Substituent Effects on Chloride Transfer Equilibrium in the Gas Phase. Intrinsic Resonance Demand of Benzyl Cation[1)]

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Relative chloride ion affinities of 48 carbocations have been measured by the chloride ion transfer equilibrium of benzyl chlorides in the gas phase. The substituent effects on the chloride affinity of benzyl cation have been analyzed in terms of the LArSR Eq., giving a $\rho=-14.0$ and an $r^+=1.29$. The r^+ value higher than the corresponding value of unity for the α-cumyl(2-phenyl-2-propyl) cation clearly indicates that the benzyl cation has an enhanced resonance demand in the intrinsic carbocation stability compared with that of the α-cumyl one. Most importantly, the unique r^+ value of 1.29 for the gas-phase benzyl cation stability has been found to be identical with the value observed for the k_c ionization process of the solvolysis of the activating substituent range of benzyl tosylates. The identity of the r^+ value, which is consistent with previous observations for the relevant benzylic carbocation systems, suggests that the intramolecular charge-delocalization in the transition state of the k_c solvolysis should be quite close to that of the carbocation intermediates. It is concluded that the exalted r^+ value observed for the k_c solvolysis of benzyl tosylates is not a correlational artifact arising as a result of the non-linearity caused by the k_c–k_s mechanistic transition but is due to the enhanced resonance stabilization of the benzyl cation compared with the α-cumyl cation.

The LArSR Eq. 1 has been widely applied to a series of benzylic solvolyses in which a positive charge is generated at the conjugative position with the aryl group.[2—6)]

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

The r^+ value indicates a degree of π-electronic interaction between aryl substituents and the charge of a reaction center. This resonance demand (r^+) was found to vary significantly with the system; e.g., from $r^+=1.00$ for the solvolysis of α-cumyl(2-phenyl-2-propyl)-chlorides to 1.39 for 1-phenyl-1-(trifluoromethyl)ethyl tosylates.[4)] Thus the r^+ value has provided quite important information on the structure of the transition state, the charge-delocalization into an aryl ring. The resonance demand of the S_N1 solvolysis of the benzyl substrate is of particular interest as a reference benzylic cation system and also as a system giving an unstable primary carbocation, in which there is current interest.[7)] Moreover, much attention is given to the reaction mechanism itself of the benzyl solvolysis because the substituent effect for the solvolysis of benzyl substrates is generally nonlinear behavior due to the solvent nucleophilic participation to this system, i.e., a change in reaction mechanism from S_N1 for the activating substituent range to S_N2 for the deactivating one.[6—11)] A mechanistic transition with a change of substituent may bring about inevitable difficulties in the correlation analysis of the substituent effect based on the LArSR Eq. 1. This point has been stressed as the cause of obscurity of the physical significance of the r^+ value from a standpoint of a single parameter analysis using σ^+ substituent constant corresponding to $r^+=1.00$ in the LArSR Eq. 1.[12)] Shorter noted that the pronounced deviation from conformity to σ^+ in a direction to $r^+\gg 1.0$ in benzyl solvolysis is considered to be due to the changing proportion of S_N1 and S_N2 mechanisms, and the r^+ value, if calculated, would not give information on the resonance stabilization of the benzyl cation.[13)] However, a mechanistic shift with a change of substituent is completely independent of whether the resonance demand for the S_N1 solvolysis of the benzyl system is comparable to that of the α-cumyl solvolysis. It would be possible to apply the LArSR Eq. 1 to a limited range of the substituent effects for the benzyl solvolysis, the electron donor substituent region where the solvent nucleophilic participation is not important. An r^+ of 1.3 and a ρ of -5.2 were in fact obtained for the acetolysis of benzyl tosylates thereby.[6a)] Thus, the k_c process via benzyl cations was characterized by a unique r^+ value higher than unity for the formation process of α-cumyl cations.

Thermodynamic stabilities of carbocations have recently become available from studies on ion-molecule equilibria in gas-phase.[14—20] The equilibrium constants are determined by the free energy difference between neutral ground state and charged molecules, mostly by the free energy of the charged molecule, and of course are absolutely free from mechanistic complexities arising from mechanistic involvement of solvent as nucleophile, i.e., a mechanistic shift from S_N1 to S_N2. Such gaseous thermodynamic stabilities of carbocations will provide important and decisive information on the inherent nature of carbocations that correspond to the intermediates and/or on the transition state of the k_c ionization process of the solvolysis. It will, therefore, be highly instructive to study the substituent effect on the stability of benzyl cation in the gas phase to clarify the real features of the substituent effect for the k_c ionization process of the benzyl substrates. This will also be a critical test for the reality and physical significance of the r^+ value for a reaction with accompanying mechanistic transition with a change of ring-substituent.

Most of data on intrinsic carbocation stability have come from gas-phase proton-transfer equilibrium between a carbocation and the corresponding olefin.[14,15,17] However, this method cannot be applicable to the case of primary carbocations like benzyl cations. Recent comprehensive studies on gas-phase ion-molecule reacions suggest that the chloride-transfer equilibrium (2) as well as the hydride-transfer equilibrium can be used for estimation of intrinsic stabilities of carbocations, and that the chloride-transfer equilibrium has some advantages over the hydride-transfer equilibrium such as the well-defined position of the positive charge in the molecule and the faster rate of attainment of equilibrium.[21—24)

(2)

In this work, we have measured relative chloride ion affinities for a series of benzyl cations together with a variety of alkyl cations. The substituent effect on the intrinsic stability of the benzyl cation has been analyzed in terms of the LArSR Eq. 1, and compared with that of the solvolysis of benzyl tosylates.

Results and Discussion

The standard free energy changes of chloride transfer equilibria (2) have been measured by the equilibrium constants with a pulsed ion cyclotron resonance (ICR) mass spectrometer at 343 K. Experimental data for the free energy changes of *m,p*-substituted benzyl cations and several relevant carbocations have been obtained based on overlapping equilibria between carbocations of nearly equivalent chloride affinity strengths as presented in Fig. 1. The scale covers a range of 28 kcal mol^{-1} from 3,5-*bis*(trifluoromethyl)benzyl cation to 1-(3,4-dimethylphenyl)ethyl cation. The internal consistency of the overlaps is better than ±0.2 kcal mol^{-1} in most cases. Chloride ion affinity values of several benzyl cations are available from the literature.[21,22] Those values were measured by a pulsed high pressure ion-source mass spectrometer (HPMS) at quite high temperature (600 K). Chloride ion affinity values of substituted benzyl cations relative to *t*-butyl cation obtained by Kebarle et al. using HPMS as well as the corrected values at 300 K tend to be greater by 1 to 2 kcal mol^{-1} compared to the corresponding values obtained in this study at 343 K. Although the causes of these discrepancies are not clear, this analysis of the substituent effect has been done only on the basis of data obtained in this study because of the good consistency of the overlaps for the entire range of chloride affinities.

Chloride ion affinities have been also measured for several substituted 1-phenylethyl cations, α-cumyl cation, and 1-phenyl-1-(trifluoromethyl)ethyl cation, of which relative stabilities were independently estimated from the gas-phase basicity measurement of the corresponding olefins (styrenes) based on the proton-transfer equilibrium. Both results are listed in Table 1. We can see that the relative chloride ion affinity of 1-phenylethyl cation is in good agreement with the corresponding basicity of styrene.

$$C_6H_5CH(CH_3)Cl + t\text{-}C_4H_9^+ \rightleftharpoons C_6H_5CH(CH_3)^+ + t\text{-}C_4H_9Cl \qquad -\Delta G^\circ = 7.7\ \mathrm{kcal\,mol^{-1}} \tag{3}$$

$$C_6H_5CH{=}CH_2 + t\text{-}C_4H_9^+ \rightleftharpoons C_6H_5CH(CH_3)^+ + (CH_3)_2C{=}CH_2 \qquad -\Delta G^\circ = 7.5\ \mathrm{kcal\,mol^{-1}}\ ^{29)} \tag{4}$$

The same is true for other substituted 1-phenylethyl cations, α-cumyl cation, and 1-phenyl-1-(trifluoromethyl)ethyl cation. There is indeed an excellent linear relationship between these quantities as shown in Fig. 2, suggesting that the chloride ion affinity values of carbocations and proton affinities of the corresponding olefins have an identical response to substituent perturbation. Therefore, free energy changes of the chloride-transfer equilibrium and the proton-transfer equilibrium will be equally referred to the relative stabilities of carbocations in the gas phase. Combining both results obtained from proton-transfer and chloride-transfer equilibria, we can find a spectrum of intrinsic stabilities of benzylic carbocations which varies significantly over 16 kcal mol^{-1} with substituent(s) attached to the central carbon atom.

R^+	$PhC(Me)_2^+ >$	$PhCHMe^+ >$	$PhCH_2^+ >$	$t\text{-}Bu^+ >$	$PhC(CF_3)Me^+$
kcal mol^{-1}	12.4	7.5	0.2	0.0	−3.8

This variation in stability of benzylic carbocations would primarily be referred to the electronic effect

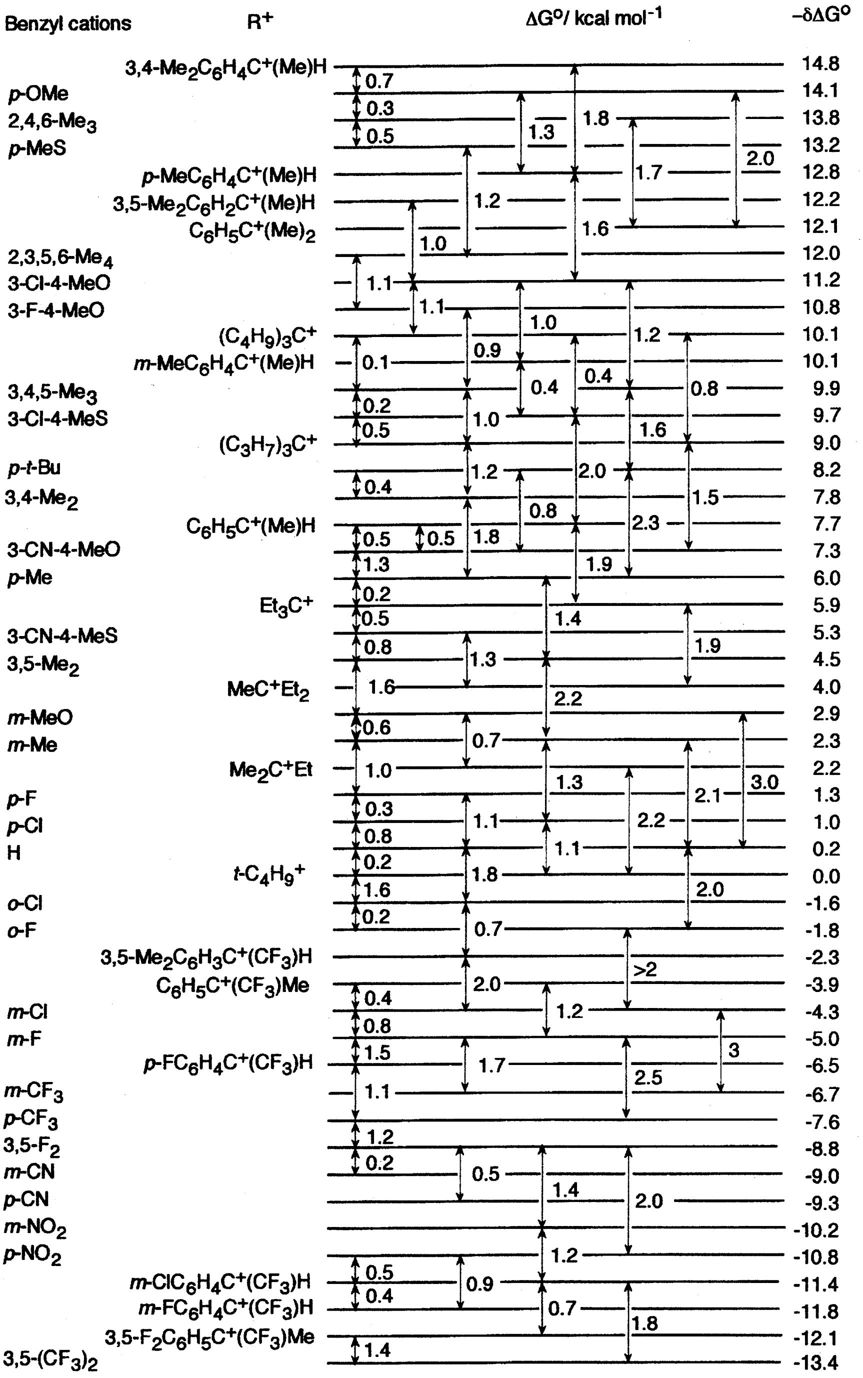

Fig. 1. Ladder of ΔG° values for chloride transfer equilibria measured at 343 K. Chloride ion affinity increases and stability of R^+ decreases from top to bottom. Selected chloride ion affinity values relative to t-butyl cation are given in the last column.

of α-substituent(s), i.e., the electron-withdrawing α-substituent(s) destabilizes a carbocation.

The relative stabilities of representative m,p-substituted benzyl cations to the unsubstituted one are summarized in Table 2. For the correlation analysis of the gas-phase substituent effects, a unique set of substituent constants very different from those in solution may be required. However, recently we have shown that the substituent effect on the gas-phase basicity of α-methylstyrene, which can be directly referred to the relative stabilities of α-cumyl cations, is excellently described by the ordinary set of σ^+ values determined in solution.[26] There seems to be no difficulty in defining a gas-phase σ^+ scale by this set of stabilities of substituted α-cumyl cations. Accordingly, the plot of relative stabilities of substituted benzyl cations against those of the corresponding α-cumyl cations shown in Fig. 3 can be regarded as the gas-phase σ^+-plot. We can clearly see that there is neither a simple linear relationship nor a monotonic curvature as seen for the substituent effect on the

Table 1. Relative Stabilities of Various Carbocations Determined from Proton and Chloride Transfer Equilibrium in the Gas Phase

Type of equilibrium	$-\delta\Delta G^\circ$/kcal mol^{-1}					
	1-Phenylethyl cations				α-Cumyl cation	1-CF$_3$-1-Phenyl ethyl cation
	H	*m*-Me	3,5-Me$_2$	*p*-Me		
Chloride transfer[a]	7.7	10.1	12.2	12.8	12.1	−3.9
Proton transfer[b]	7.5[c]	9.2[c]	11.4[c]	12.5[c]	12.6[d]	−3.6[e]

a) Free energy changes of a reaction; $ArC(R)MeCl+Me_3C^+ \rightleftharpoons ArC(R)Me^+ + Me_3CCl$.
b) Free energy changes of a reaction; $ArC(R)=CH_2+Me_3C^+ \rightleftharpoons ArC(R)Me^+ + Me_2C=CH_2$, where R=H, Me, CF$_3$. c) Ref. 30. d) Ref. 25. e) Ref. 27.

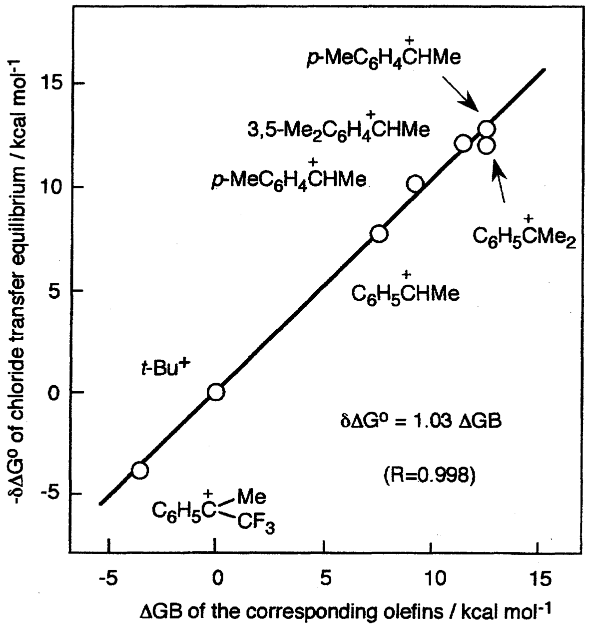

Fig. 2. Comparison between chloride ion affinities of carbocations and gas-phase basicities of the corresponding olefins.

solvolysis of this system[6] and that there is no common set of σ^+ substituent constants for the substituent effects on the gas-phase carbocation stabilities. In this figure, a good linear relationship with a slope of unity is observed for *meta* substituents and *para* π-electron attracting substituents, but all *para* π-donor substituents significantly deviate upward from the line of unit slope. The linear relationship with unit slope for non-conjugative substituents clearly suggests the same contribution of inductive/field effects to both systems. Therefore, significant deviations of *para* π-donor substituents must be due to different contribution of resonance effect between both systems. In fact, a close examination has shown that the deviations of *para* π-donors are systematic and indicate a greater stabilization by the stronger *para* π-donor substituents. Such a pattern of deviations of *para* π-donors is just what would be expected for the system of an enhanced resonance demand. Indeed, the deviations of *para* π-donors of the benzyl cation can be accurately related to the resonance substituent parameter, $\Delta\bar{\sigma}^+_R$, defined from reactivities in solution[4] with a correlation coefficient of 0.998 and a standard deviation of ±0.47 (n=23).

$$-\delta\Delta G^\circ_{\text{benzyl cation}} = 1.06(-\delta\Delta G^\circ)_{\alpha\text{-cumyl cation}} - 4.24\Delta\bar{\sigma}^+_R + 0.2$$

The effect of the p-t-butyl group on the stability of benzyl cation is unexpectedly great compared with that of the corresponding α-cumyl cation regardless of its small resonance effect. This may not be surprising because the positive charge of carbocations in the gas phase is significantly stabilized through charge-induced dipole interaction, i.e., the highly polarizable substituents can substantially stabilize the benzyl cation while this effect is not important in solution.[28,29] Excluding these particular substituents, the LArSR Eq. 1 can be equally applicable to treatment of the gas-phase substituent effect, and the benzyl cations must have an enhanced resonance demand in the intrinsic carbocation stability compared with that of the α-cumyl cation. Using gas-phase substituent constant values listed in Table 3, which are slightly modified from standard values owing to no specific substituent–solvent interaction,[26] the LArSR analysis provides an excellent correlation as shown in Fig. 4. An r^+ of 1.29 and a ρ of −14.0 obtained by this correlation are practically in complete agreement with the values given by standard substituent constants. The r^+ value of 1.29 higher than the value of unity for the α-cumyl cation clearly shows that the contribution of resonance effects of *para* π-donors involved in the substituent effect on the stability of carbocations is increased in the benzyl cation system compared with that in the α-cumyl cation. Since the unsubstituted benzyl cation is significantly less stable by 12 kcal mol^{-1} than the corresponding α-cumyl cation as noted above, this result leads to a suggestion that the more electron-deficient carbocation seems to have the greater resonance demand. This trend is consistent with previous observations for relevant benzylic carbocations as summarized in Table 4. The rather stable 1-phenylethyl carbocation has an r^+ value of 1.14, which is just in-

Table 2. Relative Stabilities of Benzyl Cations and the Corresponding α-Cumyl Cations in the Gas-Phase

	$-\delta\Delta G^\circ$/kcal mol^{-1}				
Subst.	Benzyl[a]	α-Cumyl[b]	Subst.	Benzyl[a]	α-Cumyl[b]
p-OMe	13.9	10.5	*p*-F	1.1	−0.1
3-Cl-4-OMe	11.0	6.7	*m*-F	−5.2	−5.1
3-F-4-OMe	10.6	6.7	*p*-Cl	0.8	−0.4
3-CN-4-OMe	7.1	3.0	*m*-Cl	−4.5	−4.7
p-SMe	13.0	10.0	*p*-CF$_3$	−7.8	−7.2
3-Cl-4-SMe	9.5	6.2	*m*-CF$_3$	−6.9	−6.3
3-CN-4-SMe	5.1	1.7	*p*-CN	−9.5	−9.5
m-OMe	2.7	2.1	*m*-CN	−9.2	−9.0
p-Me	5.8	4.1	3,5-F$_2$	−9.0	−8.5[c]
p-*t*-Bu	8.0	5.8	*p*-NO$_2$	−11.0	—
m-Me	2.1	1.8	*m*-NO$_2$	−10.4	−9.4
3,4,5-Me$_3$	9.7	—	3,5-(CF$_3$)$_2$	−13.6	−12.6
3,4-Me$_2$	7.6	6.1[c]	H	0.0	0.0
3,5-Me$_2$	4.3	3.5		(0.2)[d,e]	(11.9)[d]

a) Free energy changes of reactions, $ArCH_2Cl + C_6H_5CH_2^+ \rightleftharpoons ArCH_2^+ + C_6H_5CH_2Cl$.
b) Free energy changes of reactions, $ArC(Me){=}CH_2 + C_6H_5C(Me)_2^+ \rightleftharpoons ArC(Me)_2^+ + C_6H_5C(Me){=}CH_2$, Ref. 26.
c) Determined in this study. 3,4-Me$_2$; $\Delta G^\circ = 1.2$, -0.2, and -0.9 kcal mol^{-1} relative to 2-chloropyridine, trimethyl phosphate, and 2-pyrrolidone, respectively. 3,5-F$_2$; $\Delta G^\circ = 1.0$, -0.3, -1.6, and -2.8 kcal mol^{-1} relative to dimethyl carbonate, tetrahydrofuran, methyl acetate, and acetone, respectively.
d) Relative to *t*-butyl cation. e) $-\delta\Delta G^\circ$ values of 1.2 kcal mol^{-1} (303 K) and -0.2 kcal mol^{-1} (300 K) were reported (Refs. 22 and 23, respectively).

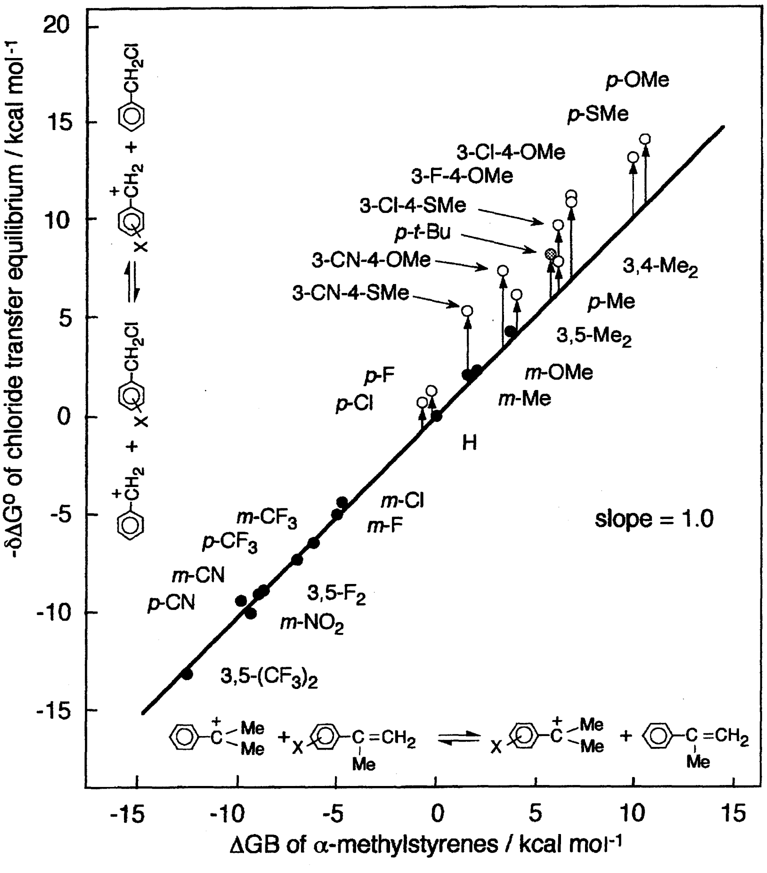

Fig. 3. Plots of relative stabilities of substituted benzyl cations against relative gas-phase basicities of the corresponding α-methylstyrenes.

Table 3. Substituent Constants Used for the LArSR Analysis of Gas Phase Substituent Effects

Subst.	σ° (g)	$\Delta\bar{\sigma}_R^+$ (g)	Subst.	σ° (g)	$\Delta\bar{\sigma}_R^+$ (g)
p-OMe	−0.10	−0.70	*p*-F	0.20	−0.17
3-Cl-4-OMe	0.22	−0.72	*p*-Cl	0.20	−0.15
3-F-4-OMe	0.22	−0.72	*m*-F	0.39	0.00
3-CN-4-OMe	0.47	−0.73	*m*-Cl	0.36	0.00
p-SMe	0.04	−0.73	3,5-F_2	0.65	0.00
3-Cl-4-SMe	0.25	−0.73	*m*-CF_3	0.50	0.00
3-CN-4-SMe	0.60	−0.73	*p*-CF_3	0.56	0.00
p-Me	−0.13	−0.20	*m*-CN	0.69	0.00
3,4-Me_2	−0.24	−0.21	*p*-CN	0.73	0.00
3,5-Me_2	−0.28	0.00	*m*-NO_2	0.73	0.00
m-Me	−0.12	0.00	*p*-NO_2	0.80	0.00
H	0.00	0.00	3,5-$(CF_3)_2$	0.98	0.00

termediate between the benzyl cation and the α-cumyl cation,[30] and the highly electron-deficient 1-phenyl-1-(trifluoromethyl)ethyl cation has an r^+ value of 1.40 higher than that for benzyl cation.[27] It is clear that the r^+ value varies substantially with the intrinsic stability of respective parent benzylic carbocations while the ρ value remains surprisingly constant in magnitude among these benzylic carbocations. A similar trend of the resonance demand was observed for a series of substituent effects on the gas-phase stability of conjugate acid ions of benzoyl systems, $ArC(OH)Y^+$: ρ and r^+, respectively, for Y=CF_3;−11.5; 1.20, H;−12.1; 1.04, Me;−12.3; 0.78, OMe;−11.9; 0.45, and NMe_2;−12.7; 0.23.[31] These facts are fully consistent with the basic concept of varying resonance demand. Thus the resonance demand is an inherent characteristic of each benzylic carbocation itself, and the primary unstable benzyl cation has been characterized evidently by a unique r^+ of 1.29 distinctly higher than the r^+ values of the tertiary α-cumyl cation and the secondary 1-phenylethyl cation.

It is highly instructive to compare this result for the gas-phase stability of benzyl cation with the solvolysis reactivity of benzyl tosylates. Substrates with activating substituents are considered to proceed predominantly through the k_c ionization process.[10] The ρ value of −5.2 obtained for the acetolysis of benzyl tosylates[6a] is significantly smaller than that for the gas-phase stabilities of benzyl cations. This may be attributed to the reduced positive charge in the rate-determining transition state due to effective solvation. Most important is the fact that the r^+ value for the acetolysis of benzyl tosylates is identical with the value of 1.29 obtained for the gas-phase stabilities of benzyl cations. This also is the case for relevant benzylic systems of which the solvolysis is well-defined as a k_c mechanism.[27,30] Similarly, the identity of the r^+ value between gas and solution phases was observed for the substituent effects on the basicity of benzoyl compounds where the chemical

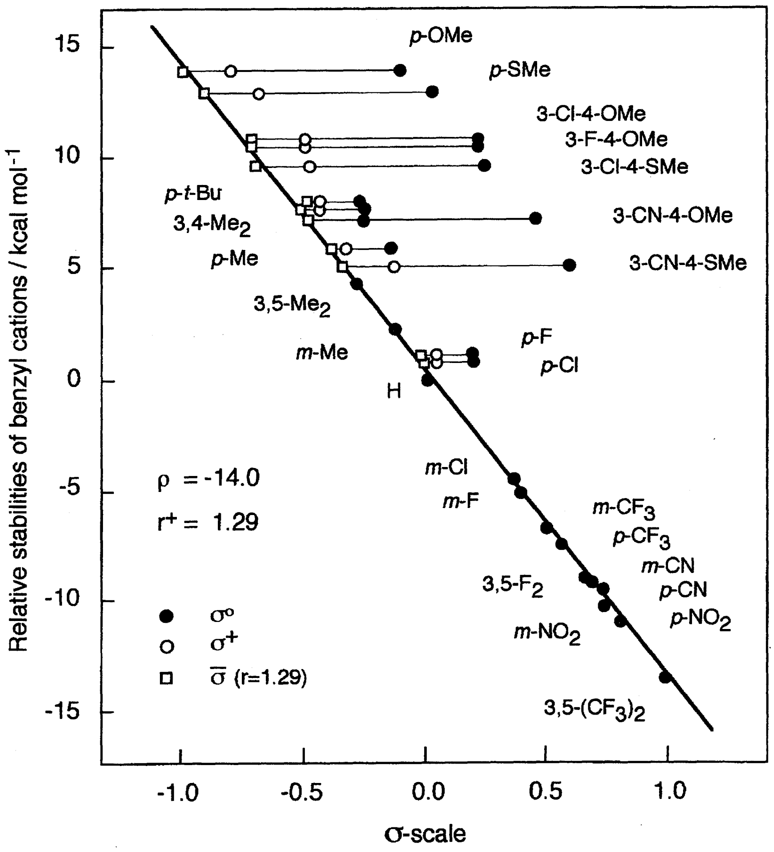

Fig. 4. LArSR plots of stabilities of benzyl cations: ●; σ°, ○; σ^+, □; $\bar{\sigma}$ (r=1.29).

Table 4. Results of LArSR Analysis for Gas Phase Stabilities of Benzylic Carbocations and the Corresponding k_c Solvolyses

$Ar\text{-}C^+(R^1)R^2$		ρ_{gas} [a]	r^+_{gas} [a]	$\rho_{solvolysis}$ [b]	$r^+_{solvolysis}$ [b]
R^1	R^2				
Me	Me	−13.0 (−9.5)[c]	1.00[c]	−4.59[d]	1.00[d]
H	Me	−13.8 (−10.1)[e]	1.14[e]	−5.45[f]	1.15[f]
H	H	−14.0 (−10.3)	1.29	−5.23[g]	1.28[g]
CF_3	Me	−14.0 (−10.3)[h]	1.40[h]	−6.29[i]	1.39[i]

a) For gas phase stabilities of carbocations in kcal mol^{-1}. Values in parentheses were obtained by multiplying the ρ values by the factor of 1000/2.303 RT. b) For the solvolysis of the corresponding substrates, $\log k/k_o$. c) Ref. 26. d) In 90% aq acetone, L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963). e) Ref. 30. f) Ref. 2 in 80% aq acetone. g) Ref. 6(a), in acetic acid. The same ρ and r^+ values were observed in 80% aq acetone, Ref. 6(b). h) Ref. 27. i) Ref. 4, in 80% aq ethanol.

process of interest was exactly the same in both phases, while the ρ values were significantly reduced in solution compared with the corresponding value in the gas phase.[32] The corollary is that the resonance demand should be an inherent feature of carbocations regardless of external solvent stabilization. Thus the solvation of a cation reduces the central charge to lower the response (the magnitude of ρ value) to substituent perturbation, essentially without change in intramolecular charge-delocalization. Accordingly, the identity of r^+ value between the solvolysis and the gas-phase stability of carbocations strongly suggests that the intramolecular charge-delocalization in the S_N1 transition state should also be quite close to that of the carbocation intermediate.

In conclusion, the exalted r^+ value of 1.3 obtained for the solvolysis of benzyl substrates is not a correlational artifact arising as a result of the non-linearity caused by the k_c–k_s mechanistic transition as suggested by Shorter,[13] but must be an intrinsic feature characterizing the nature of the transition state of k_c solvolysis of benzyl tosylate. The less stable primary benzyl cation should have an inherent resonance demand distinctly higher than the value of $r^+=1.0$ of the tertiary α-cumyl cation system. This result provides a new insight into the mechanistic transition in the benzyl solvolysis. In Fig. 5 are plotted logarithmic rate constants of the solvolysis of benzyl tosylates in acetic acid against a calculated set of LArSR substituent constants with $r^+=1.3$.[6a] A single curved correlation is observed as a whole. All activating substituents down to p-halogens construct a sufficiently linear plot, giving a ρ of −5.2 for the k_c mechanism of this system, and the plots of deactivating substituents fall on the relatively flat portion of the single curved correlation in which the approximate slope of −1 may be an acceptable value in magnitude as a ρ value for the k_s mechanism. The mechanistic transition with a change of substituent should also be a continuous function of substituent polarity, and any mechanistic change must therefore give a single smooth-curved or a bisected plot against an appropriate set of substituent constants. The significant split observed for strong π-donor substituents in the σ^+ plot indicates not only a simple failure of the σ^+-treatment but also a vital inconsistency of the interpretation in terms of the mechanistic transition. More importantly, a single curved correlation with $r^+=1.3$ has held similarly in more nucleophilic solvents like 80% aqueous acetone, while the curvature itself changes with solvent nucleophilicity, arising as a result of change in the ρ value for the k_s region.[6b] This suggests that the resonance demand for the solvolysis of benzyl tosylates remains essentially constant within the same framework of the transition state structure. It is likely that the resonance demand of a reaction is independent of the magnitude of developed positive charge in the transition state and hence the extent of cleavage of a leaving group in the transition state of the solvolysis. This is reconciled with the identity of the r^+ value between the gas-phase stabilities of carbocations and the solvolyses of the corresponding precursors. Clearly, these results have confirmed that the r^+ value is an "*inherent nature characteristic of the carbocation structure itself.*" This is our answer to the criticism against the LArSR Eq. 1 that the physical significance of the r^+ parameter is obscure even though the correlation can be improved.

Experimental

Measurements. The measurements of chloride ion transfer and proton transfer equilibria were done with the homemade pulsed ion cyclotron resonance mass spectrometer as described previously[33] and several experiments were done by using an Extrel FTMS 2001 Fourier transform mass spectrometer equipped with a 3.0 Tesla superconducting magnet and with a modified sample inlet system. The temperature of the chamber of an ICR ion-trapping cell was maintained at 70 °C. A Bayard–Alpert type ionization gauge was used to monitor pressures of neutrals with appropriate correction factors being applied to correct the gauge readings for the different ionization cross-section of various compounds.[34] A total pressure of about 10^{-6} Torr (1 Torr=133.2 Pa) was maintained for RCl and R_0Cl by controlled rates through leak valves (Anelva) from a parallel in-

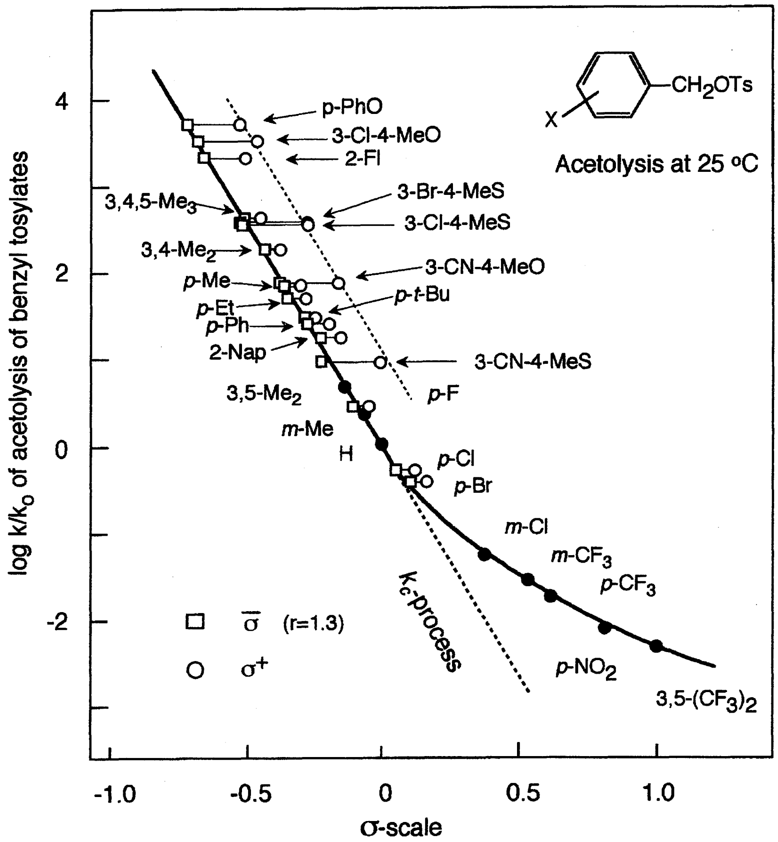

Fig. 5. Plots of log (k/k_o) of acetolysis of benzyl tosylates against $\bar{\sigma}$ ($r^+=1.3$) and σ^+.

let manifold into the vacuum chamber. After a reaction period of 1 to 3 s depending upon the reactant, an equilibrium was attained and the relative abundance of R^+ and R_0^+ was measured by signal intensities of ICR spectra. The equilibrium constant for chloride ion transfer reaction was obtained by $K=[R^+]/[R_0^+]\times[R_0Cl]/[RCl]$, then the standard free energy changes were calculated by $\Delta G^\circ=-RT\ln K$. Several measurements were done for each equilibrium at different pressures of the neutral reactants to avoid artifacts. Arithmetic mean values of K were used for the calculation of ΔG° and the average uncertainty is estimated to be better than ±0.2 kcal mol^{-1} in most cases.

Materials. Most of the alkyl chlorides used for this study were prepared from the corresponding alcohols with thionyl chloride or concentrated hydrochloric acid, and purified by general methods. These compounds were characterized as follows. All boiling points and melting points are uncorrected. 5-Butyl-chlorononane; bp 78 °C/2 mmHg (lit,[35]) bp 91.5—92.5 °C/2.5 mmHg) (1 mmHg=133.32 Pa). 4-Chloro-4-propylheptane; bp 48—52 °C/1.5 mmHg (lit,[36]) bp 78—79 °C/11 mmHg). 3-Chloro-3-ethylpentane; bp 55—57 °C/30 mmHg (lit,[37]) bp 64—65 °C/52 mmHg). 3-Chloro-3-methylpentane; bp 45 °C/41 mmHg (lit,[37]) bp 68—69 °C/160 mmHg). *p*-Trifluoromethylbenzyl chloride; bp. 85 °C/20 mmHg (lit,[38]) bp 86—87 °C/20 mmHg). *m*-Trifluoromethylbenzyl chloride; bp 80 °C/27 mmHg (lit,[39]) bp 70—71 °C/11 mmHg). *p*-Fluorobenzyl chloride; bp 89 °C/32 mmHg (lit,[40]) bp 76 °C/20 mmHg). *o*-Fluorobenzyl chloride; bp 38—39 °C/3 mmHg (lit,[40]) bp 67.5—68 °C/16 mmHg). *m*-Fluorobenzyl chloride; bp 93 °C/60 mmHg (lit,[40]) bp 67—68 °C/15 mmHg). *m*-Chlorobenzyl chloride; bp 45 °C/0.1 mmHg (lit,[41]) bp 111—111.2 °C/25.4 mmHg). *m*-Methoxybenzyl chloride; bp 124—125 °C/22 mmHg (lit,[39]) bp 87—87.5 °C/2 mmHg). *p*-*t*-Butylbenzyl chloride; bp 58—60 °C/0.2 mmHg (lit,[42]) bp 110—115 °C/6—7 mmHg). 3,4-Dimethylbenzyl chloride; bp 68 °C/1 mmHg (lit,[43]) bp 109—110 °C/16 mmHg). 2,4,6-Trimethylbenzyl chloride; mp 39—40 °C (lit,[44]) mp 37 °C). 3,4,5-Trimethylbenzyl chloride; bp 72 °C/0.7 mmHg (lit,[45]) mp 36—37 °C). 2,3,5,6-Tetramethylbenzyl chloride; mp 66—67 °C (lit,[46]) mp 67—68 °C). 3-Fluoro-4-methoxybenzyl chloride; bp 62 °C/0.2 mmHg (lit,[47]) bp 122 °C/13 mmHg). 3-Chloro-4-methoxybenzyl chloride; bp 102—103 °C/0.8 mmHg (lit,[48]) bp 130—131 °C/3 mmHg). *m*-Nitrobenzyl chloride; mp 45.5—46.2 °C (lit,[49]) mp 45.2—45.4 °C. 3,5-*Bis*(trifluoromethyl)benzyl chloride; bp 82—84 °C/30 mmHg, mp 30.0—31.2 °C. Anal. Calcd for $C_9H_5ClF_6$: C, 41.17; H, 1.92%. Found: C, 41.19; H, 1.97%. 3,5-Difluorobenzyl chloride; bp 82 °C/22 mmHg. Anal. Calcd for $C_7H_5ClF_2$: C, 51.72; H, 3.10%. Found: C, 51.62; H, 3.09%. 3-Cyano-4-methoxybenzyl chloride; mp 100—101 °C; ^{1}H NMR (CCl_4) $\delta=3.95$ (3H), 4.48 (2H), 6.85—7.57 (m, 3H); IR (Nujol) 2305 cm^{-1} (CN). Anal. Calcd for C_9H_8ClNO: C, 59.52; H, 4.44; N, 7.71%. Found: C, 59.49; H, 4.44; N, 7.58%. 3-Cyano-4-methylthiobenzyl chloride; mp 105—106 °C, ^{1}H NMR ($CDCl_3$) $\delta=2.57$ (3H), 4.52 (2H), 7.19—7.61 (m, 3H). Anal. Calcd for C_9H_8ClNS: C, 54.68; H, 4.08; N, 7.09%. Found: C, 54.75; H, 4.08; N, 6.96%. IR (Nujol) 2340 cm^{-1} (CN). 1-Phenyl-1-(trifluoromethyl)ethyl chloride; bp 83 °C/21 mmHg. Anal. Calcd for $C_9H_8ClF_3$: C, 49.00; H, 3.52, N; 8.16%. Found: C,49.01; H, 3.54; N, 8.19%. p-Methoxy and p-methylthiobenzyl chlorides were purified by vacuum line trap-to-trap distillation and characterized as follows. p-Methoxybenzyl chloride; ^{1}HNMR (CCl_4) δ=3.70 (3H), 4.42 (2H), 6.72 (d, J=7.4 Hz, 2H), 7.17 (d, J=8.4 Hz, 2H). p-Methylthiobenzyl chloride; ^{1}HNMR (CCl_4) δ=2.44 (3H), 4.47 (2H), 7.19 (4H). 3-Chloro-4-methylthiobenzyl chloride was purified by preparative GLC. ^{1}HNMR (CCl_4) δ=2.55 (3H), 4.49 (2H), 7.19—7.57 (m, 3H). Anal. Calcd for $C_8H_8Cl_2S$: C, 46.39; H, 3.89%. Found: C, 46.44; H, 3.88%. Preparation and physical constants of several 1-aryl-2,2,2-trifluoroethyl chlorides used for constructing a ladder of a chloride ion affinity scale will be described in a subsequent paper. The remaining compounds were obtained commercially or from our previous studies. All samples were checked for purity by GLC and their ICR mass spectra. Each sample was subjected to several freeze-pump-thaw cycles on the ICR inlet system to remove entrapped impurities.

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