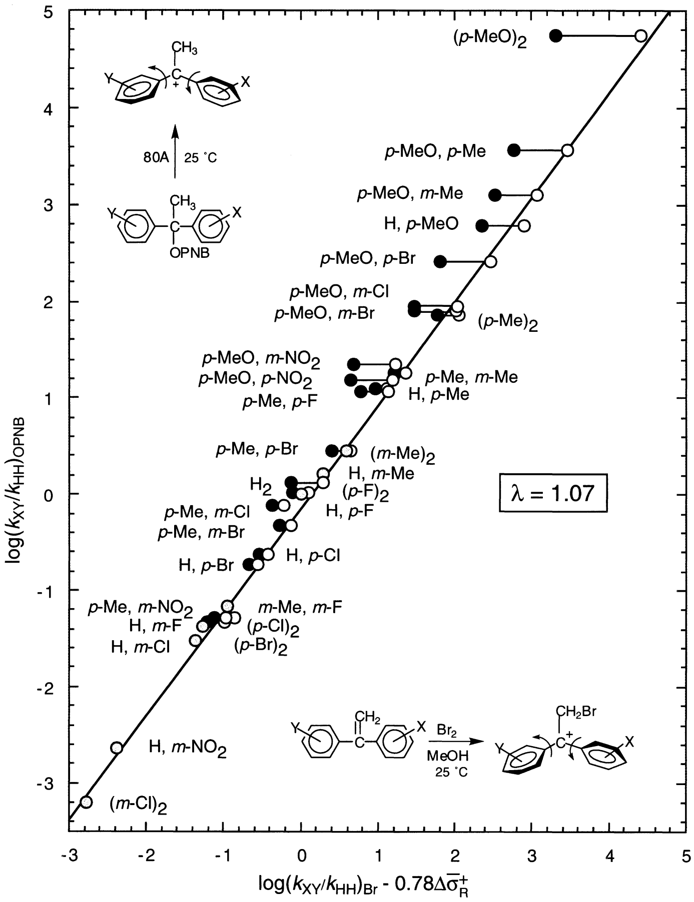


Fig. 2. A linear relationship between log $(k_{\mathrm{XY}}/k_{\mathrm{HH}})_{\mathrm{OPNB}}$ for the solvolysis of 1,1-diphenylethyl p-nitrobenzoates and log $(k_{\mathrm{XY}}/k_{\mathrm{HH}})_{\mathrm{Br}}$ for the bromination of 1,1-diphenylethylenes; log $(k_{\mathrm{XY}}/k_{\mathrm{HH}})_{\mathrm{OPNB}} = 1.07$ log $(k_{\mathrm{XY}}/k_{\mathrm{HH}})_{\mathrm{Br}} - 0.83\ \Delta\bar{\sigma}_{\mathrm{R}}^{+}$. Closed circles are plots for log $(k_{\mathrm{XY}}/k_{\mathrm{HH}})_{\mathrm{Br}}$, open circles after the correction of resonance effects, and half-toned for the resonance-invariant substrates.

subsets observed in the bromination rate process are not caused by coordinate-shifts of the transition state. Furthermore, Eq. 7b leads to an extended form, Eq. 8:

$$(\rho^{k}_{\mathrm{Br}})_{\mathrm{Y}} = \alpha(\rho^{t}_{\mathrm{Br}})_{\mathrm{Y}} = \alpha'(\rho^{k}_{\mathrm{OPNB}})_{\mathrm{Y}} \qquad (8)$$

where $\alpha' = 1/1.07$ as in Eq. 6. We have already shown that the $(\rho^{k}_{\mathrm{OPNB}})_{\mathrm{Y}}$ value changes significantly with the fixed-Y subsets without accompanying coordinate-shifts of the transition state. The constant proportionality effect of the fixed-Y substituents on the $(\rho^{k})_{\mathrm{Y}}$ for the bromination and solvolysis testify to a common reason in both reactions, whatever is the reason of the non-linearity and non-additivity behavior. It is important that α' remains constant for any fixed-Y subsets even when the $\bar{\sigma}_{\mathrm{X}}$-correlations are not linear. Evidently, the dispersion behavior in both rate-processes should be a thermodynamic but not a kinetic effect.

When either Z = H or Z = Br in Scheme 1, the elementary steps for the solvolysis/return (left half) and for the addition/elimination (right half) involve a common cation intermediate, whose thermodynamic stability controls the stabilities of both transition states. While the reaction coordinates characterizing the extent of recombination of the intermediate cation with the LG-group ion (left half) and the extent of departure of Br^{+} from the intermediate (right half) are clearly different, they can be unified in terms of the amount of the charge developed at the α-carbocationic center. It has been generally shown that Y–T-correlations for the rates and equilibria in a solvolytic process show the same characteristic r value inherent in the parent structure of the carbocation in the gas phase. This implies that the r value should be a function of the structure of the parent cation irrespective of position of the transition state. The structure of the incipient carbenium moiety $\mathrm{Ar_2C^{+}CH_3}$ of the solvolytic transition state resembles the structure of the solvolytic intermediate. In contrast, the structure of the cationic moiety changes appreciably in the bromination as the reaction progresses from the intermediate to the transition state. Hence, it is important that the r parameter for the intermediate extrapolated by Eq. 6 is appreciably lower than that expected for the ordinary bromination intermediate cation $\mathrm{Ar_2C^{+}CH_2Br}$, which should have a higher r value than that of the corresponding α-$\mathrm{CH_3}$ cation. This is reasonable because the cationic moiety of the transition state of the bromination is a 1,1-diarylmethyl cation having an α-$\mathrm{CH_2}^{-}\cdots\mathrm{Br}^{+}$ group that may be a stronger electron-donor than $\mathrm{CH_3}$. The difference in this r value from that of the intermediate cation should be a measure of the position of the transition state. It is therefore remarkable that the correlation (Eq. 6a) involves a constant differential r value, indicating a fixed position of the bromination transition state irrespective of the varying X in a fixed-Y subset.

Similarly, in the solvolytic elimination process, $Z = \mathrm{H}$ in Scheme 1, the stabilities of both transition states are also controlled by the thermodynamic stability of the intermediate. Hence it is highly plausible to expect a relationship (Eq. 9) between the two elementary steps in the process:

$$\begin{aligned}\log(k/k_\mathrm{o})_\mathbf{solv} &= \alpha\log(K/K_\mathrm{o})_\mathbf{cation} \\ &= \alpha'[\log(k/k_\mathrm{o})_\mathbf{H\text{-}addn} + \gamma\Delta\bar{\sigma}_\mathrm{R}^{+}]\end{aligned} \tag{9}$$

where γ is a coefficient referred to as the differential resonance demand between the intermediate cation and the transition state.

Whereas these results do not explain the non-linearity and non-additivity in the α,α-diarylcarbenium ion systems, we emphasize that the significant RSR-behavior observed in these four elementary reaction steps are all caused by the thermodynamic effect and are independent of coordinate shift of the transition state.

So far the significant dependence of the ρ_X values on the fixed-Y substituents suggested an interpretation based on the RSR, and the non-additivity behavior was then ascribed to coordinate-shift of the transition state.[9,10] Hence, Dubois and coworkers concluded that the variation of ρ in the hydration comes mainly from a Y-dependent change in the thermodynamic stability of the intermediate, whereas in bromination a transition-state shift is superimposed on this effect.[9,10] The present analysis argues strongly against their conclusion.

Although a non-additivity of substituent effects is evident also in the bromination of 1,1-diphenylethylenes, we do not attribute it to a significant coordinate-shift of the transition state. We believe that substituent-induced *conformational* changes of the transition state account accurately for the nonlinear substituent effects in the 1,1-diarylethyl solvolyses and in bromination and hydration of multi-substituted 1,1-diphenylethylenes. This interpretation deserves to be further tested for such systems and an analysis will soon be published.

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