Varying Resonance Demand in Carbocationic Systems

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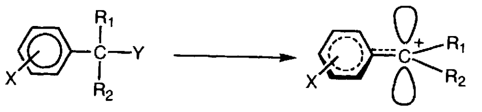
1 Introduction

In a variety of aromatic side-chain reactions, exemplified by benzylic solvolyses, where a positive charge, which can be delocalized by the π-system of the ring, is generated, (Scheme 1), the Brown equation (1) has been widely applied to correlate the substituent effects.[1]



Scheme 1 Solvolysis of benzylic precursors.

$$\log(k/k_0) = \rho^+\sigma^+ \qquad (1)$$

In eqn. (1) k (or K) is the rate (or equilibrium) constant for such a reaction of a ring-substituted derivative and k_0 or K_0 is the corresponding value for the unsubstituted compound. The electrophilic substituent constants, σ^+, were defined using the solvolysis rates of α,α-dimethylbenzyl (α-cumenyl) chlorides (**1**), $R_1=R_2=CH_3$ in Scheme 1, in 90% aqueous acetone (90A) at 25 °C. For this reaction, the reaction constant $\rho^+ = -4.54$.

The substituent effects in such systems can be more generally described by the Yukawa–Tsuno equation (2),[2]

$$\log(k/k_0) = \rho(\sigma^0 + r\Delta\bar{\sigma}_R^+) \qquad (2)$$

where σ^0 is the normal substituent constant which does not involve any additional π-electronic interaction between the substituent and the reaction centre, and $\Delta\bar{\sigma}_R^+$ is the resonance substituent constant measuring the capability for π-delocalization of the π-electron donor substituent and is defined by $\sigma^+ - \sigma^0$. The r value is a parameter characteristic for the given reaction, measuring the extent of resonance demand, *i.e.*, the degree of resonance interaction between the aryl group and the reaction site in the rate-determining transition state.[2,3] Since our proposal of this equation, the original form using σ instead of σ^0 in eqn. (2) has been widely applied.[2,3] However, we believe that the use of eqn. (2), which is a theoretically more justifiable form, is preferable.[2,3] When $r=0$, $\log(k/k_0)=\rho\sigma^0$, while when $r=1.00$ eqn. (1) is obtained. This modification of the parameter scale does not affect the original meaning and the applicability of the equation.

With the Yukawa–Tsuno (Y–T) equation (2), we introduced the concept of varying resonance demand of reactions into the analysis of substituent effects. In the general application of this equation, the r value changes widely with the reaction. Its value is not limited to lower than unity, as found for the cumenyl system ($0<r<1$), but in many cases it is significantly higher than unity ($r>1$). This fact clearly indicates that the Brown σ^+ scale [*i.e.*, eqn. (2) when $r=1.0$] does not reflect the highest extreme of benzylic resonance exaltation but is merely a single point on the r scale. This r scale permits evaluation of the nature of the transition state, and has been widely applied to the assignment and interpretation of reaction mechanisms,[3–5] involving benzylic solvolyses[3,5] and neighbouring aryl-assisted reactions,[6–10] with which we will be mainly concerned in this review.

The application and generality of the Yukawa–Tsuno relationship were adequately and precisely reviewed by Shorter,[3] and further developments of the Y–T analysis were reviewed both by Johnson[4] and recently by us.[5]

In the extensive application of eqn. (2), the correlation results were always compared with those of the Brown equation. It was pointed out that the additional r term in eqn. (2) is either necessary or superfluous.[3–5] More critical analyses cast doubt on the real merit of the r parameter,[4] and argue against its significance as a measure of the resonance demand.[4] Hence, this point will be also considered in this review.

The difficulties encountered in the analysis of substituent effects in solvolyses as a mechanistic probe mostly arise from the mechanistic involvement of the solvent.[3–5] Consequently, the behaviour of benzylic carbocations in the gas phase should be the best model

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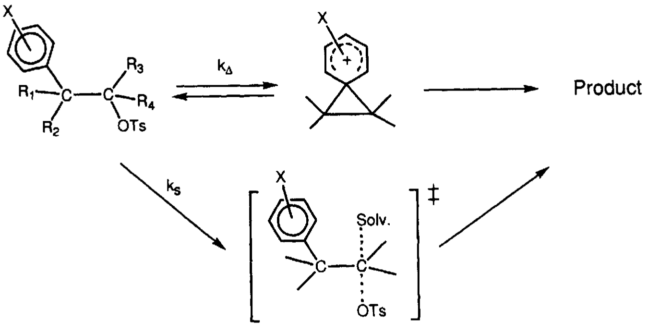
for the behaviour of the solvolysis intermediate in solution.[5] The intrinsic substituent effect on the benzylic cation stabilities in the gas phase have also been analysed by eqn. (2), and will be compared here with the substituent effects on the benzylic solvolysis reaction.[5] In our opinion, this will provide convincing evidence for the concept of varying resonance demand in solvolysis. Finally, we will analyse the mechanisms of a series of benzylic solvolysis reactions by using the concept of a continuous spectrum of varying resonance demands.

2 The Yukawa–Tsuno Analysis of Solvolyses

Most of the criticism of eqn. (2) appears to arise primarily from the relatively small change of the r value in most benzylic solvolyses.[3,4] A definite answer to such criticism will be provided by exploring the substituent effects on systems whose r values differ significantly from unity.

The β-aryl-assisted solvolysis,[6–10] *e.g.*, of neophyl brosylates (**2**),[6] where $R_1=R_2=CH_3$ and $R_3=R_4=H$ in Scheme 2, should be an appropriate model reaction for cases where the resonance demand is low since it gives an r value significantly lower than unity, whereas formation of highly electron-deficient carbocation systems,[5] such as those formed in the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates ($R_1=CH_3$, $R_2=CF_3$ in Scheme 1) should model reactions having distinctly higher resonance demand. Both systems will be shown to be far beyond the correlative ability of the Brown $\rho^+\sigma^+$ equation but to be well correlated in terms of the Y–T equation.



Scheme 2 Solvolytic process of β-arylalkyl precursors.

The results of the analysis of the varying resonance demand in solvolyses of a series of substrates are summarized in Table 1. The precision of the fit to eqn. (2) is generally found to have a standard deviation of ±0.04—0.10 in $\log k/k_0$, depending on the magnitude of the ρ value. This is comparable to the standard deviations found for the *meta*-correlation with a single σ values set, and also with similar standard deviations found in correlations when the solvent, or the leaving group, was changed. Thus, the precision index of 0.015—0.020 in σ units is taken as an appropriate reference level of acceptable conformity in the Y–T equation.

2.1 Aryl-assisted Solvolyses

The substituent effect on the acetolysis of neophyl brosylates **2** gives a reasonably good correlation with σ^+ rather than with σ constants, and this was taken as evidence for the anchimeric assistance by the β-aryl group.[6] It was suggested that the Y–T equation results in a better correlation than the simple Brown $\rho^+\sigma^+$ treatment, and this has been corroborated recently by the application of an extensive data set.[6]

The behaviour of substituents in this reaction is illustrated by the so-called Y–T plot in Fig. 1. A linear relationship for *meta* and π-accepting *para* substituents, covering four orders of magnitude in reactivity, is wide enough to define a ρ_m correlation as a rigid reference common to both the σ^+ and the Y–T analyses. The σ^+ plots (open circles) of *para* π-donor substituents consistently deviate

Table 1 Yukawa–Tsuno correlations for benzylic solvolyses

No.	System (Solv., Temp)	ρ	r	R	SD	n
1	Neophyl OBs (AcOH, 75 °C)	−3.83	0.57	0.9997	0.038	29
2	2-Arylethyl OTs (AcOH, 115 °C)	−3.87	0.63		0.035	27
3	1-Aryl-2-propyl OTs (AcOH, 100 °C)	−3.53	0.54		0.025	21
4	*threo*-3-Aryl-2-butyl OBs (AcOH, 75 °C)	−3.32	0.56		0.042	24
5	2,2-Bisarylethyl OTs (AcOH, 90.1 °C)	−4.44	0.53	0.998	0.077	16
6	2-Ar-2-(*m*-ClC_6H_4)ethyl OTs (AcOH, 90.1 °C)	−3.60	0.62	0.9994	0.037	14
7	2-Ar-2-(3,5-$Cl_2C_6H_3$)ethyl OTs (AcOH, 90.1 °C)	−3.54	0.66	0.9996	0.028	13
8	(1-Arylcyclobutyl)CH_2 OBs (AcOH, 55 °C)	−3.27	0.55		0.050	17
9	Benzyl OTs (80A, 25 °C) X≥4-MeS,3-CN[a]	−5.23	1.29	0.9995	0.040	17
9a	(AcOH, 25 °C) X≥*p*-halogens[a]	−5.23	1.29	0.9994	0.044	14
10	α-Me-benzyl Cl (80A, 45 °C)	−4.97	1.15	0.9993	0.06	25
10a	(97T, 45 °C)	−6.47	1.11	0.998	0.12	21
11	α-Bu^t-benzyl OTs (80A, 25 °C)	−5.54	1.09	0.9997	0.060	31
12	2,2-Me_2indanyl Cl (80A, 25 °C)	−5.81	1.14	0.9995	0.11	11
13	α,α-Me_2-benzyl Cl (90A, 25 °C)	−4.59	1.00			
14	Ar(Ph)CH-Cl (EtOH, 25 °C)	−4.09	1.10	0.9991	0.092	22
14a	(85A, 0 °C)	−4.58	1.15	0.9983	0.10	20
15	Ar(*m*-ClC_6H_4)CH Cl (EtOH, 25 °C)	−4.47	1.18	0.9993	0.083	18
15a	(85A, 0 °C)	−4.93	1.23	0.9982	0.11	18
16	Ar(3,5-$Cl_2C_6H_3$)CH Cl (EtOH, 25 °C)	−4.37	1.38	0.998	0.15	6
17	Ar(*p*-$NO_2C_6H_4$)CH Cl (85A, 0 °C)	−5.31	1.32	0.9975	0.14	14
18	Ar_3COH (pK_R^+, H_2O–H_2SO_4)	−11.39/3	0.76	0.999	0.40/3	11
19	α,α-$(Pr^i)_2$-benzyl Cl (80A, 45 °C)	−4.88	1.01	0.9995	0.11	14
20	α-Et,α-Me-benzyl Cl (80A, 45 °C)	−4.69	1.04	0.9993	0.079	17
21	α-Bu^t,α-Me-benzyl Cl (80A, 45 °C)	−4.28	0.91	0.9986	0.088	22
22	α-Bu^t,α-Pr^i-benzyl OPNB (50E, 75 °C)	−3.08	0.68	0.998	0.059	12
23	α,α-Bu^t_2benzyl OPNB (50E, 75 °C)	−2.19	0.26	0.994	0.07	12
24	(1-Arylcyclopropyl)CH_2 OTs (80E, 25 °C)	−1.55	0.11	0.996	0.041	8
25	BBCO OTf[b] (80E, 75 °C)	−2.17	0.01	0.989	0.008	7
26	Ar_2CCF_3 OTs (80E, 25 °C)	−4.18	1.19	0.999	0.12	12
27	Ar(Ph)CCF_3 OTs (80E, 25 °C) X≥3,4-Me_2[a]	−6.1	1.45	0.996	0.15	6
	X≤3,4-Me_2[a]	−4.33	1.26	0.999	0.074	12
28	Ar(*m*-ClC_6H_4)CCF_3 OTs (80E, 25 °C) X≥*p*-Me[a]	−6.19	1.57	0.996	0.19	7
29	Ar(3,5-$Cl_2C_6H_4$)CCF_3 OTs (80E, 25 °C) X≥H[a]	−5.95	1.69	0.998	0.18	12
30	α-CF_3benzyl OTs (50E, 25 °C)	−6.05	1.53	0.9994	0.082	15
31	α-Me,α-CF_3-benzyl OTs (80E, 25 °C)	−6.29	1.39	0.9998	0.070	28

[a] X≥Y or X≤Y: correlation for the range of substituents more electron-donating or electron-attracting than Y. [b] 4-Methylbenzobicyclo[2.2.2]octen-1-yl triflates.

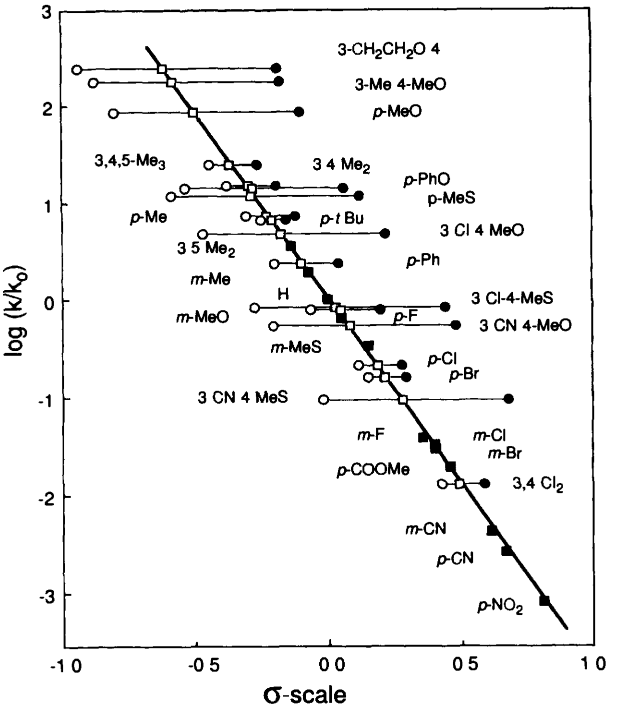


Figure 1 The Y–T plot for acetolysis of neophyl brosylates (**2**) at 75 °C ○, plots against σ^+, ●, against σ^0, □, against substituent parameter scale $\bar\sigma$ given by the Y–T equation with r=0 57, ■, for plots of substituents having invariant σ for the three scales The figure is reproduced with permission from *Bull Chem Soc Jpn* 1990, **63**, 1121

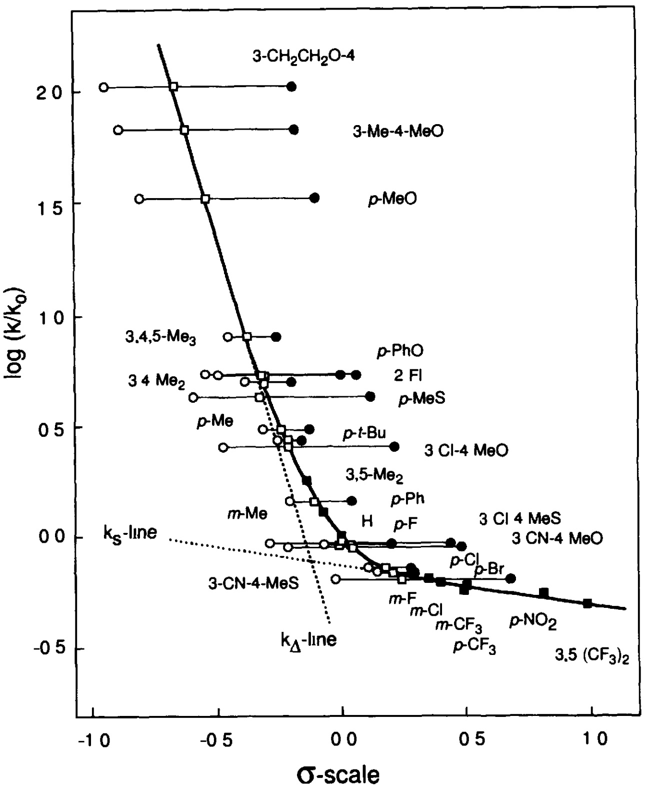


Figure 2 The Y–T plot for acetolysis of 2 phenylethyl tosylates (**3**) at 115°C ○, plots against σ^+ , ●, against σ^0, □, against σ with r=0 63, ■, for the plots of substituents having invariant σ for the three scales The figure is reproduced with permission from *Bull Chem Soc Jpn* 1987, **60**, 1091

downwards from the reference *meta* substituents correlation line The line segments between σ^+ and σ^0 values for *para* π-donor substituents reflect the resonance capabilities of these substituents, i e the $\Delta\bar\sigma^+_R$ values The ρ_m correlation line divides all the line segments at a constant internal ratio, corresponding to the r value of the system Thus, the Y–T correlation line can be defined as a unique line intersecting all line segments for *para* π-donors at such a constant ratio, i e , at a substituent parameter $\bar\sigma$ scale with a characteristic r value, even without the need to use the *meta* substituents

The solvolysis of **2** is considered to proceed through a rate-determining aryl-assisted transition state which leads to the tertiary carbenium ion [6] The substituent effect on the rate should reflect only that on the aryl assisted ionization step and therefore the observed r value of 0 57 should be characteristic of this step This exalted r value can be rationalized in terms of a direct π-interaction between the aryl π system and the β-carbocation centre at the rate-determining transition state

Most solvolyses of β-arylalkyl arenesulfonates involve a mechanistic complication arising from a concurrent solvent-assisted (k_s) process, as shown in Scheme 2 [7,8] The measured rate constant k_t of the solvolysis should be a sum of the rate constants for aryl-assisted k_Δ and unassisted k_s processes In practice, substituent effects on these competitive processes can be directly analysed by using a non-linear least squares method based on the assumption of independent Y–T correlations for both k_Δ and k_s processes, i e eqn (3)

$$k_t = k^{\mathrm{H}}_{\Delta}10^{\rho_\Delta(\sigma^0 + r_\Delta \Delta\sigma_{\mathrm{R}})} + k^{\mathrm{H}}_{s}10^{\rho(\sigma^0 + r\,\Delta\sigma_{\mathrm{R}})} \qquad (3)$$

The treatment was simplified by applying r_s=0 for the k_s process of this reaction

However, it is instructive to apply a classical method of analysis The Y–T plot for the acetolysis of β-arylethyl tosylates **3**, all R's being H in Scheme 2, is shown in Fig 2 [7] In this reaction, only compounds carrying strongly electron-donating substituents react predominantly by the aryl assisted k_Δ process Clearly, we see the same pattern of the Y–T plot for these reactive substrates which react predominantly by the k_Δ process as for the acetolysis of **2** The Y–T correlation line with an r value of 0 63 passes through the points dividing the $\Delta\sigma^+_R$ line segments as a constant internal ratio of 0 63 and collapses into the single smooth correlation curve for the r-independent electron-withdrawing substituents reacting by the k_s mechanism

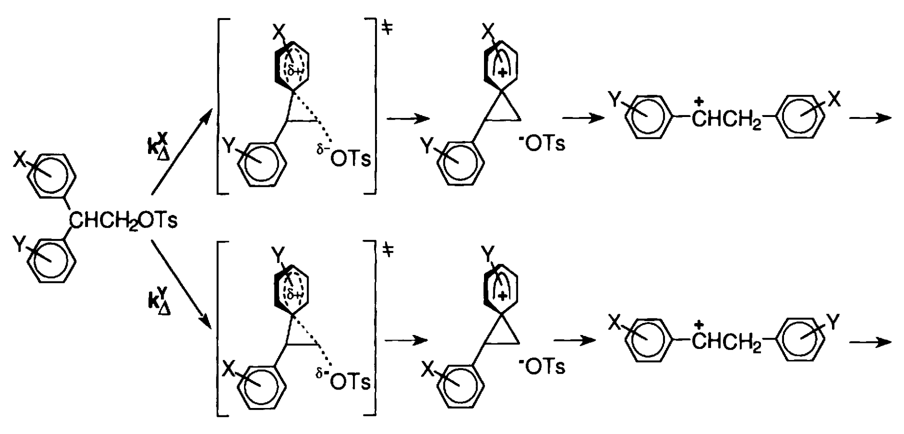
The same behaviour was observed for the solvolyses of *threo*-3-aryl-2-butyl brosylates[8] and (1-arylcyclobutyl)methyl brosylates [9] Rates of these solvolyses were previously reported to correlate linearly with σ^+ without a significant break, implying the operation of only the k_Δ mechanism without a concurrent k_s process [9] The simple Brown $\rho^+\sigma^+$ treatment appears to be incapable of providing a correct interpretation of the mechanistic details

The Y–T correlations for the acetolysis of 2,2-diarylethyl tosylates **4** (entries 5—7 in Table 1) are instructive, since the nature of the phenonium transition state may be modified by the presence of the non-participating aryl group, keeping the mechanism essentially the same [10]

The acetolysis of differently disubstituted diarylethyl systems **4**(X,Y) proceeds through two competitive assisted pathways either by the X-substituted phenyl (k^{X}_Δ) or by the Y-substituted phenyl group (k^{Y}_Δ), as shown in Scheme 3

The substituent effect on the symmetrically disubstituted bis-arylethyl tosylates, i e **4**(X=Y), can be described accurately in terms of the Y–T relationship with ρ= −2 22 and r=0 53 The Y–T plot is excellently linear against an apparent substituent scale $\bar\sigma$ with r=0 53 for the whole set of substituents, indicating a uniform mechanism for all of them

When Y≠X, the overall solvolysis rate constant k_t corresponds to the sum of the rate constants, k^{X}_Δ+ k^{Y}_Δ, and hence k_t cannot be employed directly in the Y–T analysis The acetolysis of mono-substituted diphenylethyl tosylates gave a nonlinear Y–T correlation, which is ascribed to a competitive X-substituted aryl-assisted pathway k^{X}_Δ and the unsubstituted phenyl-assisted k^{H}_Δ pathway By application of an iterative nonlinear least-squares method to eqn (3), where the subscripts Δ and s are now replaced by the k^{X}_Δ and k^{H}_Δ pathways, respectively, the substituent effect on k_t was dissected into a k^{X}_Δ correlation with ρ_Δ=−3 53, r_Δ=0 60, and an unassisted (by aryl-X-substituents) correlation for the phenyl-assisted k^{H}_Δ mechanism correlated with σ^0 having ρ_{H}= −0 88 The ρ_Δ and r_Δ values for



Scheme 3 Solvolysis processes of 2,2-diarylethyl tosylates 4

the effects of assisting aryl substituents are quite close to those for **2**, whereas the low ρ_H value with the unexalted σ^0 constants for the unassisting aryls is compatible with a remote β-aryl effect.

In the acetolysis of 2-aryl-2-(3,5-dichlorophenyl)ethyl tosylates **4**(X,Cl_2), the strongly electron-withdrawing 3,5-dichlorophenyl group does not compete in an aryl-assistance pathway with any other aryl groups carrying more electron-releasing substituents than *p*-Cl. A Y–T correlation with $r=0.66$ for 13 substituents in the range down to *m*-chloro was obtained, demonstrating that a single X-substituted phenyl-assisted pathway takes place.

Similarly, for the acetolysis of 2-aryl-2-(*m*-chlorophenyl)ethyl tosylates **4**(X,Cl), eqn (2) gives a linear correlation with $r=0.63$ for substituents more electron-releasing than H. This may reflect the Y–T correlation for the X-substituted aryl-assisted pathway. The r and ρ values are comparable with those for the aryl-assisted k_Δ pathway of the mono-substituted diphenylethyl system and also with those for other k_Δ solvolyses, *e.g.* neophyl brosylates, suggesting a close similarity of the aryl-assisted mechanisms.

On the other hand, the acetolysis of 2-aryl-2-(*p*-methoxyphenyl)ethyl tosylates **4**(X,*p*-MeO), probably proceeds uniformly through the *p*-methoxyphenyl-assisted pathway. There is a linear Hammett correlation against σ^0 (or σ), attributed to the effect of the unassisting-aryl X-substituents in the *p*-methoxyphenyl-assisted mechanism.

The ρ value for symmetrical bis-arylethyl **4**(X=Y) systems appears too small compared with those of the neophyl system with the single aryl group. This can be accounted for by the fact that only one of the two β-aryl groups participates in the rate-determining aryl-assisted transition state, while the other one affects the unassisted mechanism, and both routes must be additive. Consequently, when we apply a ρ value of -0.8 for the latter route, we obtain a Y–T correlation for the k_Δ route [eqn (4)]

$$\log(k/k_0)_\Delta = -2.22\times2(\sigma^0+0.53\Delta\bar{\sigma}_R^+)-0.8\sigma^0=-3.6(\sigma^0+0.61\Delta\bar{\sigma}_R^+) \quad (4)$$

which is practically identical to those for the k_Δ processes of Y-fixed **4**(X,Y) systems.

In the 2,2-diphenylethyl system **4**, all the r_Δ values are within a narrow range of 0.62 ± 0.04 and tend to increase only slightly as the substituent in the unassisting aryl becomes more electron-withdrawing. This r value of 0.6 can be referred to the resonance demand characteristic of the β-aryl assisted solvolyses.

2.2 Benzylic Solvolyses generating Stable Carbocations

Most benzylic solvolyses generating relatively stable carbocations may belong to the category to which the Brown σ^+ constants are effectively applicable. A broad applicability of the Brown $\sigma^+\rho^+$ equation has been demonstrated for solvolyses of a wide series of tertiary α,α-dialkylbenzyl *p*-nitrobenzoates.[4,10] The solvolysis of α-phenylethyl chlorides **5** in 80% aqueous acetone (80A), gives an excellent linear correlation ($R=0.999$) with eqn (2) with an r value of 1.15,[10] whereas the Brown σ^+ treatment gave a bisected rather than a single linear correlation.[11] Whereas the exalted r value as well as the concave Brown plot may be attributed to the nucleophilic solvent participation for the region of electron-attracting substituents in nucleophilic solvents, the finding of a strict linear correlation with the same r value in the less nucleophilic aqueous trifluoroethanol (TFE)[5,12] argues against the importance of solvent nucleophilicity in this case.

Any S_N1–S_N2 mechanistic complication should be absent in the solvolysis of α-*tert*-butylbenzyl tosylates **6**, having a neopentyl-type structure.[12] Indeed, the substituent effect is accurately described by eqn (2) with an r value of 1.09 differs from the $r=1.0$ for the α-cumenyl chlorides solvolysis.[12] From the linearity of substituent effects between the solvolyses of **5** and **6** in 80A, an S_N1–S_N2 mechanistic duality is unlikely to be the cause of the exalted r value observed in the solvolysis of **5**.

The slightly lower r value for the solvolysis of system **6** than for the α-methyl analogue **5** is presumably due to incomplete coplanarity of the aryl group with the cationic p-orbital in the transition state of **6**.[12] In the solvolysis of 2,2-dimethylindan-1-yl chlorides (entry 12 in Table 1), the vacant p-orbital developed at the benzylic position is in an appropriate stereoelectronic conformation to overlap the benzene π-system.[13] Hence, this system attains a full resonance stabilization at the transition state and the r value of 1.14 is practically identical with that observed for the solvolysis of chlorides of **5**.[12] Consequently, the resonance demand for the S_N1 solvolysis of secondary α-alkylbenzyl must be appreciably and intrinsically higher than that for the transition state for the solvolysis of tertiary α,α-dialkylbenzyl.

Benzhydryl solvolyses (entries 14—17 in Table 1) show Y–T correlations with similar resonance demand and the magnitude of r is significantly dependent on the electron-withdrawing effect of the second aryl groups.[2,14]

Substituent effects in the solvolysis of the triphenylmethyl system are reported to give r values close to unity. The pK_R^+ values for symmetrically trisubstituted triarylmethanols give a complete linear Y–T correlation against a $\bar{\sigma}$ scale with an r value of 0.76 for the substituent range from *p*-dimethylamino to *p*-nitro.[2] This contrasts sharply with the less satisfactory Y–T correlation obtained for the pK_R^+ values for monosubstituted triphenylmethanols or for the log (k/k_0) values for the solvolysis of the corresponding chlorides, in which the strong π-donor *p*-methoxy substituent requires a higher r-value than that for the other weaker electron-donating groups. The three aryl rings in the triarylmethyl cation are twisted out of coplanarity with the vacant orbital by steric interaction.[4] The propellor conformation of the symmetrical triarylmethyl cation prevents the aryl groups from exerting their maximum stabilizing effect on the carbocation. However, in the monosubstituted cation, only the strong π-donor substituted aryl can be coplanar with the cationic orbital, exerting its maximum π-effect. Hence, deviations from the correlation line are indicative of resonance loss due to reduced conjugation caused by twisting.

The solvolysis of benzyl tosylates **7** is a typical case where a significant mechanistic shift occurs when the substituent is changed

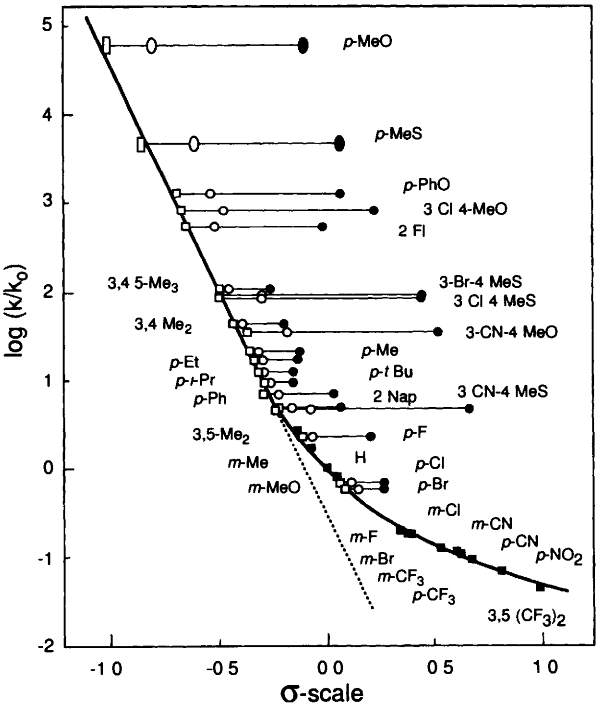


Figure 3 The Y–T plot for solvolysis of benzyl tosylates (7) in 80% acetone at 25 °C, $r=1\ 29$ For symbols, see Fig 1 caption The graph is reproduced with permission from *Bull Chem Soc Jpn*, 1990, **63**, 1146

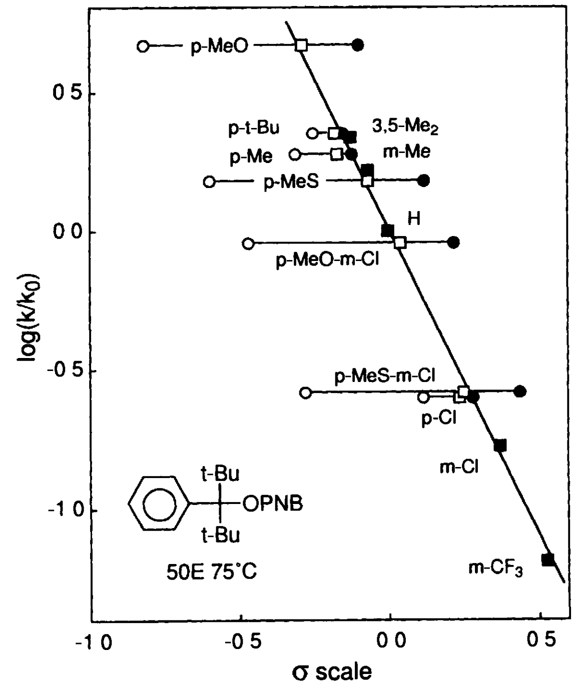


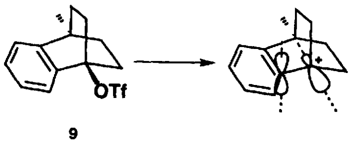
Figure 4 The Y–T plot for solvolysis of α,α di *tert* butylbenzyl OPNB (8) in 50% aq EtOH at 75 °C, $r=0\ 26$ For interpretation of symbols, see Fig 1 caption Reproduced with permission from *Tetrahedron Lett* 1991, **32**, 2929

The bisected (bilinear) correlation with σ^+ values gives different ρ^+ values for the regions of electron-donating and electron-withdrawing substituents, this was reasonably ascribed to a change from the S_N1 mechanism for the former substituents to the S_N2 mechanism for the latter substituents Since this mechanistic transition is clear we do not expect a single linear relationship for the whole range of substituents Fig 3 shows a σ^+ plot for the solvolysis in 80A[15] which is neither linear nor bilinear but displays a significantly split pattern of apparently parallel curvatures with significant gaps In contrast, the Y–T correlation (Fig 3) *vs* $\bar{\sigma}$ scale with $r=1\ 29$ gives a linear plot over a range of reactivity of 10^4 for substituents more reactive than 4-MeS-3-CN, and is connected to the concave plot covering the range of more electron-withdrawing substituents The solvolysis in the less nucleophilic 97% aqueous TFE (97T) gives a straight-line correlation with an identical r value of 1 27 for a wider range of substituents more electron-donating than the *meta* halogens [15] The enhanced r value of this solvolysis is independent of the mechanistic complexity involving nucleophilic solvent assistance in the region of electron-withdrawing substituents

2.3 Solvoyses with Low *r*-Values

β-Aryl assisted solvolyses characteristically show r values of 0 5—0 6 The solvolysis of (1-arylcyclopropyl)methyl tosylates,[16] an analogue of the neophyl system, gave an excellent Y–T correlation with an extremely low r value of 0 11, suggesting a different mechanism from that of other β-aryl-assisted solvolyses

The intrinsic resonance demand of a carbenium ion may be reduced effectively by reduced coplanarity between the reaction centre and the phenyl ring (*vide infra*) Thus a diminished r value may be observed in the solvolysis of highly congested benzylic precursors A well known example is the solvolysis of α,α-di-*tert*-butylbenzyl *p*-nitrobenzoates **8** having two bulky *tert*-butyl groups at the reaction centre [17] The application of eqn (2) affords an excellent linear correlation (Fig 4), with $\rho=-2\ 19$ and $r=0\ 26$ [17] This r value is comparable to that for the pK_a of benzoic acids on which the Hammett σ scale is based



9

The solvolysis of 4-methylbenzobicyclo[2 2 2]octen 1-yl triflates **9** would be an excellent model of such a system where any exalted π-delocalization interaction should be completely prohibited The carbocation orbital developed at the bridgehead of the bicyclic skeleton is rigidly orthogonal to the benzo π-orbital, and in addition, any back-side attack by a nucleophile is prohibited Logarithmic rates are in fact correlated directly with conventional σ^0 parameters giving $\rho=-2\ 17$ [18] Thus the substituted effect on this solvolysis can be referred to by the so-called resonance unexalted σ^0 reactivity with $r=0\ 0$, being the lowest limit of exalted π-delocalization

2.4 Highly Electron-deficient Carbocation Systems

The solvolyses of benzylic substrates carrying a strongly electron-withdrawing α-substituent (entries 26—31 in Table 1) generate highly electron-deficient carbocations[5] [19] and are expected to show highly exalted resonance demand [5] Analyses of the substituent effects in this class of solvolyses have been reported in the last 10 years [19—24]

The solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates **10** was analysed by eqn (2) [20] [21] In the Y–T plot of this reaction (Fig 5), *meta*-substituents and *para*-π-acceptors covering five orders of magnitude in reactivity fall on a single straight line, and the σ^+ plot (open circles) of the *para*-π-donor substituents deviates upwards from the correlation line The linear Y–T plot (squares) against the $\bar{\sigma}$ scale with $r=1\ 39$, *i e*, the correlation line dividing all the resonance line-segments ($\sigma^+-\sigma^0$) of *para*-π-donor substituents by an external ratio of 1 39, contrasts sharply with the poor linear plot against σ^+

Substituent effects on the solvolysis of 1-aryl-2,2,2-trifluoroethyl tosylates **11** can also be described in the same way, to give a high r value of 1 53 [22] [23]

The behaviour of the α-trifluoromethyl-α,α-diarylmethyl system **12** was also analysed by eqn (2) [24] The substituent effect on the symmetrically substituted bis-aryl derivative **12** (X=Y) can be described accurately by the Y–T relationship with $\rho=-4\ 18$ and $r=1\ 19$ The Y–T plot is linear over the whole range of substituents, indicating the absence of any mechanistic change with change in substituent The unsymmetrically substituted derivatives **12** (X,Y) with a series of fixed Y=H, *m*-Cl and *m*,*m*′-Cl₂, afford slightly bisected Y–T plots

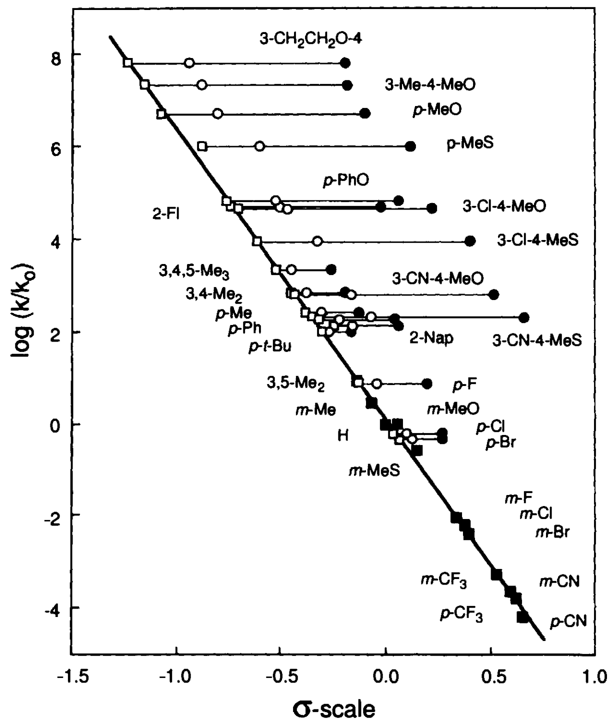


Figure 5 The Y–T plot for solvolysis of α-CF_3-α-CH_3-benzyl-OTs (**10**); $r = 1.39$. For symbols, see Fig. 1 caption. The graph is redrawn from the data in ref. 21.

with highly exalted r values; those for the electron-donating substituent range are 1.45, 1.57 and 1.69 for these Y groups. Both ρ and r values are appreciably reduced in the range of electron-withdrawing substituents in all the sets. The deviation from the linear Y–T relationship may be attributed to the deviation of the two aryl groups from coplanarity; a convincing example is afforded by the Y–T correlation of $pK_R{}^+$ for triarylmethanols. Since the r value obtained for **12** (X=Y) is reduced due to the conformation with reduced coplanarity, the resonance demand of the (hypothetical) planar system **12** should be higher than the value of unity in the α-cumenyl system.

Whereas we have achieved remarkable success with the Y–T analysis, most studies of solvolyses of this class have so far been based on eqn. (1), and it was suggested that exceptionally high ρ^+ values in the range of -10 to -12 are a characteristic feature of these highly electron-deficient carbocation-forming reactions.[23] However, as summarized in Table 2,[5,22] all these solvolyses showed significantly nonlinear Brown σ^+ correlations; $\rho^+_D = -10$ for the electron-donating range of substituents while $\rho^+_A = -5$ to -6 for the region of electron-attracting substituents.[22] Since the nonlinear relationship rules out the operation of a single mechanism for the whole range of substituents, all these solvolyses, without exception, should involve a mechanistic change with a break in the σ^+ plot in the vicinity of the unsubstituted derivative.

It is remarkable that all but one of the 19 sets in Table 2 give good linear relationships (R>0.99) against the log $(k/k_0)_{10}$ values from the solvolysis of **10** in the corresponding solvents and none shows a significantly higher slope than unity. This simple linearity suggests that the r values as well as ρ values must be very similar for these systems. For the solvolysis of $ArCH(OMs)PO_3Et_2$,[25] a good linear free energy relationship is obtained against log $(k/k_0)_{10}$ in 80T without a significant break. On the other hand, the solvolysis of $ArCH(OMs)PS(OEt)_2$[25] is the only case which shows a clear break in the plot against $\log(k/k_0)_{10}$, and it evidently indicates significant thio group participation for deactivating substrates. No mechanistic change seems to take place in any of the other reactions. An electrophilic substituent parameter $\bar{\sigma}$ scale with a high resonance demand (r=*ca.* 1.4) should be required for a proper description of the substituent effects in these extremely electron-deficient benzylic systems. A ceiling to the magnitude of the resonance demand in benzylic solvolyses appears to be an r value of 1.5—1.7.

3 Stabilities of Carbocations in the Gas Phase

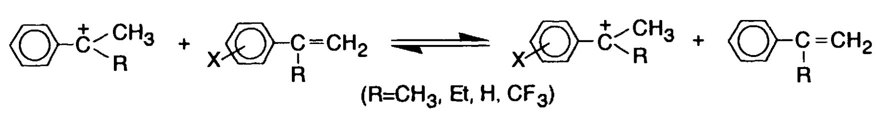
The mechanistic involvement of the solvent is an important cause of the misunderstanding of substituent effects on benzylic solvolyses. An effective approach to overcome this difficulty in the solvolytic studies, and towards a general theory of substituent effects in benzylic system directly comparable with the theoretical results, is to investigate the behaviour of carbocations in the gas phase, a medium free of solvent participation and other complicating factors. The intrinsic stabilities of benzylic carbocations have now become available from ion cyclotron resonance mass spectroscopic determinations in the gas phase.[26,27]

The relative stabilities of carbocations can be estimated from the free energy changes of the ion–molecule proton-transfer equilibria of the corresponding olefins [eqn. (5)], or those of the gas-phase

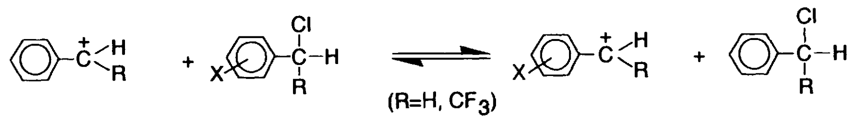
Table 2 Substituent effects in the extremely electron-deficient systems

		Brown eqn.[b]		Log k-log k eqn.[c]	
System[a]	Solv.	ρ^{+b}_D	ρ^{+b}_A	Slope[c]	R
$Ar(3,5\text{-}Cl_2C_6H_4)CCF_3$-OTs	80E	−9.6	—	1.17	0.995
$Ar(m\text{-}ClC_6H_4)CCF_3$-OTs	80E	−9.1	−4.7	1.01	0.996
$Ar(Ph)CCF_3$-OTs	80E	−7.7	−4.6	0.79	0.991
ArC(CN)Me-OMs	TFE		−6.70	0.881	0.998
$ArC(CF_3)_2$-OTs	TFA	−10.7		1.12	0.999
$ArC(CN)CF_3$-OTs	TFA	−12.1		1.32	
Ar-α-ketoNB-OTf[d]	EtOH	−5.69	−4.15	0.726	0.998
$ArC(CF_3)Me$-OTs	80E	−8.8	−6.4	1.000[e]	
$ArC(CF_3)Me$-Br		−10.3			
$ArC(SO_2Ph)Me$-OMs	MeOH	−8.0		0.921	0.9999
ArC(SOPh)Me-OMs	TFE	−7.2		0.778	0.9995
$ArCH(OMs)\text{-}P(=O)(OEt)_2$	TFE	−10.1	−6.1	0.918	0.993
	97HFIP	−10.3		1.123	0.9998
$ArCH(OMs)\text{-}P(=S)(OEt)_2$	AcOH	−7.15	−2.99	0.69[f]	0.985
				0.45[g]	0.9988
$ArCH(CF_3)OTs$	TFA		−6.7	1.05	0.993
	97HFIP	−9.1		1.020	0.994
	TFE	−9.8		1.046	0.997
	AcOH	−10.1		1.08	
	aq.EtOH	−11.9−−9.7		0.982	0.998

[a] Most of data are taken from ref. 22; otherwise see text. [b] ρ^+_D and ρ^+_A are the Brown ρ^+ values for electron-*donor* and -*acceptor* substituents, respectively. [c] Slope of logarithmic rates against the log $(k/k_0)_{10}$ for the solvolysis of $ArCMe(CF_3)OTs$ (**10**) in the corresponding solvent. [d] 2-Aryl-3-oxobicyclo[2.2.1]heptan-2-y triflates. [e] By definition. [f] More reactive than 3,4-Me_2. [g] Less reactive than 3,4-Me_2.



(5)



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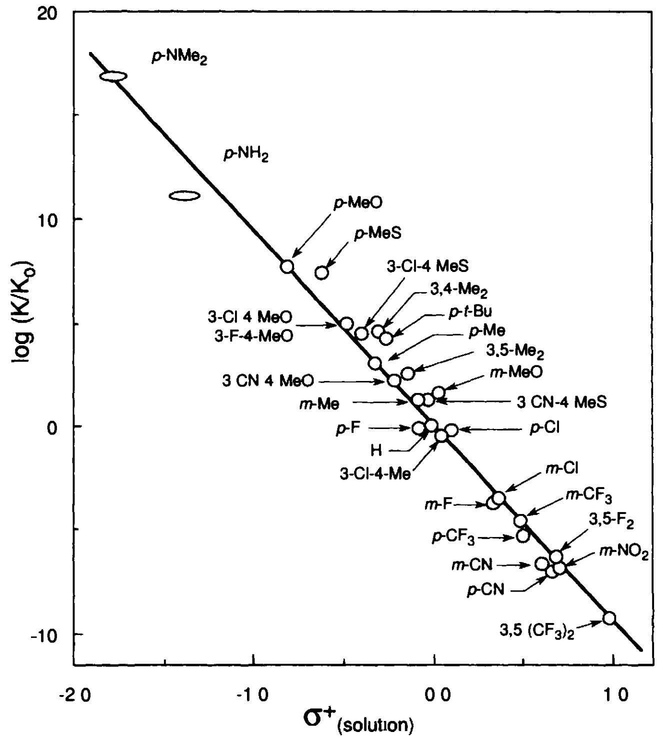


Figure 6 The plots of gas phase stabilities of substituted α cumenyl cations ($1C^+$) against Brown's σ^+ in solution. The figure is redrawn from the data in ref 26.

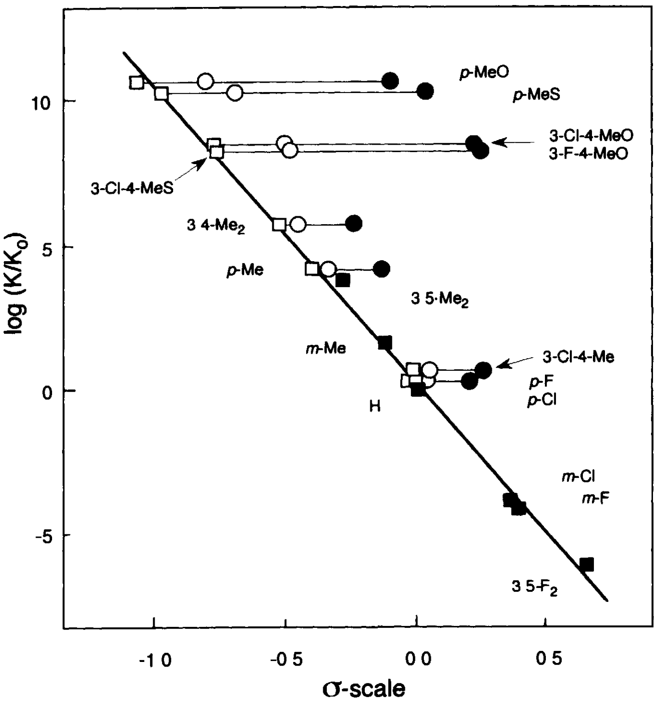


Figure 7 The Y–T plot of gas phase stabilities of substituted benzyl cations ($7C^+$), $r = 1.29$. For symbols, see Fig 1 caption. Data taken from ref 27.

halide-transfer equilibria of corresponding benzylic halides [eqn (6)].[26,27]

The substituent effect on the stability of the α-cumenyl cations $1C^+$ based on the proton transfer equilibrium of α-methylstyrenes[26] can be correlated directly with the ordinary set of solution σ^+ values (Fig 6). Unexpectedly, the correlation covering the substituent range from p-NMe$_2$ to 3,5-(CF$_3$)$_2$ is excellent, and there is no difficulty in defining the gas-phase σ^+ scale for $r = 1.00$ by using these gas-phase stabilities of substituted $1C^+$ cations.[26]

The relative stabilities of substituted benzyl cations are correlated with eqn (2) (Fig 7) with a higher resonance demand parameter $r = 1.29$ than for the cumenyl system ($r = 1.00$). This linear correlation for the whole range of substituents contrasts sharply with the concave Y–T plot (Fig 3) of the solvolytic reactivities of **7**. Furthermore, the r value for the gas-phase stabilities of $7C^+$ is identical with the value assigned for the S_N1 solvolysis of tosylates of **7**. Hence, the r value of 1.29 must be an intrinsic feature of the S_N1 solvolysis mechanism of **7**, rather than a correlational artifact of the nonlinear relation due to involvement of the solvent.

Consequently, the Y–T equation is applicable to the gas-phase substituent effects on the intrinsic stabilities of benzylic cations in exactly the same manner as it applies to the solution phase. The r value significantly increases as the stability of parent carbocation decreases, while the ρ value remains constant for a series of benzylic carbocations. It is remarkable that the resonance demand parameters characterizing the stabilities of a series of benzylic cations in the gas phase are linearly related to the intrinsic gas-phase stabilities of the parent carbocations (Fig 8). Furthermore, it is very surprising that the r value for the gas-phase stabilities of the cations and of the corresponding benzylic S_N1 solvolyses have identical magnitude (Table 3). From this linearity, the varying resonance demand in solvolysis should be an essential feature of the incipient carbocation intermediate as well as of the solvolysis transition state. The r value of benzylic solvolyses should be essential in the intrinsic resonance demand of generated cations, which should in turn depend on the instability of the cation. The r value for the solvolysis of α-cumenyl chlorides, which generates a higher stable tertiary benzylic carbocation, should be in the lowest range of the r values for benzylic solvolyses. Consequently, any ordinary benzylic solvolysis should rarely show an r value significantly lower than unity. More stable carbocation systems showing significantly low resonance demand from the aryl group will be those having strongly electron-donating α-substituents, *e.g.*, —OR, —NR$_2$ *etc.* Significantly low r values as well as identity between solution and gas phase r values have also been observed in the protonation equilibria ($pK_{BH}{}^+$ values) of benzoyl compounds.[28] However, solvolytic reactions of benzoyl derivatives are often complicated by subsidiary reactions of the highly polar α-substituents.

The gas-phase stability of the ethylene-phenonium ion $3C^+$ and its ring substituted derivatives has also been determined by the bromide-transfer equilibria [analogous to eqn (6)] of β-arylethyl bromides and gave an excellent Y–T correlation with $\rho = -12.8$ and $r = 0.60$ (Fig 9).[29] The ρ value is significantly larger than those observed for benzylic carbocations, but is similar to that obtained for the stabilities of benzenium ions.[29] It should be particularly noted that the r value of 0.60 is identical with the value observed for the corresponding solvolysis which proceeds *via* an intermediate phenonium ion.[6–11]

Clearly, there is a continuous spectrum of intrinsic resonance demand of the stabilities of benzylic carbocations in the gas phase

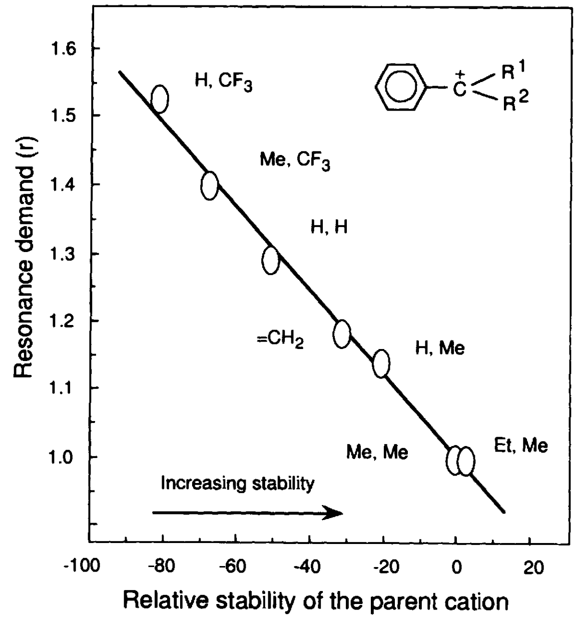


Figure 8 Plot of the *r* values for gas-phase cation stabilities against the stabilities of parent cations. Reproduced with permission from *Chem. Lett.*, 1992, 1085.

Table 3 Yukawa–Tsuno correlations for the gas-phase stabilities of benzylic cations

α-Rs in benzylic cation	$\Delta G_0{}^a$	Y–T-correlation ρ_g	r_g	r_{solv}
CF_3,H	81.6	−10.6	1.53	1.53
CF_3,Me	67.8	−10.2	1.40	1.39
H,H	51.0	−10.3	1.29	1.29
$H_2C{=}C^b$	31.4	−10.2	1.18	
H,Me	21.8	−9.9	1.14	1.15
Me,Me	0.0	−9.5	1.00	1.00
Me,Et	−1.7	−9.5	1.00	1.04
Me,Bu^t	4.6	−9.1	0.86	0.91
$CH_2{-}CH_2{}^c$	41.8	−12.8	0.60	0.63

[a] Relative stability of respective parent carbocations estimated from proton-transfer or chloride-transfer equilibria, in kJ mol^{-1}. [b] α-Arylvinyl cation Ar-$C^+{=}CH_2$. Ethylenephenonium ion $3C^+$.

This leads to the important conclusion that the resonance demand characterizing the S_N1 solvolytic transition state should in principle be determined by the intrinsic resonance demand of the carbocation intermediate.

4 Relation between *r* and Molecular Structure Parameters

The characteristic change of the *r* value in the solvolysis reaction and for the corresponding carbocation should provide important information concerning the solvolysis transition state. The value of *r*, reflecting the π-delocalization within the cationic species, appears to remain essentially the same in solution as in the gas phase, and the degree of charge delocalization in the transition state of the solvolytic ionization should also resemble that in the carbocation intermediate. Moreover, the *r* value is directly related to the intrinsic stability of the parent cation. Thus, *ab initio* calculations can be used to find the underlying relationship between quantum chemical quantities and experimental *r* values.[30] The relation between the *r* values and theoretical indices provides the basis for the physical meaning of the *r* parameter.

For a series of benzylic cations, several bond lengths, optimized at the RHF/6–31G* level, are plotted against the *r* values in Fig. 10. The $C^1{-}C^7$ bond length decreases significantly with increased resonance demand. As the *r* value increases, the $C^1{-}C^2$ and $C^3{-}C^4$ bonds are lengthened, but the $C^2{-}C^3$ bond is shortened. The $C^1{-}C^7$ bond length at $r{=}0$ is estimated to be 1.52 Å, which is close to the normal C–C single bond length, whereas at $r{=}1.51$ the $C^1{-}C^7$ bond length is 1.35 Å which is close to the normal C=C double bond length. The $C^1{-}C^2$, and $C^2{-}C^3$ and $C^3{-}C^4$ bond lengths at $r{=}0$ are all identical, being 1.39 Å, similar to the benzene C–C bond length. The Wiberg bond order also changed consistently with the corresponding bond

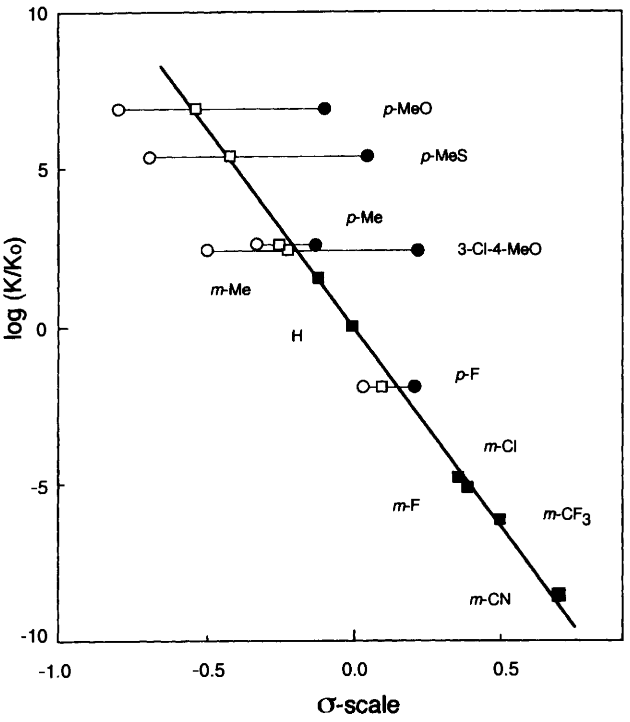


Figure 9 The Y–T plot of the stabilities of gas-phase phenonium ions; $r{=}0.60$. For symbols, see Fig. 1 caption. The graph is redrawn from the data in ref. 29.

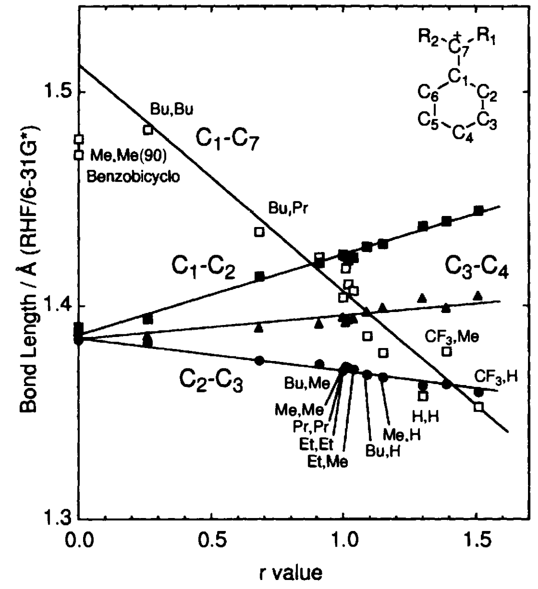
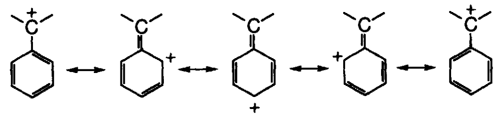


Figure 10 Bond lengths *vs*. *r* values for benzylic cations. Data taken from ref. 30.



I II III IV V

Scheme 5

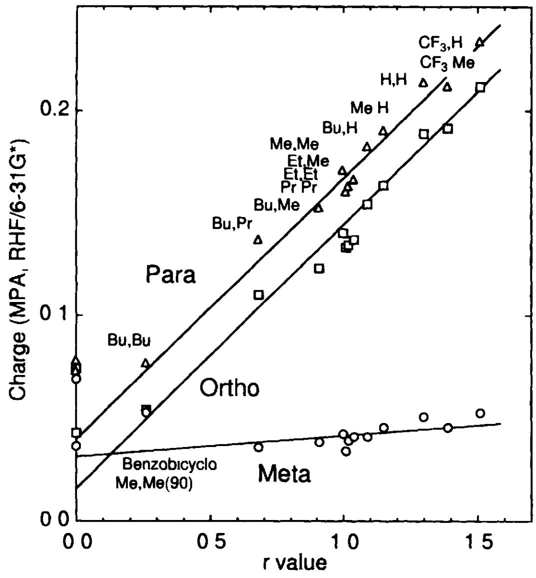


Figure 11 Mulliken population at *ortho*, *meta* and *para*-positions of phenyl ring (RHF/6-31G*) *vs* *r* values for benzylic cations. Data taken from ref 30.

lengths. The C^1-C^7 bond length or bond order at $r=0$ clearly reflects contribution from structures I and V.

The contributions of resonance structures II–IV become more important on increasing the resonance interaction between the benzylic pπ orbital and the benzene π system. This tendency reveals that the *r* value changes linearly with the degree of overlap between the two orbitals, thus reflecting the relative importance of the contribution of canonical structures I–V. The behaviour of *r* is completely consistent with what is envisaged for the resonance demand, indicating that the varying resonance interaction between C^7 and the aromatic moiety changes in parallel with the *r* value.

The Mulliken charge distribution at the respective atomic positions should be regarded as reflecting the demand of the α-cationic centre of benzylic carbocations for the π-electron delocalization from those atomic positions and should be directly related to the *r* value. As seen in Fig. 11, there are linear correlations of the charge populations as the *para-* and *ortho*-position against the *r* value but there is no significant change in the population at the *meta*-position. As the *r* value increases, the charge at the *para*-position increases significantly to +0.2 at $r=1.5$, whereas the charge at the *meta*-position changes much less. This trend of charge delocalization for benzylic cations is consistent with the varying degree of the resonance stabilization. Deviations are significant for the two cations **9C**$^+$ and **1C**$^+$ (90° twisted) at $r=0$, in which the benzylic pπ orbitals and the benzene π orbitals are orthogonal, the bonding σ orbitals of the α-substituents and the benzene π^* orbital are in the approximate conformation for overlap and the deviation may be attributed to the mixing of these two orbitals.

5 Steric Loss of Resonance Interaction

The variation of the *r* parameter has been discussed in terms of the varying extent of substituent–reaction site resonance interactions from one reaction series to another. The carbenium-like orbital in the transition state for the solvolysis of a benzylic substrate carrying two bulky α-alkyl groups may be twisted out of coplanarity, as exemplified by the solvolysis of **8**,[17] resulting in a markedly reduced *r* value. The observation of steric control of resonance demand is also important in clarifying the origin of the *r* value in the Yukawa–Tsuno correlation.

The degree of steric inhibition of resonance largely depends on the bulk of the α alkyl substituents.[31] The efficiency of resonance interaction should be proportional to $\cos^2\theta$, where θ is the dihedral angle between the two overlapping p orbitals as in equation (7).

Table 4 Calculated Torsional Angles (θ degree) between Alkyl Groups and Benzene Ring

Ar C$^+$R^1,R^2		θ_{calc}			θ_{expt}^{a}
R^1	R^2	3-21G	6-31G*	MP2(FU)/6-31G*	
Me	Me	5	5	7	0
Bu^t	Me	24 (14)^c	24 (15)^c		17(22^b)
Bu^t	Pr^i	37	33		32
Bu^t	Bu^t	77 (63)^c	76 (60)^c	69	59
BBCO^{+d}		90	90		90

^{a} Given by $r/r_{max}=\cos^2\theta$ where $r_{max}=1.00$ for planar α,α-dimethylbenzyl system. ^{b} Based on gas phase data. ^{c} For the *p*-MeO derivative. ^{d} 4-methylbenzobicyclo[2.2.2]octen-1-yl cation **9C**$^+$.

$$r=r_{max}\cos^2\theta \qquad (7)$$

where r_{max} is the intrinsic *r* for the coplanar *tert*-benzylic system, given by $r=1.00$ for the α,α-dimethylbenzyl system. The *r* values and the dihedral angles θ based thereon are compared in Table 4 for a series of α,α-dialkylbenzylic precursors.

The gas-phase stabilities of α-*tert*-butyl-α-methylbenzyl cations have been found to be correlated linearly by eqn (2) with $r=0.86$,[32] a value close to $r=0.91$ derived from the solvolysis.[32] The similarity between the empirical *r* values for the solvolysis transition state and the corrresponding gas-phase cation appears to comprise both sterically twisted and untwisted systems. The optimized structure of the carbenium ion derived from theoretical calculations should be able to model that of the solvolytic transition state as well as the intermediate immediately following it.

All the dihedral angles of the twisted *tert*-benzylic cations in the optimized structures (Table 4) are in good agreement with the 'experimental' angles of the solvolysis transition states deduced from eqn (7).

In the 6-31G* optimized structure of the carbenium ion **8C**$^+$, the calculated dihedral angle of 76° for the unsubstituted ion is lower than the angle estimated from the solvolysis *r* value, whereas the calculated angle of 60° in the optimized structure of *p*-methoxy-**8C**$^+$ is in a better agreement with it. This is as expected since the enhanced delocalization by the *p*-methoxyphenyl groups should increase its coplanarity with the reaction centre and hence the *r* value for the solvolysis of **8** should be slightly higher (see Fig. 4).

The close similarity between the theoretically calculated and the empirically observed dihedral angle assigned for twisted benzylic systems corroborates the characterization of the empirical parameter *r* in the Yukawa–Tsuno equation as a parameter reflecting the degree of π-delocalization interaction between the aryl group and the reaction site.

6 Varying Resonance Demand in Solvolyses

The characteristic change of the *r* value in both the solvolysis reaction and the corresponding carbocation provides important information concerning the solvolysis transition state.

In a typical two-step S_N1 mechanism with a single dominant transition state, the *r* values of closely-lying transition states for the various nucleophile–cation reactions should all be predominantly controlled by the intrinsic resonance demand of the intermediate cation, the substituent effect should be described by a single scale of substituent constants ($\bar{\sigma}$) with an *r* value characteristic of the system. In fact, in a recent laser flash photolysis study on the recombination of stable trityl and benzhydryl carbocations with nucleophiles and solvents,[33] McClelland *et al* have demonstrated that the substituent effects on the solvent-recombination processes can be correlated by eqn (2) with the same *r* values observed in the solvolyses and with smaller ρ values. The effect of the coplanarity change was also observed similarly.[33] The identity of *r* values has been recognized also in various benzylic cation–nucleophile recombination reactions.[34]

These facts imply that either the reverse of the k_c ionization or the recombination step of the carbocation with various nucleophiles should be described by a Y–T $\bar{\sigma}$ scale with the same r value as for the ionization step This is reminiscent of the Ritchie N_+ relationship of constant susceptibility to the nucleophile regardless of the cation,[35] which requires that the ρ for the recombination reaction with any nucleophile should be a constant of the cation regardless of nucleophile

The energy profile in the vicinity of the transition state and the intermediate in the solvolysis process should be essentially noncrossing For solvolyses involving higher endothermic ionization processes, the Hammond shift in the transition state coordinate relative to the intermediate is reflected almost exclusively in the ρ value, without affecting the r value The Brønsted-type analysis, the so-called rate–equilibrium relationship in terms of a common Y–T $\bar{\sigma}$ scale, can be applied precisely for systems involving an appreciably wide shift of solvolytic transition states

For the uniform applicability of eqn (2) with either a non-unity or a non-zero r value, Johnson suggested that the reaction conforming to the Y–T equation with $r \neq 1\ 00$ may be a two-step process

$$A \overset{K_1}{\rightleftharpoons} [B] \xrightarrow{k_2} [C] \rightarrow$$

involving a pre-equilibrium K_1 followed by a rate-determining k_2 step where one of these steps correlates with σ^0 (or σ) and the other with σ^+ [eqn (8)] [4]

$$\log k/k_0=\rho_1\sigma^0+\rho_2\sigma^+=(\rho_1+\rho_2)(\sigma^0+\frac{\rho_2}{\rho_1+\rho_2}\Delta\bar{\sigma}^+_R) \qquad (8)$$

Whereas this scheme is logically capable of reproducing the Y–T correlations, this cannot be general as the cause of observing non-unity r values, since we can generally find widely varying resonance demand for the intrinsic stabilities of benzylic cations in the gas phase

As the Y–T equation implies, the unification of a substituent parameter scale in terms of varying r leads to a unique additivity relationship of substituent effects, for the system of $k=k_1\ k_2\ \ k_j$ [eqns (9a) and (9b)]

$$\sum(\log k/k_0)_j=\sum\rho_j\sigma^0+\sum\rho_j r_j\Delta\bar{\sigma}^+_R \qquad (9a)$$

$$=\rho'(\sigma^0+r'\Delta\bar{\sigma}^+_R) \qquad (9b)$$

where $\rho'=\sum\rho_j$ and $r'=\sum\rho_j r_j/\sum\rho_j$ Eqns (9a) and (9b) allow in theory the assignment of any reasonable r_j value for each step Thus, for the above overall pre-equilibrium mechanism, the overall substituent effect can be represented as a single linear Y–T correlation with an apparent r' value, the Johnson pre-equilibrium scheme is a special case of $r_1=0$ and $r_2=1\ 00$, which cannot be general [5] It is of great importance that this equation can be applicable also to the simultaneous contribution of different substituent effects on a single reaction step We have already discussed additivity of the substituent effects on the solvolysis of bis-arylethyl tosylates **4**(X=Y)

The simple additivity inherent in the Y–T relationship makes eqn (2) a useful tool for analysis of reaction mechanisms, but at the same time caution should be exercised in order to avoid its interpretation being misleading

In conclusion, we want to emphasize that in spite of the wide spectrum of observed r values the intrinsic resonance demand is an inherent property of the intermediate or the transition state of respective reactions, and is therefore characteristic of the structure of intermediate This is the basis of mechanistic analysis by using the Yukawa–Tsuno relationship

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