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## GAS PHASE SUBSTITUENT EFFECTS. STABILITIES OF 1-ARYL-2,2,2-TRIFLUOROETHYL CATIONS

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Summary: Gas-phase stabilities of 1-aryl-2,2,2-trifluoroethyl cations were determined based on chloride-transfer equilibria. The substituent effect was analyzed based on the LArSR Eq., giving a remarkably high r of 1.53 and a  $\rho$  of -14.6.

The previous study<sup>1</sup> has shown that the substituent effect for the gas-phase stabilities of 1-aryl-1-(trifluoromethyl)ethyl cations can be described excellently in terms of our LArSR equation  $(1)^2$  with an r of 1.40 and a  $\rho$  of -14.0.

$$\delta \Delta G^{O} = \rho (\sigma^{O} + r \Delta \overline{\sigma}_{R}^{+})$$

The r value of 1.40 indicates remarkably greater  $\pi$ -delocalization of the positive charge into the aryl  $\pi$ -system compared with that in cumyl (1-methyl-1-phenylethyl) cation (r=1.00).<sup>3</sup> Furthermore, the exalted r value is in complete agreement with that for the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates, supporting the conclusion that an r value for this solvolysis must reflect the intrinsic resonance demand of a highly electrondeficient cationic transition state in the  $S_N$  1 ionizing process.<sup>4</sup> The substituent effect for a highly electron-deficient carbocation system has been characterized by a unique r value distinctly higher than unity, and an exalted resonance demand may be expected for all electron-deficient systems. Indeed, we recently found a remarkably high r of 1.51 with a  $\rho$  of -6.20 (for log k/k<sub>o</sub>) for the solvolysis of a strongly destabilized secondary system, 1-aryl-2,2,2-trifluoroethyl tosylates.<sup>5</sup> These results indicate the failure of a simple  $\sigma^+$ correlation to the substituent effect for highly electron-deficient carbocation reactions. Nevertheless, Tidwell et al. analyzed this solvolysis on the basis of the  $\sigma^+$ -correlation, giving  $\rho^+$  values of -9 to -10 in most solvents.<sup>6</sup> Similarly, the remarkably large  $\rho^+$ values were reported for relevant destabilized benzylic solvolyses from several groups.<sup>7-9</sup> The previous authors concluded that the range of -10 to -12 appears to be a temporary ceiling on the magnitude of  $\rho^+$  values for benzylic solvolyses.<sup>6</sup> As evidence for this conclusion, such large  $\rho^+$  values for the solvolysis were pointed out to be comparable with those for gas-phase stabilities of cumyl cations and 1-phenylethyl cations. Accordingly, we have examined in this study the substituent effect for the gas-phase stabilities of 1-aryl-2,2,2-trifluoroethyl cations 1 in order to clarify the intrinsic resonance demand of this system.

The relative stabilities of 1-aryl-2,2,2-trifluoroethyl cations 1 can be estimated from

$$x \xrightarrow{O} \stackrel{+}{C} \stackrel{CF3}{\leftarrow} + \underbrace{O} \stackrel{-}{C} \stackrel{CHCF3}{\leftarrow} \xrightarrow{T} x \xrightarrow{O} \stackrel{-}{C} \stackrel{CHCF3}{\leftarrow} + \underbrace{O} \stackrel{+}{C} \stackrel{CF3}{\leftarrow} (2)$$

the free energy changes of the chloride-transfer equilibrium by the same technique which was successfully applied to the determination of the stabilities of benzyl cations.<sup>10,11</sup> The equilibrium constants for the chloride-transfer reaction (2) were determined stepwise based on overlapping equilibria between carbocations of nearly equivalent chloride affinity strengths by means of a pulsed ion cyclotron resonance mass spectrometer.

Relative chloride ion affinities ( $\Delta$ CIA) of 1-aryl-2,2,2-trifluoroethyl cations 1 to the unsubstituted cation, which correspond to negative values of the free energy changes of the reaction (2), are listed in Table 1. Chloride ion affinity of 1-phenyl-2,2,2-trifluoroethyl cation is found to be higher by 7.5 kcal mol<sup>-1</sup> than the corresponding benzyl cation;<sup>10</sup> this result is attributed to strong destabilization of the cation by CF<sub>3</sub> group. Combining the present result with relevant results obtained so far yields a spectrum of the stabilities of the parent benzylic carbocation (ring substituent=H). Their stabilities significantly decrease as the substituent(s) linked to the central carbon is (are) changed from the methyl group to the electron-withdrawing CF<sub>3</sub> group.<sup>1,3,10,12</sup> This order holds exactly for the reactivity of the solvolysis for the corresponding substrates, suggesting a relationship







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-19.5

H\_+\_CFs

	$\delta \Delta G^{O}/kcal mol^{-1} a$			
Subst.	H,CF <sub>3</sub> (1)	CH3, CH3(2)		
p-MeO	17.2	10.5		
3-C1-4-MeO	13.0	6.7		
3-F-4-MeO	12.9	6.7		
3-CN-4-MeO	10.6	3.0		
p-MeS	17.6	9.8		
3-C1-4-MeS	13.5	6.2		
p-Me	5.9	4.1		
3-C1-4-Me	1.2	-0.6		
m-Me	1.9	1.8		
3,4-Me,	8.2	6.3		
3,5-Me,2	4.8	3.5		
p-t-Bu	7.2	5.8		
p-F	0.3	-0.1		
p-Cl	0.4	-0.4		
m-F	-5.0	-5.1		
m-Cl	-4.6	-4.7		
3,5-F,	-8.6	-8.5		
m-CF <sub>3</sub>	-7.3	-6.3		
p-CF3	-7.7	-7.2		
н	0.0 (-6.8) <sup>b</sup>	0.0 (12.7) <sup>b</sup>		

Table 1. Relative Stabilities of  $ArC^+(R^1)R^2$ 







between kinetics and thermodynamics of cation formation.

In Figure 1 are plotted the relative stabilities of carbocations 1 against the corresponding values of cumyl cations 2. This plot may be regarded as a gas-phase  $\sigma^+$ -plot because the gas-phase stabilities of 2 are described excellently by the ordinary solution set of  $\sigma^{+,3}$  There is no simple linear relationship as a whole, indicating inapplicability of the  $\sigma^+$ -analysis to this system. However, there seems to exist a good linear relationship with a slope of unity for meta substituents and para  $\alpha$ ,  $\alpha$ ,  $\alpha$ -trifluoromethyl group, and all para  $\pi$ -donor substituents significantly deviate upward from the line. The line of a unit slope for meta substituents and para  $\pi$ -acceptor suggests that the stabilization of the cation by these substituents must be identical for both systems regardless of the large difference in carbocation stability. Deviations of para  $\pi$ -donors are systematic, i.e., the stronger para  $\pi$ -donor substituent shows the wider deviation, suggesting a greater stabilization by resonance effects of the para  $\pi$ -donor substituents in the carbocation 1. Indeed, application of the LArSR Eq. 1 to 1 provides an r of 1.53 remarkably higher than the value of unity for cumyl cation, whereas a  $\rho$  of -14.6 is comparable to that for cumyl cation. The r value of 1.53 higher than those for not only cumyl cation but also destabilized 1-aryl-1-(trifluoromethyl)ethyl cation indicates the extremely strong  $\pi$ -interaction between the cation center and the aryl  $\pi$ -system in 1. The less stable carbocation should have substantially the higher resonance demand. This is consistent with our previous observation for relevant benzylic carbocations summarized in Table 2. The r value significantly increases as the carbocation is destabilized by  $\alpha$ -substituents while the ρ value remains surprisingly constant within a series of benzylic carbocations regardless of large variation of the stability in the carbocation. The plots of the r values against the relative stabilities of the respective parent carbocations give a good linear relationship as shown in Fig. 2. There is a continuous spectrum of varying resonance demands

Table	2.	LArSR	Corre	lations	of	Gas-phase
		Stabili	tion of	Dong	-No	Cotiona

C	$) - \dot{c} < \frac{R^1}{2}$			
x R <sup>1</sup>	R <sup>2</sup>	ρ	r	note
CF3	Н	-14.6	1.53	
CF3	Me	-14.0	1.40	a
н	н	14.0	1.29	b
н	Me	-13.6	1.14	С
Me	Me	-13.0	1.00	đ

a) Ref. 1. b) Ref. 3. Preliminary result gave an r of 1.31 and a  $\rho$  of -13.7, ref. 10. c) Ref. 11. d) Ref. 3.



Fig. 2. Relationship between resonance demands and stabilities of parent carbocations.

characteristic of the stabilities of carbocations. The degree of the  $\pi$ -delocalization of the charge in a cation into aryl  $\pi$ -system reflects the attenuation from  $\alpha$ -substituent(s). This is also consistent with the fact that the r value for the gas-phase stability of conjugated acid of Y-substituted benzoyl compound system (Ar-CO-Y) decreases with the increase in electron-donating ability of Y-substituent.<sup>13</sup> Thus, the r value has physical significance for characterizing the nature of a carbocation. These findings substantiate the conclusion that the varying resonance demand is the essential requirement for the substituent effect analysis,<sup>14</sup> which is the basic concept introduced into the LArSR Eq. 1.

Finally, it should be noted that the r value of 1.53 for gas-phase stabilities of carbocations 1 is in complete agreement with that for the solvolysis of 1-aryl-2,2,2-trifluo-roethyl tosylates. This reveals that the r value for its solvolysis must reflect the intrinsic resonance demand of a highly electron-deficient cationic transition state in the  $S_N$  1 ionizing process of this solvolysis in the same manner as those in ordinary benzylic solvolyses and that a simple  $\sigma^+$  with a fixed resonance demand of r=1.00 can no longer be applicable to highly electron-deficient carbocation reactions. The remarkably large  $\rho^+$  values of -10 to -12 regarded as a characteristic feature of highly destabilized benzylic solvolyses are an artifact of an improper analysis based on a  $\sigma^+$  correlation.

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