Bull. Chem. Soc. Jpn., ***70***, *1163—1169 (1997)*

Gas-Phase Substituent Effects in Highly Electron-Deficient Systems. II. Stabilities of 1-Aryl-2,2,2-trifluoroethyl Cations Based on Chloride-Transfer Equilibria[1)]

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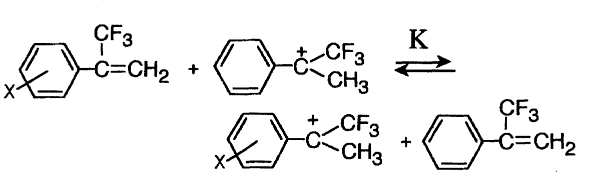
(Received December 16, 1996)

The relative stabilities of 1-aryl-2,2,2-trifluoroethyl cations were determined based on the chloride ion-transfer equilibria in the gas phase. An application of the Yukawa–Tsuno equation to this substituent effect on the equilibrium constants gave a remarkably larger r^+ of 1.53 and a ρ of -10.6, supporting our previous conclusion that the highly electron-deficient benzylic carbocation systems are characterized by extremely high resonance demands. This r^+ value, furthermore, conformed a linear relationship between the r^+ value and the relative stability of the unsubstituted member of the respective benzylic carbocations, clearly demonstrating a continuous spectrum of varying resonance demands characteristic of the stabilities of carbocations. The π-delocalization of the positive charge into the aryl π-system increases with the destabilization of a carbocation by the α-substituent(s) linked to the central carbon. In addition, the r^+ value of 1.53 for 1-aryl-2,2,2-trifluoroethyl cations was found to be in complete agreement with that for the solvolysis of 1-aryl-2,2,2-trifluoroethyl tosylates in 80% aq acetone. This reveals that the r^+ value observed for this solvolysis must be the intrinsic resonance demand of a highly electron-deficient cationic transition state in the S_N1 ionizing process. The identity of the r^+ value was consistent with our previous observation for other benzylic carbocation systems, indicating that the degree of the π-delocalization of the positive charge is identical between the cationic transition state and an intermediate cation for all benzylic systems, which cover a wide range of reactivity and stability of the carbocation. This leads us to the conclusion that the geometry of the transition state in the ionizing process of the S_N1 solvolysis, which is a highly endothermic reaction, closely resembles the high-energy product, an intermediate cation.

In our preceding paper[2)] it was shown that the substituent effect on the gas-phase stability of the 1-phenyl-1-(trifluoromethyl)ethyl cation, determined based on proton-transfer equilibria (Eq. 1), could be excellently described in terms of the Yukawa–Tsuno (Y–T) equation (Eq. 2)[3,4)] with an r^+ of 1.41 and a ρ of -10.0.



(1)

$$\log K/K_o = -\delta\Delta G^\circ/RT = \rho(\sigma^\circ + r^+\Delta\bar{\sigma}_R^+). \qquad (2)$$

In Eq. 2 σ° and $\Delta\bar{\sigma}_R^+$ are a normal substituent constant and a resonance substituent constant ($\Delta\bar{\sigma}_R^+ = \sigma^+ - \sigma^\circ$), respectively, and r^+ is a resonance demand parameter, which represents the degree of the π-interaction between a *para* π-donor substituent and the positive charge. The ρ value is a susceptibility parameter of the system. The r^+ value of 1.41 for the 1-aryl-1-(trifluoromethyl)ethyl cation system indicates greater π-delocalization of the positive charge into the aryl π-system, compared with that in the α-cumyl (1-methyl-1-phenylethyl) cation.[5)] Furthermore, this r^+ value was found to be in complete agreement with the value for the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates in aq 80% acetone, supporting that the r^+ value of 1.39 observed for this solvolysis must reflect the intrinsic resonance demand of a highly electron-deficient cationic transition state of the S_N1 ionizing process.[6)] From this result we concluded that the significant curvature or break in the plot of logarithms of rate constants vs. σ^+ ($r^+=1.00$) observed for the solvolysis of a deactivated benzylic system is not due to a mechanistic change along with a change of substituents from electron-releasing to electron withdrawing, but is due to an improper analysis of the substituent effect. Thus, the highly electron-deficient carbocation system is far beyond the scope of the simple Brown $\rho^+\sigma^+$ treatment, and has been characterized by a unique r^+ value that is distinctly higher than the value of unity. An exalted resonance demand may be expected for all electron-deficient carbocation systems. In fact, we recently found a remarkably high r^+ value of 1.53 with a normal-size ρ value of -6.05 for the solvolysis of 1-aryl-2,2,2-trifluoroethyl tosylates in 50% aq ethanol, although the range of the substituent points is not wide enough, because of a very low reactivity of the substrates.[7)] On the other hand, Tidwell et al.

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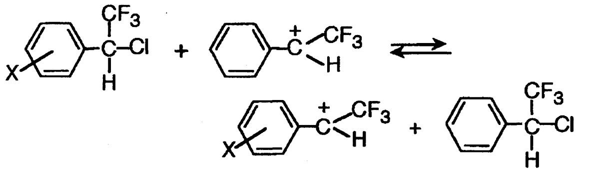
previously analyzed the substituent effect of this solvolysis based on a simple $\rho^+\sigma^+$ treatment, and reported remarkably large ρ^+ values of -9 to -12 in most solvents.[8] The large negative ρ^+ value was taken to be evidence for the k_c mechanism, and was attributed to a strong destabilization of the incipient cation by the α-CF_3 group. However, the magnitude of the ρ^+ value is incredibly large for the transition state of the solvolysis, because these values are comparable to, or even larger than, that of the substituent effect on the proton-transfer equilibrium between α-cumyl cations and α-methylstyrenes in the gas phase,[5,9,10] where there is no solvation stabilization of carbocations. It is therefore interesting to study the substituent effect on the gas-phase stability of the 1-phenyl-2,2,2-trifluoroethyl cation, which corresponds to an intermediate cation of the S_N1 solvolysis of the 1-phenyl-2,2,2-trifluoroethyl substrate. This will provide direct information on the substituent-effect behavior of such an extremely electron-deficient carbocation system. Furthermore, we are particularly interested in the substituent effect of this system, because we found an excellent linear relationship between the resonance demands (r^+) and the intrinsic stabilities ($\Delta\Delta G^\circ_{X=H}$) of the unsubstituted member of a respective series of benzylic carbocations.[11,12] The resonance demand of an extremely electron-deficient carbocation will serve to expand this relationship. Accordingly, we determined the intrinsic stabilities of 1-phenyl-2,2,2-trifluoroethyl cations by measuring the chloride ion-transfer equilibria (Eq. 3) in the gas phase. This method was successfully applied to determining the stabilities of the primary benzyl cation system.[13—15]



(3)

Results and Discussion

The measurements of the equilibrium constants of chloride ion-transfer reactions were performed on a pulsed-ion cyclotron resonance mass spectrometer and on a Extrel FTMS-2001 in the same manner as that used for determining the stabilities of benzyl cations.[15] The relative chloride ion affinity (CIA) values[16] were determined stepwise based on the overlapping equilibria between a given carbocation and a reference carbocation of known chloride-ion affinity. The relative chloride-ion affinities of the reference carbocations used in this study were previously determined in our laboratory.[15] The standard free energy changes for each equilibrium are shown in Fig. 1. The chloride-ion affinity of the unsubstituted 1-phenyl-2,2,2-trifluoroethyl cation is 6.8 kcal mol^{-1} higher than that of the *t*-butyl cation. This value means that the 1-phenyl-2,2,2-trifluoroethyl cation is less stable by 7 kcal mol^{-1} than the primary benzyl cation, because the latter is 0.2 kcal mol^{-1} more stable than the *t*-butyl cation. We recently found a good linear relationship with a slope of near unity between the chloride-ion affinities of various carbocations and the gas-phase basicities of olefins, which give the corresponding carbocation by protonation.[15] There therefore seems to be no difficulty to combine both data of the chloride-ion affinities and the gas-phase basicities to construct a single scale of relative stabilities of the carbocations. Thus, we can see a spectrum of intrinsic stabilities of the unsubstituted member of the respective benzylic carbocations, as shown below.

$$\begin{array}{lccc} R^+ & PhC(Me)_2^+ > & RhCHMe^+ > & PhCH_2^+ \\ \Delta\Delta G^\circ_{X=H}/\text{kcal mol}^{-1} & 0.0 & 5.2 & 12.0 \\ & & > PhC(CF_3)Me^+ > & PhC(H)CF_3^+ \\ & & 16.2 & 19.5 \end{array}$$

The stability of the 1-phenyl-2,2,2-trifluoroethyl cation is the lowest among these benzylic carbocations, as expected from a strong electron-withdrawing effect of the CF_3 group. The variation in the stability of the benzylic carbocations would primarily be referred to as an electronic effect of the α-substituents, and would be controlled by the combined effects of two α-substituents, though there is no simple additivity.

Substituent Effect. The relative chloride-ion affinity values of the 1-aryl-2,2,2-trifluoroethyl cations are summarized in Table 1, which cover a sufficiently wide range to analyze in detail the substituent effect. Figure 2 shows plots of the relative chloride-ion affinities of the 1-phenyl-2,2,2-trifluoroethyl cations against the corresponding values of the gas-phase basicities of the α-methylstyrenes, which correspond to the stabilities of the α-cumyl cations. This plot can be regarded as being a gas-phase σ^+-plot, because the stabilities of the α-cumyl cations could be described excellently by the ordinary solution set of the σ^+ values.[5] At a glance, it is found that there is no simple linear relationship for a whole set of substituents, clearly indicating the inapplicability of a simple σ^+-analysis to this system. If limited only to non-conjugate substituents, *meta* substituents and the *para* trifluoromethyl group, there could exist a good linear relationship with a slope of 1.08. All *para* π-donor substituents show positive deviations from this line. The slope of near unity means that the effects of non-conjugate substituents on the stability of carbocations are identical in both systems in spite of the large difference in the stability of the unsubstituted member of the respective carbocations. The upward deviations of *para* π-donors are systematic, i.e., the stronger *para* π-donor substituent shows a greater deviation. This trend of the *para* π-donors suggests that the resonance stabilization from *para* π-donor substituents must be greater in the 1-phenyl-2,2,2-trifluoroethyl cation system than that in the α-cumyl cation. In fact, these deviations of the *para*-π-donor substituents are related to the resonance substituent constant values, $\Delta\overline{\sigma}^+_R$ (Eq. 2).

$$\begin{aligned} &-\delta\Delta G^\circ_{(PhC^+(CF_3)H)} \\ &= 1.08(-\delta\Delta G^\circ)_{\alpha-\text{cumyl cation}} - 7.64\Delta\overline{\sigma}^+_R + 0.1. \end{aligned} \tag{4}$$

Such correlations are observed whenever there is a large difference in the stabilization of the positive charge by the res-

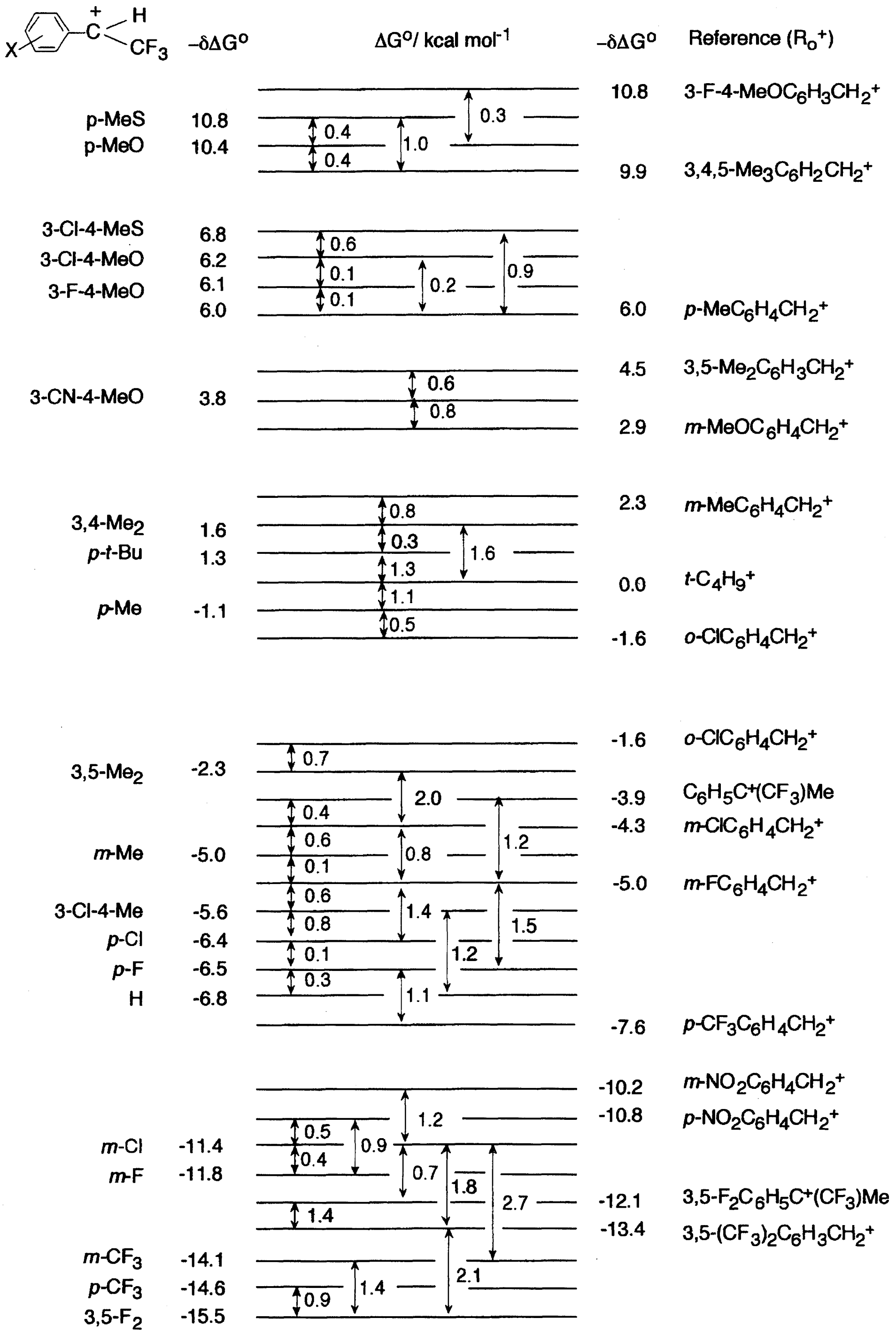


Fig. 1. Ladder of ΔG° values for chloride ion-transfer equilibrium (Eq. 3) measured at 343 K. Values of $-\delta\Delta G^\circ$ are relative to *t*-butyl cation and positive values denote lower chloride ion affinity, i.e., higher stability of a carbocation. The scale of $-\delta\Delta G^\circ$ of reference carbocations was taken from our previous study.[15]

onance effect of *para* π-donors between two systems.[12,15,17] An application of the Y–T equation to the present system in terms of the equilibrium constants gave an r^+ of 1.53 and a ρ of -10.6 with high precision, as shown in Fig. 3 and Table 2. In this correlation analysis, the *p*-SMe, 3-Cl-4-SMe, and 3-CN-4-OMe groups were excluded, and these substituents deviate upward from the regression line, indicating an exalted stabilization effect of these substituents. Although the cause of these deviations is not clear at present, it seem that this can be attributed in part to an exalted contribution of the polarizability effect of these substituents in a highly electron-deficient carbocation system.[18] Further study may be necessary to clarify in detail this behavior. The r^+ value of 1.53, given by well-behaved substituents, is obviously higher than not only the value of unity for the α-cumyl cation, but also that of the 1-phenyl-1-(trifluoromethyl)ethyl cation, which

Table 1. Relative Chloride Ion Affinities of 1-Aryl-2,2,2-trifluoroethyl Cations[a)]

Subst.	$-\Delta$CIA/kcal mol^{-1}	Subset.	$-\Delta$CIA/kcal mol^{-1}
p-MeO	17.2	3,5-Me$_2$	4.5
3-Cl-4-MeO	13.0	*p*-*t*-Bu	8.1
3-F-4-MeO	12.9	*p*-F	0.3
3-CN-4-MeO	10.6	*p*-Cl	0.4
p-MeS	17.6	*m*-Cl	−4.6
3-Cl-4-MeS	13.5	*m*-F	−5.0
p-Me	5.7	*m*-CF$_3$	−7.3
3-Cl-4-Me	1.2	*p*-CF$_3$	−7.8
m-Me	1.8	3,5-F$_2$	−8.7
3,4-Me$_2$	8.4	H	0.0(−6.8)[b)]

a) Negative values of the free energy changes of chloride ion-transfer equilibria (Eq. 3). b) Relative to *t*-butyl cation.

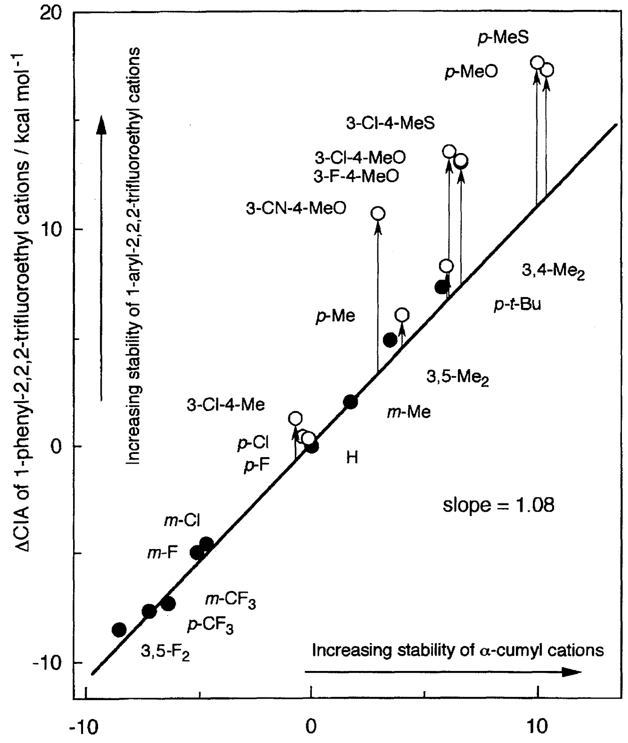


Fig. 2. Plots of stabilities of 1-aryl-2,2,2-trifluoroethyl cations vs. those of α-cumyl cations: Open circles; *para* π-donor substituents, closed circles; *meta* substituents.

is one of the highly electron-deficient carbocation systems. Consequently, destabilization of a carbocation by the α-substituent linked to the central carbon essentially causes an exaltation of the resonance demand.

Varying r^+ Values with the System. In previous studies we found an excellent linear relationship between the resonance demands (r^+) and the intrinsic stabilities ($\Delta\Delta G^\circ_{X=H}$) of the unsubstituted member of the respective series of benzylic carbocations.[11,12)] The r^+ value of 1.53 for the present system obeys this linear correlation, as shown in Fig. 4. Including an sp hybridized carbocation, a vinyl cation, there is an excellent linear relationship between these two quantities with a correlation coefficient of 0.997 and a standard deviation of ±0.02.

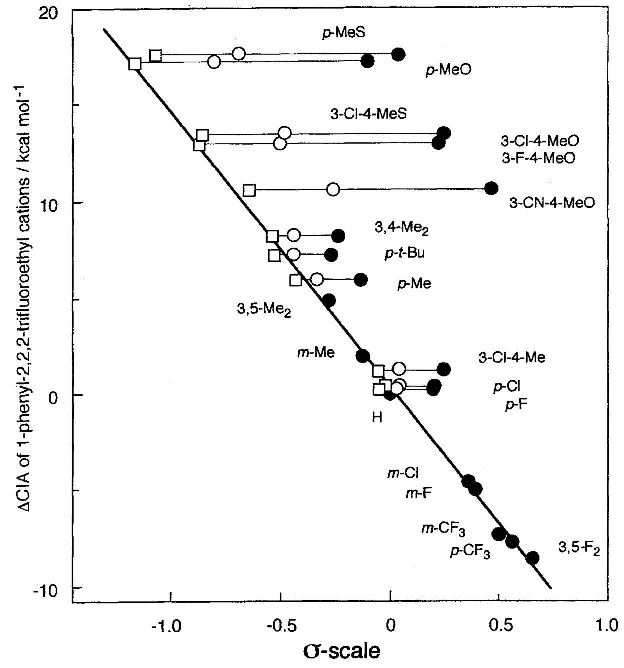


Fig. 3. The Y–T plot of stabilities of 1-aryl-2,2,2-trifluoroethyl cations against: σ^+ (open circles), σ° (closed circles), and $\overline{\sigma}$ with r=1.53 (squares).

$$r^+ = 0.0261\Delta\Delta G^\circ_{X=H} + 1.00. \tag{4}$$

This correlation clearly demonstrates that the resonance demand substantially varies with the intrinsic stability of a given carbocation, showing a continuous spectrum of the r^+ values. This fact also suggests that the origin of the varying resonance demand is the intrinsic stability of the parent carbocations. It is interesting to correlate this variation of the r^+ value with the substituent constants describing the electronic effects of the α-substituents, because such a correlation has practical use to expect an r^+ value for a new system of which the resonance demand is unknown. Using the σ°_p and $\Delta\overline{\sigma}^+_R$ substituent constants as a first approximation for parameters describing the electronic effects of α-substituents (R^1 and R^2), respectively, the following correlation was given with a satisfactory precision (R=0.9992, SD=±0.01):

$$r^+ = 0.45\Sigma\sigma^\circ + 0.40\Sigma\Delta\overline{\sigma}^+_R + 1.28. \tag{5}$$

where $\Sigma\sigma^\circ = \sigma^\circ_p(R^1) + \sigma^\circ_p(R^2)$ and $\Sigma\Delta\overline{\sigma}^+_R = \Delta\overline{\sigma}^+_R(R^1) + \Delta\overline{\sigma}^+_R(R^2)$. Equation 5 is further transformed into the LSFE equation form based on $\sigma^\circ = \sigma_i + \sigma^+_\pi$ and·$\Delta\overline{\sigma}^+_R = 0.415\ \sigma^+_\pi$, where σ_i and σ^+_π are field/inductive and π-electronic effect substituent constants, respectively,[19)]

$$r^+ = 0.45\Sigma\sigma_i + 0.62\Sigma\sigma^+_\pi + 1.28. \tag{6}$$

This result indicates that the r^+ value as well as the intrinsic stability of the parent carbocation are affected by both field/inductive and π-electronic effects of the R^1 and R^2 substituents, in spite of the variation in the central carbon from the primary to tertiary carbon. Furthermore, we have recently

Table 2. Results of the Y–T Analysis for Gas-Phase Stability of Benzylic Cations and for the Solvolysis of the Corresponding Substrates

$ArC^+(R^1)R^2$		$\Delta\Delta G^\circ_{X=H}$ [a)]	Gas-phase stability			Solvolysis	
R^1	R^2		ρ [b)]		r^+	ρ	r^+
CF_3	H	19.5	−10.6	(−14.2)	1.53	−6.05[h)]	1.53[h)]
CF_3	Me	16.2	−10.0[c)]	(−13.7)[c)]	1.41[c)]	−6.29[i)]	1.39[i)]
H	H	12.2	−10.3[d)]	(−14.0)[d)]	1.29[d)]	−5.20[j)]	1.30[j)]
H	Me	4.9	−10.1[e)]	(−13.8)[e)]	1.14[e)]	−5.45[k)]	1.15[k)]
Me	Me	0.0	−9.5[f)]	(−13.0)[f)]	1.00[f)]	−4.59[l)]	1.00[l]
Me	Et	−0.4	−9.5[g)]	(−13.0)[g)]	1.00[g)]	−4.7[m)]	1.04[m)]

a) In kcal mol^{-1}. Relative stabilities of the unsubstituted member of respective series, based on proton-transfer or chloride ion-transfer equilibria, see also Ref. 2. b) Values in parentheses are obtained by multiplying the ρ of $\log K/K_\circ$ by the factor $2.303RT/1000$, i.e., kcal mol^{-1} $\overline{\sigma}^{-1}$ unit c) Ref. 2. d) Ref. 13. e) M. Mishima, S. Usui, M. Fujio, and Y. Tsuno, *Nippon Kagaku Kaishi*, **1989**, 1269. f) Ref. 5. g) M. Mishima, H. Nakamura, K. Nakata, M. Fujio, and Y. Tsuno, *Chem, Lett*, **1994**, 1607. h) Tosylates in 50% aq ethanol at 25 °C, Ref. 7. i) Tosylates in 80% aq ethanol at 25 °C, Ref. 6. j) Tosylates in 80% aq acetone at 25 °C: M. Fujio, M. Goto, T. Susuki, I. Akasaka, M. Mishima, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **63**, 1146 (1990). k) Chlorides in 80% aq acetone: M. Fujio, T. Adachi, Y. Shibuya, A. Murata, and Y. Tsuno, *Tetrahedron Lett.*, **25**, 4557 (1984). ρ value corrected to 25 °C. l) Chlorides in 90% aq acetone at 25 °C: H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1944 (1957); **80**, 4979 (1958); L. M. Stock and H. C. Brown *Adv. Phys. Org. Chem.*, **1**, 35 (1963). m) Chlorides in 90% aq acetone: M. Fujio, K. Nakata, T. Kuwamura, H. Nakamura, Y. Saeki, M. Mishima, S. Kobayashi, and Y. Tsuno, *Tetrahedron Lett.*, **34**, 8309 (1993).

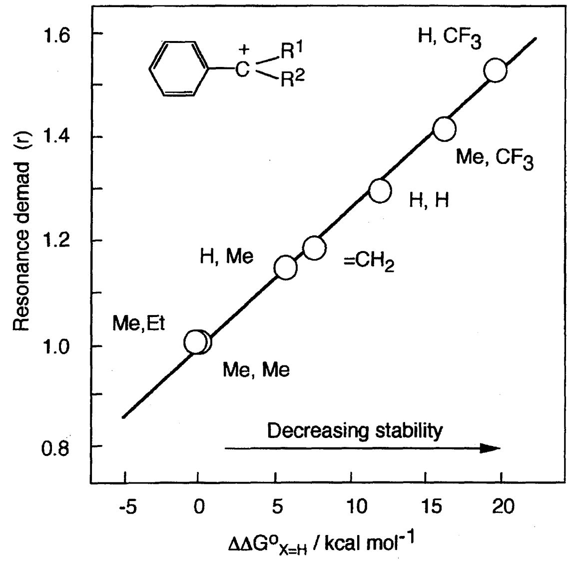


Fig. 4. Linear relationship between resonance demands and relative stabilities of parent carbocations (ring substituent= H).

found that the r^+ values are correlated linearly with theoretical parameters given by ab initio molecular-orbital calculation at the RHF/6-31G* level such as the charge (Mulliken populations) on the *para* position of the phenyl ring and the Wiberg bond order or bond length of C_1–C_7, which are associated with the concept of a resonance interaction.[20)] Thus, the r^+ value has physical significance for characterizing the intrinsic nature of a carbocation, itself. The π-delocalization of the charge into the aryl π-ring is competitive to the stabilization from the α-substituent(s). The same conclusion was reached by the fact that the r^+ value for the gas-phase stability of the conjugate acid of the R-substituted benzoyl (ArCOR) system decreases along with an increase in the electron-donating ability of the R-substituent.[17)]

Comparison with Substituent Effects in Solution. It becomes clearer that the r^+ value is an inherent nature of the structure of a given carbocation. This provides us an important criterion for understanding the mechanisms of the benzylic solvolysis. It is therefore interesting to the compare substituent effects of the gas-phase carbocations with those of the solvolysis of the corresponding substrates. The r^+ value of 1.53 for the gas-phase stabilities of 1-aryl-2,2,2-trifluoroethyl cations is in complete agreement with that for the solvolysis of 1-aryl-2,2,2-trifluoroethyl tosylates in 50% aq ethanol.[7)] Such an agreement of the r^+ value has generally been observed for other benzylic carbocation systems, as summarized in Table 2. Concerning this result, we recently found that the solvation of a cation reduces the central charge to lower the response to substituent perturbation, essentially without changing the magnitude of the r value.[17)] Accordingly, the identity of the r^+ value between the stabilities of carbocations and solvolysis means that the degree of the charge-delocalization in the rate-determining transition state of the solvolysis is very close to that of the carbocation intermediate. The r^+ value of 1.53, observed for the solvolysis of 1-aryl-2,2,2-trifluoroethyl tosylates, is not a correlational artifact, but must be the resonance demand reflecting a highly electron-deficient cationic transition state of the limiting S_N1 ionizing process in the same manner as that of the solvolysis of ordinary benzylic substrates to give stable carbocations. In addition, the ρ value given by the Y–T analysis of this solvolysis is a normal size, as large as that of the solvolysis of the α-cumyl and 1-phenylethyl halides. This is in sharp contrast with the remarkably large ρ^+ values given by the simple σ^+ treatment, suggesting 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. Although the σ^+ value may be a good average of the substituent constants, which are applicable to ordinary benzylic solvolysis generating stable carbocation intermediates, the resonance demand essentially varies with the systems, and the highly electron-

Table 3. Physical Data of 1-Aryl-2,2,2-trifluoroethyl Chlorides

Subst.	Bp/°C (mmHg)j) [Mp/°C]	Carbon (%)		Hydrogen (%)		Nitrogen (%)	
		Found	Calcd	Found	Calcd	Found	Calcd
p-MeO	61—63(1)a)	48.04	48.13	3.62	3.59		
3-F-4-MeO	68—69(2)	44.36	44.56	2.97	2.91		
3-Cl-4-MeO	101(1)	41.48	41.73	2.72	2.72		
3-CN-4-MeO	[49.6—50.1]	47.98	48.12	2.90	2.83	5.71	5.61
p-MeS	b)	45.16	44.92	3.32	3.35		
3-Cl-4-MeS	b)	39.40	39.29	2.55	2.56		
3-Cl-4-Me	113(20)	44.68	44.48	2.92	2.90		
p-Me	93—94(30)c)	51.79	51.82	3.81	3.87		
m-Me	84—85(20)	51.88	51.82	3.78	3.87		
3,4-Me_2	103(25)	53.87	53.95	4.56	4.53		
3,5-Me_2	111—113(47)	53.96	53.95	4.52	4.53		
p-*t*-Bu	78—79(2)	57.41	57.49	5.49	5.63		
H	113(110)d)	49.30	49.38	3.08	3.11		
p-F	70(25)e)	45.22	45.20	2.36	2.37		
m-F	80—81(35)f)	45.09	45.20	2.43	2.37		
3,5-F_2	67(23)	41.86	41.68	1.82	1.75		
p-Cl	84—85(15)g)	41.91	41.95	2.22	2.20		
m-Cl	90(15)h)	42.02	41.95	2.23	2.20		
m-CF_3	71—72(16)i)	41.09	41.17	1.93	1.92		
p-CF_3	83—85(35)	41.03	41.17	1.88	1.92		

a) Lit,22) 57.5—59.5 °C/1 mmHg. b) Purified by GLC. c) Lit,22) 89—90 °C/27 mmHg. d) Lit,22) 70—71 °C/27 mmHg. e) Lit,23) 75—77 °C/24 mmHg. f) Lit,23) 72 °C/22 mmHg. g) Lit,22) 95—95.5 °C/24 mmHg. h) Lit,23) 114—115 °C/4 mmHg. i) Lit,22) 75.5—76.5 °C/25 mmHg. j) 1 mmHg=133.322 Pa.

deficient carbocation system is quite far beyond the scope of the simple $\rho^+\sigma^+$ treatment. In conclusion, the present results are strong evidence for the validity of the Y–T analysis of the solvolysis of 1-aryl-2,2,2-trifluoroethyl tosylates, and indicate that the enhanced resonance demand is an essential feature of the electron-deficient benzylic carbocation system.

Finally, it should be noted that the degree of the π-delocalization of the positive charge is identical between the cationic transition state and an intermediate cation for all series of benzylic systems, although the solvolysis rate constants vary remarkably by over 10^{12} fold from α-cumyl substrate to 1-phenyl-2,2,2-trifluoroethyl substrate. This finding is also consistent with the fact that a change in the solvent does not affect the r^+ value of the solvolysis, although the rate constants vary remarkably along with a change of the solvent. These facts lead us to the conclusion that the geometry of the transition state in the ionizing process of S_N1 solvolysis, which is a highly endothermic reaction, closely resembles the high-energy product, an intermediate cation. Thus,the intrinsic behavior of carbocations in the gas phase provides an important basis for better understanding of the real features of the transition state of organic reactions in solution.

Experimental

Materials. 1-Aryl-2,2,2-trifluoroethyl chlorides were prepared by general procedures from the corresponding alcohols,[22,23] which were available from our previous studies.[7] The physical properties of these compounds are summarized in Table 3. All of the samples were purified by distillation or GLC just before use, and were checked for purity by their ICR mass spectra. Each sample was subjected to several freeze-pump-throw cycles on the ICR inlet system to remove entrapped volatile impurities.

ICR Measurements. The equilibrium constant measurements of the chloride ion transfer (Eq. 7) were performed on a home-made pulsed ion cyclotron resonance mass spectrometer equipped with a capacitance bridge detector[24] and on a Extrel FTMS 2001 spectrometer with a modified inlet system.

$$\text{R–Cl} + \text{R}_\text{o}^+ \rightleftharpoons \text{R}^+ + \text{R}_\text{o}\text{–Cl} \tag{7}$$

$$K = [\text{R}_\text{o}\text{–Cl}/\text{R–Cl}]\cdot[\text{R}^+/\text{R}_\text{o}^+], \tag{8}$$

$$\Delta G^\circ = -RT\ln K. \tag{9}$$

The equilibrium constant is expressed by Eq. 8, where R–Cl and R_o–Cl are a given substituted 1-aryl-2,2,2-trifluoroethyl chloride and a reference chloride, respectively. 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 readings for the different ionization cross-sections of the various compounds.[25,26] 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 2 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 ±0.2 kcal mol^{-1} in most cases. More than two reference compounds were used to ensure the internal consistency of the data. The chloride ion affinities of the reference cations were previously determined in our laboratory.[13]

The authors gratefully acknowledge support for this research by a Grant-in-Aid for Scientific Research from Ministry of Education, Science, Sports and Culture.

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