Gas-Phase Substituent Effects in Highly Electron-Deficient Systems. I. Intrinsic Stabilities of 1-Aryl-1-(trifluoromethyl)ethyl Cations[1]

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The relative stabilities of 1-aryl-1-(trifluoromethyl)ethyl cations were determined by measuring the proton-transfer equilibria of 1-aryl-1-(trifluoromethyl)ethylenes or the chloride-transfer equilibria of 1-aryl-1-(trifluoromethyl)ethyl chlorides in the gas phase. The stability of 1-phenyl-1-(trifluoromethyl)ethyl cation was found to be 16 kcal mol^{-1} lower than that of the α-cumyl (1-phenyl-1-methylethyl) cation. The substituent effect on the stability of this cation can be correlated in terms of the Yukawa–Tsuno equation, giving an r^+ of 1.41 and a ρ of -10.0 (in $\log K/K_o\overline{\sigma}^{-1}$ unit). While the ρ value is nearly identical to that of the α-cumyl cation series, the r^+ value is remarkably higher than the value of unity for the α-cumyl cation, indicating that such a highly electron-deficient carbocation system should be characterized by an extremely large r^+ value compared with that of the stable α-cumyl cation. In addition, this r^+ value agrees with that for the S_N1 solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates. Such agreement of the r^+ values between the gas phase and solvolysis reactions has been generally observed for the benzylic carbocation systems. It is concluded that the enhanced r^+ value for the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates must reflect the intrinsic resonance demand characteristic of the parent 1-phenyl-1-(trifluoromethyl)ethyl cation, itself, and that the extremely large ρ^+ values given by a simple correlation with σ^+ ($r^+ = 1$) are an artifact due to an improper analysis of underestimating the resonance demand for such highly deactivated substrates.

The solvolysis of extremely deactivated benzylic substrates with an electron-withdrawing group at a reaction site has been characterized by a remarkably high response of the rate due to aryl substituents.[2—5] For a typical "highly electron-deficient carbonation" system, the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates, Liu et al. noticed a remarkably large ρ^+ value of -10 based on the simple Brown σ^+ correlation.[2b] Similarly, large ρ^+ values of -10 to -12 were reported for other deactivated benzylic solvolyses by several research groups.[3—5] These ρ^+ values were merely inferred from the electron-donor portion of the substituents, whereas the electron-withdrawing portion gave relatively smaller ρ^+ values of -6 to -7. This is quite serious because the significant curvature or break in the σ^+ plot forces us to conclude that a mechanistic change occurs along with the change of substituents from electron-releasing to electron-withdrawing. However, the ρ^+ values of -6 to -7 for the electron-withdrawing portion of the plots seem to be too large in magnitude to be assigned to any processes of solvolysis other than the k_c ionization process, because this size of the ρ^+ value is comparable to, or even larger than, that for the ordinary benzylic substrates, such as substituted α-cumyl (1-methyl-1-phenylethyl) chlorides and substituted 1-phenylethyl chlorides, which are considered to proceed through the k_c ionization mechanism.[6] On the other hand, an application of the Yukawa–Tsuno (Y–T) equation (Eq. 1)[7] to the substituent effects of solvolyses of deactivated benzylic substrates with an electron-withdrawing group at a reaction site gave very high r^+ values compared with the value of unity defined for the α-cumyl solvolysis and ρ values of normal size,[8,9]

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

In equation (1) σ° and $\Delta\overline{\sigma}_R^+$ are the normal substituent constant and the resonance substituent constant, respectively, and r^+ is the resonance demand parameter, representing the degree of π-delocalization of the positive charge into the aryl π-system. For example, the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates in aq 80% ethanol was excellently correlated with an r^+ value of 1.39 and a ρ value of -6.29.[8] This correlation does not show any curvature or break in the plot, indicating the involvement of no mechanistic change with a variation of substituents from electron-releasing to electron-withdrawing, in contrast to a simple σ^+ correlation. Thus, the conclusion from analysis of the solvolysis of deactivated benzylic substrates by Eq. 1 apparently disagrees with that from the simple σ^+-analysis.

The thermodynamic stabilities of carbocations can be determined by measuring the equilibrium constants of ion–molecule reactions in the gas phase,[10—15] which are free from mechanistic complexities. Such gaseous thermodynamic data of carbocations would therefore provide important information concerning the inherent nature of carbocations which correspond to the intermediate and transition state of the k_c ionization process of the solvolysis.[13—18] It is instructive to study substituent effects on the stability of highly electron-deficient benzylic cations in the gas phase in order to clarify the nature of the substituent effects for the k_c ionization process. This would provide decisive evidence as to whether our analysis of the substituent effect based on Eq. 1 properly describes the reaction mechanism of the solvolysis of highly deactivated benzylic substrates. In this paper we report on the substituent effect of the gas-phase stability of 1-phenyl-1-(trifluoromethyl)ethyl cation as an example of a highly electron-deficient benzylic cation system.

Results and Discussion

The gas-phase stabilities of the 1-aryl-1-(trifluoromethyl)ethyl cations were determined by measuring the equilibrium constants for the proton-transfer reaction of 1-aryl-1-(trifluoromethyl)ethylenes with reference bases of known basicity (Eq. 2). Measurements of the equilibrium constants were performed on a pulsed ion cyclotron resonance mass spectrometer built in our laboratory[19] and on an Extrel FTMS 2001. The standard free-energy changes for the respective equilibria are given in Table 1. The uncertainty in most of the ΔG° values reported was estimated to be ± 0.2 kcal mol^{-1}. For some derivatives with electron-withdrawing substituents, particularly the 3,5-F_2 derivative, which had a very low basicity, the reliability of the data may be low, because the gas-phase basicity (GB) values of the reference compounds are not established well.[12] The GB of the m-CF_3 derivative could not be determined, because the amount of its conjugate acid ion generated under the present conditions was too small to be accurately measured. Accordingly, we also measured the equilibrium constants for chloride-ion transfer reactions (Eq. 3) of the 1-aryl-1-(trifluoromethyl)ethyl chlorides, which gave the corresponding carbocations by electron-impact ionization. The chloride-transfer equilibrium method may have an advantage in that the position of the positive charge in the molecule is well defined in contrast with protonation of an olefin, where protonation occurs at the most basic site in the molecule.[17,18,20] The relative chloride ion affinity (CIA) values are given in Table 2.


(2)

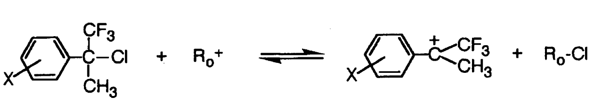

(3)

Table 1. Standard Free Energy Changes of Proton-Transfer Equilibria and Selected GB Values of 1-Aryl-1-(trifluoromethyl) ethylenes

Subst.	Reference base	[GB][a]	$-\Delta G^{\circ}$[b]	GB[c]
p-MeO	i-Pr_2O	[197.6]	−0.2	197.4
	i-PrC_2O	[196.0]	1.5	
	3-Cl-4-MeO[d]	[194.3]	3	
	3-F-4-MeO[d]	[194.3]	3	
p-MeS	i-Pr_2O	[197.6]	−0.6	196.8
	$cyclo$-$PrCOCH_3$	[196.3]	0.5	
	Bu_2CO	[195.9]	0.5	
	i-Pr_2CO	[196.1]	0.6	
	Pr_2CO	[195.1]	1.4	
	3-Cl-4-MeS[d]	[194.2]	2.6	
3-Cl-4-MeO	p-MeO[d]	[197.4]	−3	194.3
	Pr_2CO	[195.1]	−0.8	
	$cyclo$-Hexanone	[194.0]	0.3	
	Pr_2O	[193.9]	0.3	
3-F-4-MeO	p-MeO[d]	[197.4]	−3	194.3
	p-MeS[d]	[196.8]	−2.6	
	Pr_2CO	[195.1]	−0.8	
	$cyclo$-Hexanone	[194.0]	0.4	
	Pr_2O	[193.9]	0.4	
3-Cl-4-MeS	$cyclo$-Hexanone	[194.0]	0.2	194.2
	Pr_2O	[193.9]	0.4	
p-Me	i-PrCN	[185.7]	3.0	188.5
	Acetone	[187.9]	0.4	
p-t-Bu	$cyclo$-Pentanone	[190.5]	−0.4	190.1
	THF	[190.4]	−0.2	
	MeOAc	[189.2]	1.0	
3,4-Me_2	EtCOMe	[190.7]	−0.1	190.6
	$cyclo$-pentanone	[190.5]	0.0	
	THF	[190.4]	0.3	
3,5-Me_2	Acetone	[187.9]	−0.2	187.9
	Isobutene	[186.4]	1.8	
	i-PrCN	[185.7]	2.2	
m-Me	Dioxane	[185.1]	−0.2	185.0
	PrCN	[184.8]	0.3	
3-Cl-4-Me	i-PrCHO	[184.0]	0.3	183.7
	EtCN	[183.6]	0.3	
	PrCHO	[183.0]	0.7	
	PrOH	[182.0]	1.8	
H	BuOH	[182.5]	0.3	182.9
	PrOH	[182.0]	1.0	
	EtOH	[179.8]	3.0	
p-F	EtCN	[183.6]	−0.4	183.2
	PrCHO	[183.0]	0.2	
	BuOH	[182.5]	0.6	
	PrOH	[182.0]	1.4	
p-Cl	EtCN	[183.6]	−0.5	183.2
	PrCHO	[183.0]	0.2	
	PrOH	[182.0]	1.3	
m-Cl	MeOH	[174.1]	4.0	178.0
	CF_3CO_2Et	[176.8]	1.5	
	C_5F_5N	[177.1]	0.7	
m-F	MeOH	[174.1]	3.6	177.9
	CF_3CO_2Pr	[177.9]	0.4	
	CF_3CO_2Bu	[178.0]	0.0	
3,5-F_2	CF_3CO_2Me	[171.0]	2.4	174.2±0.9
	CH_3NO_2	[171.7]	2.0	
	MeOH	[174.1]	1.5	

All values in kcal mol^{-1}, 1 cal=4.184 J. a) Reference bases used (and their GB values). Ref. 12 and private communication from R. W. Taft. These GB values were anchored by $NH_3=195.6$ kcal mol^{-1}. b) Directly measured for the proton transfer equilibrium at 343 K between a given and a standard base, $ArC(CF_3)=CH_2+B_oH^+ \rightleftarrows ArC^+(CF_3)CH_3+B_o$. A positive sign of $-\Delta G^{\circ}$ means that the given base is stronger than the reference base, in kcal mol^{-1} c) Selected GB values. d) Subsitutent of α-trifluoromethylstyrenes.

The GB of the unsubstituted 1-phenyl-1-(trifluoromethyl)ethylene was found to be 3.5 kcal mol^{-1} lower than that of isobutene to give t-butyl cation by the addition of a proton, indicating that 1-phenyl-1-(trifluoromethyl)ethyl cation is less stable than t-butyl cation. This difference in the GB value is in good agreement with the value of the standard free-energy change of the chloride transfer equilibrium between 1-phenyl-1-(trifluoromethyl)ethyl chloride and t-butyl cation (Eq. 3). Recently, we found a good linear relationship with a slope of unity between the relative chloride ion affinity

Table 2. Standard Free Energy Changes of Chloride-Transfer Equilibria[a)]

R^+	$R_o^{+b)}$	[ΔCIA[c)]]	$-\Delta G^{\circ d)}$	$-\delta\Delta G^{\circ e)}$
$C_6H_5C^+(CF_3)CH_3$	m-$ClC_6H_4CH_2^+$	[4.3]	0.4	−3.9(0.0)
	m-$FC_6H_4CH_2^+$	[5.0]	1.2	
m-$FC_6H_4C^+(CF_3)CH_3$	m-$CNC_6H_4CH_2^+$	[9.0]	−0.2	−9.1(−5.2)
	p-$CNC_6H_4CH_2^+$	[9.3]	0.2	
m-$CF_3C_6H_4C^+(CF_3)CH_3$	m-$FC_6H_4C^+(CF_3)CH_3$	[9.1]	−0.8	−10.1(−6.2)
	p-$CNC_6H_4CH_2^+$	[9.3]	−0.9	
3,5-$F_2C_6H_3C^+(CF_3)CH_3$	3,5-$(CF_3)_2C_6H_3CH_2^+$	[13.4]	1.4	−12.1(−8.2)
	m-$ClC_6H_4C^+(H)CF_3$	[11.4]	−0.7	

a) All values in kcal mol^{-1}. b) Reference carbocations. c) Chloride affinity values of reference carbocations relative to *t*-butyl cation, in kcal mol^{-1}. Taken from Ref. 18. d) Directly measured free energy change for the chloride-transfer equilibrium between a given and a reference cation. $ArC(CF_3)(Me)Cl + R_o^+ \rightleftarrows ArC^+(CF_3)CH_3 + R_oCl$. e) A positive sign of $-\Delta G^\circ$ means that the given cation is of lower affinity than the reference cation. f) Selected chloride affinity values relative to *t*-butyl cation. Values in parentheses are relative to the unsubstituted 1-phenyl-1-(trifluoromethyl)ethyl cation.

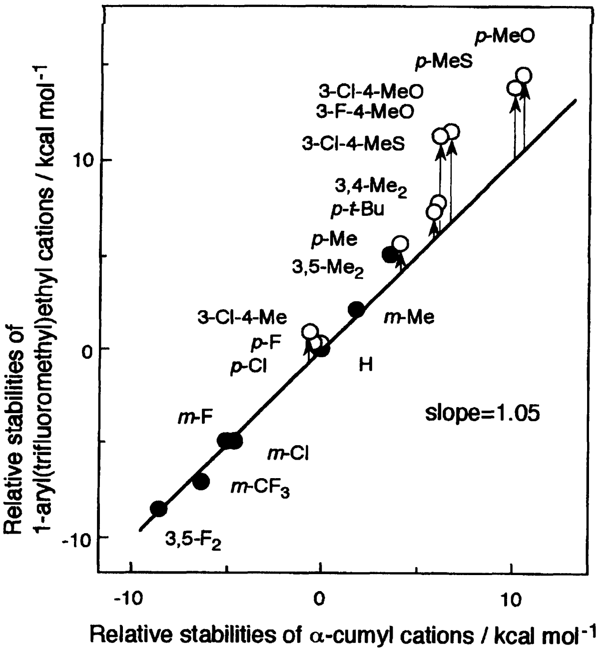


Fig. 1. Plot of gas-phase stabilities of 1-aryl-1-(trifluoromethyl)ethyl cations against the corresponding α-cumyl cations: Open circles; *para* π-donor substituents, closed circles; *meta* substituents.

Table 3. Relative Gas Phase Stabilities of Carbocations[a)]

	$-\delta\Delta G^\circ$/kcal mol^{-1}	
Subst.	Me, $CF_3^{b)}$	Me, Me[c)]
p-MeO	14.5	10.5
3-Cl-4-MeO	11.4	6.7
3-F-4-MeO	11.4	6.7
p-MeS	13.9	10.0
3-Cl-4-MeS	11.2	6.2
p-t-Bu	7.2	5.8
3,4-Me_4	7.7	6.1
p-Me	5.6	4.1
3-Cl-4-Me	0.8	−0.7
m-Me	2.1	1.8
3,5-Me_2	5.0	3.5
p-F	0.3	−0.1
p-Cl	0.3	−0.4
m-Cl	−4.9	−4.7
m-F	−5.1[d)]	−5.1
m-CF_3	−6.2[e)]	−6.3
3,5-F_2	−8.5[d)]	−8.5
H	0.0	0.0
	(−3.5)[f)]	(12.7)[f)]
	(−3.9)[g)]	(12.1)[g)]

a) A positive value means a more stable carbocation. b) 1-Aryl-1-(trifluoromethyl)ethyl cations. c) 1-Aryl-1-methylethyl cations. ΔGB values of α-methylstyrenes, Ref. 15. d) Average value of ΔCIA and ΔGB. e) ΔCIA value. f) GB values of the corresponding olefins relative to that of isobutene. g) CIA value relative to *t*-butyl cation.

values of carbocations and the gas-phase basicities of the corresponding olefins, which lead to the same carbocations by the addition of a proton.[18)] It seems reasonable that both the relative chloride ion affinities and the gas-phase basicities should be combined to give a single scale of stabilities of the 1-aryl-1-(trifluoromethyl)ethyl cations, so that the variation of the substituents covers a sufficient range for a correlation analysis of the substituent effects. Thus, we have constructed a scale of relative stabilities of 1-aryl-1-(trifluoromethyl)ethyl cations which covers a range of over 23 kcal mol^{-1} from p-MeO to 3,5-F_2 derivatives. The relative stabilities of the 1-aryl-1-(trifluoromethyl)ethyl cations are summarized in Table 3 together with those of the α-cumyl cations.

Substituent Effects. A plot of the relative stabilities of the 1-aryl-1-(trifluoromethyl)ethyl cations against those of the corresponding α-cumyl cations is shown in Fig. 1. This plot of the $\delta\Delta G^\circ_{ArC^+(CF_3)CH_3}$ vs. $\delta\Delta G^\circ_{ArC^+(CH_3)_2}$ corresponds to a σ^+-plot in the gas phase, because the substituent effect on the gas-phase basicity of the α-methylstyrenes, which can be related to the relative stabilities of the α-cumyl cations formed, is excellently described by the ordinary set of σ^+ values in solution.[17)] Figure 1 clearly shows that there exists no simple linear relationship between these two quantities for the whole set of substituents, suggesting that there is no common set of σ^+ substituent constants for the substituent effects on the gas-phase carbocation stabilities. A closer inspection of this figure indicates that while *meta* sub-

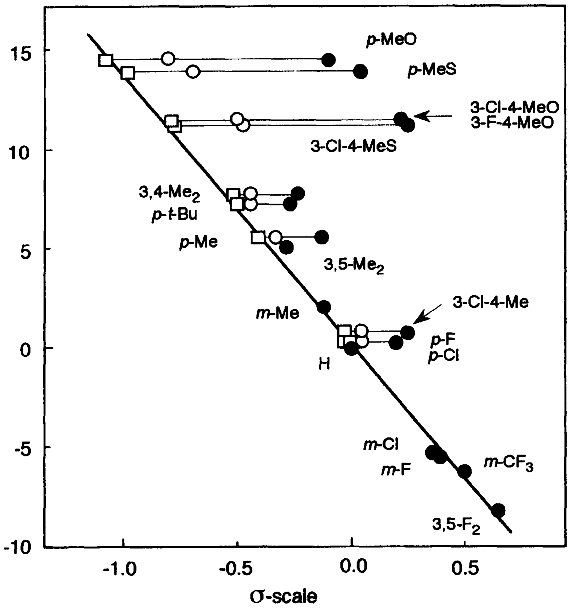


Fig. 2. Hammlet plots of intrinsic stabilities of 1-aryl-1-(trifluoromethyl)ethyl cations against: σ^+ (open circles), σ° (closed circles), and $\overline{\sigma}$ with r=1.41 (squares).

stituents provide an excellent linear relationship with a slope of 1.05, all *para* π-donor substituents show systematic positive deviations from the *meta*-line, i.e., the stronger *para* π-donor substituents cause a greater stabilization in the 1-phenyl-1-(trifluoromethyl)ethyl cation. This is indicative of an exalted resonance effect of such substituents in the 1-phenyl-1-(trifluoromethyl)ethyl cation compared with that in the α-cumyl cation. The deviations of the *para* π-donors are indeed related to the resonance substituent parameter, $\Delta\overline{\sigma}_R^+$ $(=\sigma^+ - \sigma^\circ)$, as shown by an analysis based on the following equation, which gives a correlation coefficient of 0.998 and a standard deviation of ±0.46 (n=18):

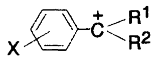
$$-\delta\Delta G^\circ_{\mathrm{ArC^+(CF_3)CH_3}} = 1.05(-\delta\Delta G^\circ_{\mathrm{ArC^+(CF_3)_2}}) - 5.27\Delta\overline{\sigma}_R^+ + 0.2. \quad (4)$$

This correlation also tells us that the Y–T equation (Eq. 1) is applicable to an analysis of this substituent effect, since Eq. 4 is equivalent in form to Eq. 1, in so far as $-\delta\Delta G^\circ_{\mathrm{ArC^+(CH_3)_2}}$ is described by σ^+ $(=1.00\sigma^\circ + 1.00\Delta\overline{\sigma}_R^+)$.[17)]

$$-\delta\Delta G^\circ = \rho'(\sigma^\circ + r^+\Delta\overline{\sigma}_R^+) \quad (5)$$

In fact, the application of Eq. 5 to the stabilities of the 1-aryl-1-(trifluoromethyl)ethyl cations gave a ρ' of −13.7 and r^+ of 1.41 with a correlation coefficient of 0.998 and a standard deviation of ±0.4 kcal mol^{-1} (Fig. 2). The ρ' value is similar to that observed for the relevant benzylic carbocations in spite of differences in the stabilities of the parent carbocations (ring-substituent=H). In contrast with the ρ' value, the r^+ value of 1.41, higher than that of unity for the α-cumyl cation, clearly indicates that the resonance effects of the *para* π-donors are exalted in the 1-phenyl-1-(trifluoromethyl)ethyl cation system compared with those in the α-cumyl cation. The magnitude of the r^+ value of 1.41 also appears to fit the trend observed for other benzylic carbocation systems, indicating that the less stable carbocations intrinsically have the greater resonance demand (Table 4). This reveals that the resonance demand parameter is a function of the structure of a carbocation, itself,[1,16,21)] and that 1-phenyl-1-(trifluoromethyl)ethyl cation is characterized by an r^+ value of 1.41, which is merely a unique point within a continuous spectrum of resonance demands of benzylic carbocations. The dependence of the r^+ value on the stability of the parent carbocation may be interpreted as follows. The π-interaction between the vacant p-orbital of a carbocation and the π-orbital of the benzene ring would be stronger in a highly electron-deficient carbocation system with an electron-withdrawing group at the cation site than that in a relatively stable carbocation, such as α-cumyl cation. This makes the Ph–C$^+$ bond shorten, i.e., increase the double-bond character, and results in a large decrease in the electron density at the *para* position of the benzene ring. Such a molecular structure enhances the π-interaction between the *para* π-donor substituents and the positive charge. As a result, exalted r^+ values are observed for the electron-deficient carbocation system. Recently, we in fact found that the empirical r^+ values are linearly related to theoretical resonance indices, such as bond length, bond

Table 4. Results of Subsituent Effect Analysis by Eq. 1 for the Gas-phase Stability of Benzylic Cations and for the Solvolysis of Corresponding Substrates

		$\Delta G^\circ_{\mathrm{ST}}$ [a)]	Gas-phase stability			Solvolysis reactivity	
R^1	R^2	kcal mol^{-1}	ρ'	(ρ)[b)]	r^+	ρ	r^+
CF$_3$	Me	16.2	−13.7	(−10.0)	1.41	−6.29[e)]	1.39[e)]
H	H	12.2	−14.0	(−10.3)[c)]	1.29[c)]	−5.23[f)]	1.28[f)]
H	Me	4.9	−13.8	(−10.1)[d)]	1.14[d)]	−5.45[g)]	1.15[g)]
Me	Me	0.0	−13.0	(−9.5)	1.00	−4.59[h)]	1.00[h)]

a) In kcal mol^{-1}. Relative stabilities of respective parent carbocations estimated from proton-transfer or chloride-transfer equilibria, see also Ref. 18. A positive value indicates a lower stability. b) Values in parentheses are obtained by multiplying the ρ' of gas-phase stability by the factor 1000/2.303RT, i.e., log $K/K_\circ\,\overline{\sigma}^{-1}$ unit c) Ref. 18. d) Ref. 17. e) Tosylates in 80% aq ethanol at 25 °C, Ref. 8. f) Tosylates in 80% aq aceton at 25 °C, Ref. 24. g) Chlorides in 80% aq acetone, Ref. 7b and M. Fujio, T. Adachi, Y. Shibuya, A. Murata, and Y. Tsuno, *Tetrahedron Lett.*, **25**, 4557 (1984). ρ value corrected to 25 °C. h) Chlorides in 90% aq acetone at 25 °C, H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1944 (1957); *J. Am. Chem. Soc.*, **80**, 4979 (1958); L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, **1**, 35 (1963).

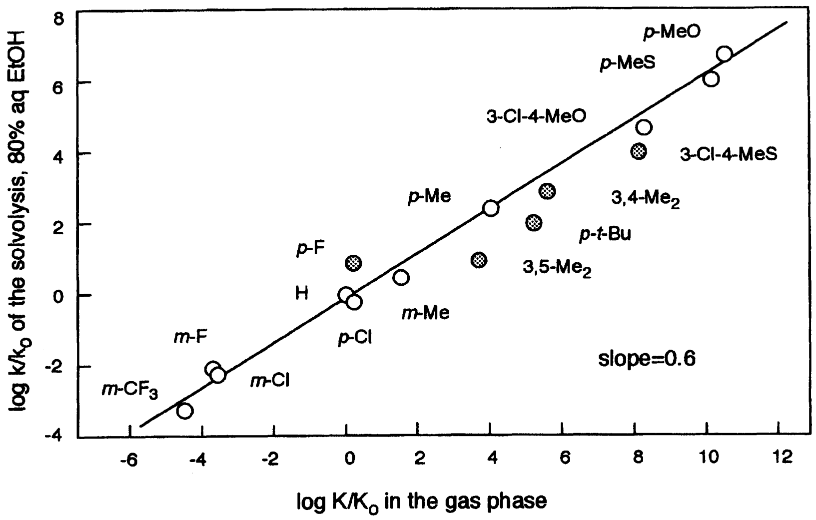
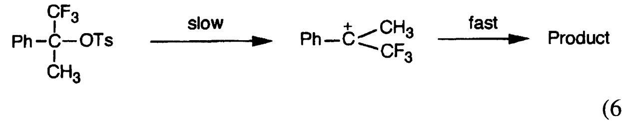


Fig. 3. Comparison of substituent effects between solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates and gas-phase stabilities of 1-aryl-1-(trifluoromethyl)ethyl cations.

order, and population based on ab initio MO calculations.[22] Thus, the variation in the r^+ value with the system is consistent with the concept of resonance theory, supporting the idea that the r^+ value is a good parameter for indicating the degree of the resonance interaction between the benzylic vacant p-orbital and the benzene π-system.

Comparison with Substituent Effects in Solution. We can now compare the present results with those of the substituent effects on the S_N1 solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates to give the same carbocation intermediates as formed in the gas phase (Eq. 6). Figure 3 shows a plot of the logarithms of the rate constants for this solvolysis in 80% aq ethanol[8] against the corresponding values of the equilibrium constants for the proton- or chloride-transfer equilibria in the gas phase. At first glance a linear relationship between the two quantities is less than excellent. However, excluding polarizable substituents and the p-fluoro group, it improves the linearity significantly, so there is no observable trend in the data, such as a curvature or change in the slope along with a variation of substituents from electron-releasing to electron-withdrawing. This suggests that both substituent effects are correlated with a common set of substituent constants.



$$\mathrm{Ph{-}C(CF_3)(CH_3){-}OTs} \xrightarrow{\text{slow}} \mathrm{Ph{-}\overset{+}{C}(CH_3)(CF_3)} \xrightarrow{\text{fast}} \text{Product} \qquad (6)$$

Substituents excluded from the correlation in Fig. 3 show similar deviations when the substituent effects in the solution are compared with those in the gas phase, suggesting that it may be necessary to use a different set of substituent constants for these substituents in the gas phase.[15] In fact, substituent constants, which are modified slightly from the standard values determined in solution, were used for these substituents in the gas-phase.[23] The negative deviations of p-t-Bu, 3,4-Me_2, 3,5-Me_2, and m-Me groups are presumably due to a polarizability effect because their stabilization of the positive charge of a cation is only effective in the gas phase.[25] A small deviation of 3-Cl-4-SMe may be attributed to the same cause. Although the cause of the positive deviation of the p-fluoro group is not yet clear, this trend is commonly observed in comparisons of the substituent effects between the gas- and solution-phases.[15—18] There is generally no difficulty in comparing the correlation results of solvolyses with those of the gas-phase carbocation stabilities based on the substituent constants in the gas phase, because the substituent constant values are normally applicable to both solution- and gas-phase substituent effects with only a few exceptions.

Indeed, the Y–T analysis of the solvolysis data of 28 substituted 1-aryl-1-(trifluoromethyl)ethyl tosylates gave an r^+ value of 1.39,[8] which, surprisingly, is identical with that observed for the carbocation stabilities in the gas phase. In addition, there is no break in this correlation, as shown in Fig. 3. If a mechanistic change occurs along with a change in the substituent, the Y–T correlation with a proper r^+ value does indeed show a smooth curvature with changing polarity of the substituents, as observed for substituent effects upon the solvolysis of primary benzyl tosylates.[24] This is also consistent with the result from the graphical analysis mentioned above.

Such an identity of the r^+ value has generally been observed for other benzylic carbocation systems.[1,15—18,21] This agreement suggests that the degree of π-delocalization of the positive charge into the substituted phenyl ring relative to charge-delocalization by the inductive/field effect will remain essentially the same in the gas phase as in the solution. The solvation of a cation reduces the central charge to lower the response to substituent perturbation, essentially without changing the nature of the intramolecular charge-delocalization. Furthermore, this fact suggests that the charge-delocalization in the transition state of the S_N1 solvolysis should also be quite close to that of the carbocation intermediate. Accordingly, the enhanced r^+ value of 1.39 obtained for the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates must

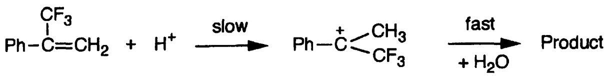
Table 5. Physical Data of 1-Aryl-1-(trifluoromethyl) ethylenes and 1-Aryl-1-(trifluoromethyl)ethyl Chlorides

Subst.	Bp	(mmHg)	Carbon (%)		Hydrogen (%)	
	°C		Found	Calcd	Found	Calcd
α-Trifluoromethylstyrenes						
p-MeO	102—102	(24)	59.13	59.41	4.47	4.49
p-MeS	133—134	(24)	54.75	55.04	4.14	4.16
3-F-4-MeO	113—114	(25)	54.35	54.55	3.65	3.66
3-Cl-4-MeO	136—137	(24)	50.66	50.76	3.47	3.41
3-Cl-4-MeS	a)		47.51	47.53	3.25	3.19
3-Cl-4-Me	140—142	(80)	54.34	54.44	3.63	3.65
3,4-Me_2	105—108	(42)	65.90	65.99	5.51	5.54
3,5-Me_2	a)		65.75	65.99	5.66	5.54
m-Me	158—162	(760)	64.41	64.51	4.91	4.87
H	138—143$^{b)}$	(760)	62.90	62.79	4.00	4.10
p-F	145—148	(760)	56.60	56.85	3.05	3.18
p-Cl	165—170	(760)	52.18	52.32	2.96	2.93
m-F	142—142$^{c)}$	(760)	56.82	56.85	3.20	3.18
m-CF_3	153—156	(760)	49.71	50.01	2.48	2.52
3,5-F_2	143—145	(760)	51.87	51.94	2.37	2.42
1-Aryl-1-(trifluoromethyl)ethyl chlorides						
H	83	(21)	51.75	51.82	3.87	3.87
m-F	a)		47.87	47.71	3.16	3.11
m-CF_3	a)		43.26	43.42	2.64	2.55
3,5-F_2	75—76	(28)	44.36	44.20	2.55	2.47

a) Purifield by GLC. b) Lit,[28] 148—151 °C. c) Lit,[28] 157—158 °C.

reflect the intrinsic resonance demand characteristic of the parent 1-phenyl-1-(trifluoromethyl)ethyl cation, itself. The ρ value of this solvolysis given by the Y–T analysis is as large as that of the solvolysis of the α-cumyl and 1-phenylethyl halides in contrast with the remarkably large ρ^+ values given by the σ^+ plot. This indicates that the large ρ^+ values observed for highly deactivated substrates, which were emphasized as an inherent feature of such substrates, must be an artifact arising from an improper σ^+ analysis. The break in the correlation observed in the simple σ^+ -plot, which implies a mechanistic shift with the change of substituents, is also an artifact. In conclusion, the present results are strong evidence for the validity of the Y–T analysis of the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates, and indicate that the enhanced resonance demand is an essential feature of the electron-deficient benzylic carbocation system.

Acid-catalyzed hydration of a carbon–carbon double bond is an alternative route to generate a carbocation intermediate in solution. It is therefore of interest to compare the gas-phase substituent effect with that of the acid-catalyzed hydration of 1-aryl-1-(trifluoromethyl) ethylenes, since protonation on the double bond to give 1-phenyl-1-(trifluoromethyl)ethyl cation is assumed to be a rate-determining step of this reaction (Eq. 7).[26)]



$$\text{Ph–}\overset{CF_3}{\text{C}}\text{=CH}_2 + H^+ \xrightarrow{\text{slow}} \text{Ph–}\overset{+}{\text{C}}(CH_3)(CF_3) \xrightarrow[+H_2O]{\text{fast}} \text{Product} \quad (7)$$

The application of Eq. 1 to available data of hydration of the1-aryl-1-(trifluoromethyl) ethylenes in acetic acid–water–sulfuric acid at $H_o=-7.50$[25)] gives an r^+ of 1.15 and a ρ of −4.77. The ρ value is somewhat smaller than that of the solvolysis of 1-phenyl-1-(trifluoromethyl) ethylenes tosylates, but is still as large as that of ordinary benzylic S_N1 solvolysis. This ρ value therefore seems to be consistent with the currently accepted mechanism of a rate-determining formation of 1-phenyl-1-(trifluoromethyl) ethylenes cation. In contrast to the ρ value, the r^+ of 1.15 for the hydration is noticeably smaller than that of the corresponding cation in the gas phase and of the solvolysis. Although the data used for this correlation involve only five substituents, the small r^+ value seems unlikely to be a correlational artifact, because a similar reduction of the r^+ values is generally observed for the acid-catalyzed hydration of styrenes, α-methylstyrenes, and phenylacetylenes.[16)] One may expect that the external stabilization of the transition state by solvation decreases the r^+ values as well as the ρ value. As discussed above, the solvation of a cation reduces the central charge and lowers the response to substituent perturbation, apparently without changing the nature of the intramolecular charge-delocalization. Accordingly, the disagreement of the r^+ value between the hydration rates and the gas-phase carbocation stabilities or solvolysis rates suggests that the structure of the transition state of the acid-catalyzed hydration is appreciably different from the corresponding stable cationoid intermediates or S_N1 transition state with respect to π-delocalization of the positive charge at the reaction center. For further understanding of the nature of the transition state of the hydration reaction theoretical calculations may be helpful.[27)]

Experimental

Materials. Substituted 1-aryl-1-(trifluoromethyl) ethylene were prepared by heating the corresponding alcohols with P_2O_5 at atmospheric pressure, as described.[28] Most of the 2-aryl-1,1,1-trifluoropropan-2-ols were available from our previous studies.[8] Several alcohols were prepared from α,α,α-trifluoroacetophenones by the addition of methylmagesium iodide, and were characterized as follows: 2-(3,5-Difluorophenyl)-1,1,1-trifluropropan-2-ol; bp 135—137 °C/104 mmHg (1 mmHg=133.322 Pa). 2-(3-Chloro-4-methylphenyl)-1,1,1-trifluoropropan-2-ol; bp 145°C/21 mmHg. 2-Aryl-2-chloro-1,1,1-trifluoropropanes were prepared from the corresponding alcohols by heating with PCl_5. The physical properties of the styrenes and chlorides are summarized in Table 5. All of the samples were purified by distillation or GLC just before use, and were checked for purity based on their ICR mass spectra. Each sample was subjected to several freeze-pump-throw cycles on the ICR inlet system to remove entrapped volatile impurities.

Measurements. The equilibrium constant measurements of a proton-transfer reaction (Eq. 8) and a chloride-ion transfer (Eq. 9) were performed on a homemade pulsed ion cyclotron resonance mass spectrometer equipped with a capacitance bridge detector[29] and on an Extrel FTMS 2001 spectrometer with a modified inlet system. The details concerning the experimental techniques used for the measurements of the equilibrium constants (K) are described elsewhere:[19]

$$\mathrm{B} + \mathrm{B_oH^+} \rightleftarrows \mathrm{BH^+} + \mathrm{B_o} \tag{8}$$

$$\mathrm{R{-}Cl} + \mathrm{R_o{}^+} \rightleftarrows \mathrm{R^+} + \mathrm{R_o{-}Cl} \tag{9}$$

$$\mathrm{K} = [\mathrm{B_o}/\mathrm{B}]\cdot[\mathrm{BH^+}/\mathrm{B_oH^+}] \text{ or } [\mathrm{R_o{-}Cl}/\mathrm{R{-}Cl}]\cdot[\mathrm{R^+}/\mathrm{R_o{}^+}] \tag{10}$$

$$\Delta G^\circ = RT\ln K. \tag{11}$$

The equilibrium constants is expressed by Eq. 10, where B refers to a given substituted α-trifluoromethylstyrene and B_o is a reference base. R–Cl and R_o–Cl are a given substituted 2-chloro-2-phenyl-1,1,1-trifluoropropane and a reference alkyl chloride, respectively. All of the measurements were performed at 1.3 T magnetic-field strength, or 3 T on an Extrel FTMS 2001. The pressures of the neutral reactants were measured by means of a Bayard–Alpert type ionization gauge with appropriate correction factors being applied to correct the gauge reading for the different ionization cross-sections of the various compounds.[30,31] The overall pressures of the reagents were maintained at 1 to 3×10^{-4} Pa by controlled rates through leak valves (Anelva) from a parallel inlet manifold into the vacuum chamber. After a reaction period of 1 to 3 s, depending upon the reactant, the equilibrium was attained and the relative abundances of the ions were measured by the signal intensities of the ICR spectra. Each experiment was performed at several ratios of the partial pressures and at different overall pressures. The arithmetic means of the values of K were used to calculate ΔG° at 343 K, the average uncertainty being $\pm0.2\ \mathrm{kcal\,mol^{-1}}$ in most of these cases. More than two reference compounds were used to ensure the internal consistency of the data. The GB values for the reference compounds were taken from the literature.[12] The chloride ion affinities of the reference cations were previously determined in our laboratory.[18]

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References

1) Preliminary report: M. Mishima, H. Inoue, M. Fujio, and Y. Tsuno, *Tetraheron Lett.*, **30**, 2101 (1989).

2) a) K.-T. Liu and C.-F. Shu, *Tetrahedron Lett.*, **21**, 4901 (1980); b) K.-T. Liu, M.-Y. Kuo, and C.-F. Shu, *J. Am. Chem. Soc.*, **104**, 211 (1982); c) K.-T. Liu and Y.-W. Wu, *J. Chem. Res. (S)*, **1984**, 408.

3) P. G. Gassman and T. T. Tidwell, *Acc. Chem. Res.*, **16**, 279 (1983); T. T. Tidwell, *Angew. Chem., Int. Ed. Engl.*, **23**, 20 (1984); P. G. Gassman and T. L. Guggenheim, *J. Org. Chem.*, **47**, 3023 (1982).

4) X. Creary and T. L. Underiner, *J. Org. Chem.*, **50**, 2165 (1985); X. Creary, M. E. Mehrsheikn-Mohammadi, and M. D. Eggers, *J. Am. Chem. Soc.*, **109**, 2435 (1987).

5) A. D. Allen, I. C. Ambidge, C. Che, H. Micheal, R. J. Muir, and T. T. Tidwell, *J. Am. Chem. Soc.*, **105**, 2343 (1983); A. D. Allen, V. M. Kanagasabapathy, and T. T. Tidwell, *J. Am. Chem. Soc.*, **108**, 3470 (1986).

6) C. D. Johnson, "Hammett Equation," Cambridge University Press, New York (1973).

7) a) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.*, **45**, 1198 (1972); b) Y. Tsuno, Y. Kusuyama, M. Sawada, T. Fuji, and Y. Yukawa, *Bull. Chem. Soc. Jpn.*, **48**, 3337 (1975); c) Y. Tsuno, W.-Y. Chong, Y.Tairaka, M. Sawada, and Y. Yukawa, *Bull. Chem. Soc. Jpn.*, **51** 596 (1978).

8) A Murata, M. Goto, R. Fujiyama, M. Mishima, M. Fujio, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **63** 1129 (1990).

9) A. Murata, S. Sakaguchi, R. Fujiyama, M. Mishima, M. Fujio, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **63** 1138 (1990).

10) D. H. Aue and M. T. Bowers, "Gas Phase Ion Chemistry," ed by M. T. Bowers, Academic Press, New York (1979), Vol. 2, pp. 2—51.

11) R. W. Taft, *Prog. Phys. Org. Chem.*, **14**, 247 (1983).

12) S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, **13**, 695 (1984).

13) A. G. Harrison, R. Houriet, and T. T. Tidwell, *J. Org. Chem.*, **49**, 1302 (1984).

14) F. Marcuzzi, G. Modena, and C. Paradisi, *J. Org. Chem.*, **50**, 4973 (1985).

15) M. Mishima, S. Usui, M. Fujio, and Y. Tsuno, *Nippon Kagaku Kaishi*, **1989**, 1262.

16) M. Mishima, T. Ariga, T. Matsumoto, S. Kobayashi, H. Taniguchi, M. Fujio, Y. Tsuno, and Z. Rappoport, *Bull. Chem. Soc. Jpn.*, **69**, 445 (1996).

17) M. Mishima, S. Usui, M. Fujio, and Y. Tsuno, *Nippon Kagaku Kaishi*, **1989**, 1269.

18) M. Mishima, K. Arima, H. Inoue, S. Usui, M. Fujio, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **68**, 3199 (1995).

19) M. Mishima, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, **14(2)**, 365 (1984).

20) R. B. Sharma, D. K. S. Sharma, K. Hiraoka, and P. Kebarle, *J. Chem. Soc.*, **107**, 3747 (1985).

21) M. Mishima, H. Inoue, M. Fujio, and Y. Tsuno, *Tetraheron Lett.*, **31**, 685 (1990).

22) K. Nakata, M. Fujio, Y. Saeki, M. Mishima, Y. Tsuno, and K. Nishimoto, *J. Phys. Org. Chem.*, **9**, 561 (1996).

23) Substituent constants used for the present analysis of gas-phase substituent effects were taken from Ref. 18.

24) R. W. Taft, *Prog. Phys. Org. Chem.*, **16**, 1 (1987).

25) M. Fujio, M. Goto, T. Susuki, I. Akasaka, M. Mishima, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **63**, 1146 (1990); M. Fujio, M. Goto, T. Susuki, M. Mishima, and Y. Tsuno, *J. Phys. Org. Chem.*, **3**, 449 (1990).

26) K. M. Koshy, D. Roy, and T. T. Tidwell, *J. Am. Chem. Soc.*, **101**, 357 (1979).

27) Our preliminary results of ab initio molecular orbital calculations (HF/6-31G) suggest that the structure of the transition state of acid-catalyzed hydration of styrene is close to styrene while that of the S_N1 transition state is very close to an intermediate carbocation. It is likely that this difference in the transition state structure is the cause for the reduced r^+ value in the acid-catalyzed hydration.

28) P. Tarrant and R. E. Taylar, *J. Org. Chem.*, **24**, 238 (1959).

29) R. T. McIver, Jr., R. L. Hunter, E. B. Ledford, Jr., M. J. Locke, and T. J. Francl, *Int. J. Mass. Spectrom. Ion Phys.*, **39**, 65 (1981).

30) J. Otovos and D. P. Stevensen, *J. Am. Chem. Soc.*, **78**, 546 (1955).

31) a) J. E. Bartmess and R. M. Georgiadis, *Vacuum*, **3**, 149 (1983); b) K. J. Miller, *J. Am. Chem. Soc.*, **112**, 8533 (1990).