

GAS PHASE SUBSTITUENT EFFECTS IN A HIGHLY ELECTRON DEFICIENT SYSTEM. INTRINSIC RESONANCE
DEMAND OF 1-ARYL-1-(TRIFLUOROMETHYL)ETHYL CATION

Masaaki MISHIMA, Hiroki INOUE, Mizue FUJIO, and Yuho TSUNO*

Department of Chemistry, Faculty of Science,
Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812, Japan

Summary: Gas phase stabilities of 1-aryl-1-(trifluoromethyl)ethyl cations were determined based on the proton transfer equilibrium. The LArSR analysis of the substituent effect gave a unique r value of 1.40 with a ρ value of -14.0. This r value is identical with that for the corresponding solvolysis.

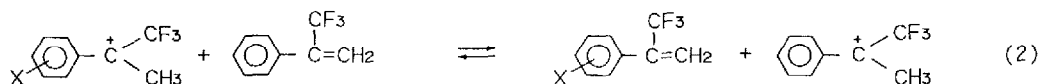
The solvolysis of extremely deactivated benzylic substrates with an electron-withdrawing group at a reaction site has recently been characterized by remarkably high response of the rate to aryl substituents.¹⁻⁵ For a typical "highly electron-deficient carbocation" system, the solvolysis of 1-aryl-1-(trifluoromethyl)ethyl tosylates, we reported an r value of 1.39 with a ρ value of -6.26^{6,7} by the analysis in terms of LArSR Eq. (1).⁸

$$\log(k/k_0) = \rho (\sigma^0 + r \Delta\sigma_R^+)$$
 (1)

The substituent effect for such a deactivated system was characterized by a unique r value remarkably higher than the value of unity defined for 1-methyl-1-phenylethyl (cumyl) solvolysis. On the other hand, Liu et al. noticed a remarkably large ρ^+ value of -10 for the same solvolysis based on the simple Brown σ^+ correlation.² Similarly, large ρ^+ values of -10 to -12 were reported for many such deactivated benzylic solvolyses.³⁻⁵ However, such ρ^+ values were merely inferred from the electron-donor portion of the substituents, whereas the electron-withdrawing portion gave smaller ρ^+ values of the ordinary size (-6 to -7). This is quite serious, since the significant curve break in the σ^+ -plot leads us to conclude the involvement of mechanistic change with the variation of substituents from electron-donor portion to electron-withdrawing portion. Nevertheless, ρ^+ values of -6 to -7 for the electron-withdrawing portion seem to be too large in magnitude to assign to any processes of solvolysis other than the k_c ionization process.⁷

Thermodynamic data of stabilities of carbocations in the gas phase which are absolutely free from mechanistic complexities will provide direct information on the inherent behavior of the carbocation intermediate of the S_N1 solvolysis.⁹ The relative stabilities of carbocations can be estimated from the free energy changes of ion-molecular equilibria in the gas phase.

In the present study, we have chosen 1-aryl-1-(trifluoromethyl)ethyl cation **1**, as an electron deficient benzylic carbocation. The gas phase stabilities of carbocations **1** were determined by measuring the equilibrium constants for the proton transfer reaction of the corresponding olefin (1-aryl-1-(trifluoromethyl)ethylene) with suitable reference cations of known stability by means of a pulsed ion cyclotron resonance mass spectrometer at 343 K. Stabilities of **1** relative to 1-phenyl-1-(trifluoromethyl)ethyl cation are summarized in Table 1.



We recently found a surprisingly excellent linear relationship for the gas-phase stabilities of cumyl (1-methyl-1-phenylethyl) cations **2** against the ordinary solution set of σ^+ as shown in Fig. 1.^{10,11} There seems to be no difficulty in defining a reference gas-phase σ^+ by this set of stabilities of **2**. Thus the plot of the gas phase stabilities of **1** against the corresponding stabilities of **2** shown in Fig. 2 corresponds to the gas phase σ^+ plot. Obviously, no simple linear relationship is observed as a whole in this plot, suggesting a limitation of the σ^+ analysis. The scattering must be referred to the intrinsic nature of carbocation **1**. For meta substituents, a good linear relationship with a slope of unity is observed, and all para π -donor substituents significantly deviate upward from the line of a unit slope. Deviations of para π -donors are systematic, and indicate a greater stabilization by the strong para π -donor substituents. The deviation behavior is just what would be expected for the system of an enhanced resonance demand,^{6,7} and in fact, application of the LArSR Eq. 1 provides an r of 1.40 and a ρ of -14.0 for **1** with satisfactory precision. The r value of 1.40 is remarkably higher than the value of unity for **2**. Thus, the carbocation **1** less stable by 16 kcal mol⁻¹ than **2** should have an inherent resonance demand distinctly higher than unity for **2**. This is supported further by the results for relevant benzylic

Table 1. Relative Gas Phase Stabilities^a of Carbocations

subst.	$\delta\Delta G^\circ/\text{kcal mol}^{-1}$	
	1 ^b	2 ^c
p-MeO	14.8	10.5
p-MeO-m-Cl	11.5	6.7
p-MeO-m-F	11.3	6.7
p-MeS	13.9	10.0
p-MeS-m-Cl	11.2	6.2
p-Me	5.8	4.1
p-Me-m-Cl	0.7	-0.6
m-Me	2.1	1.8
3,5-Me ₂	4.8	3.5
p-t-Bu	7.2	5.8
H	0.0	0.0
	(-12.7) ^d	(3.5) ^d
p-F	0.4	-0.1
p-Cl	0.4	-0.4
m-Cl	-4.3	-4.7
m-F	-4.8	-5.1

a) Negative values of acidities (GA) of cations. b) 1-Aryl-1-(trifluoromethyl)-ethyl cations. c) 1-Aryl-1-methylethyl cations. d) Relative to ammonium ion (GA(NH₄⁺)=195.6 kcal mol⁻¹).

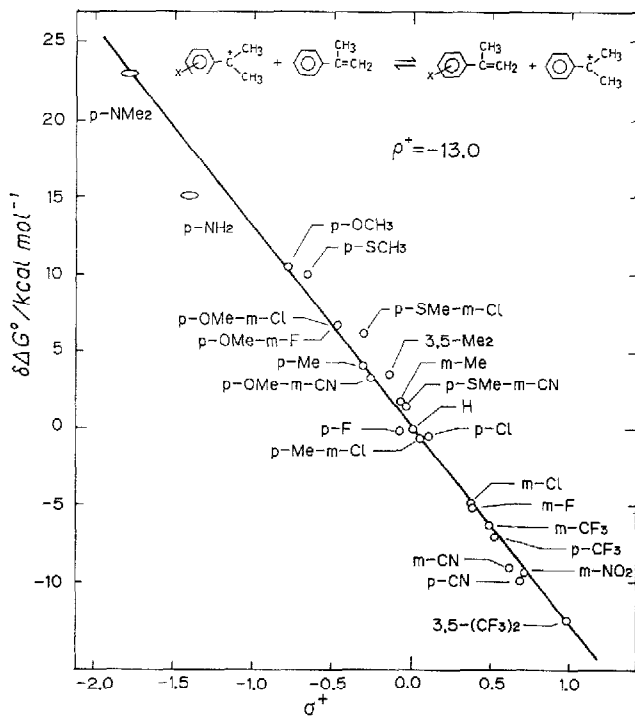


Fig. 1. Gas-phase stabilities of cumyl cations vs. σ^+ in solution.

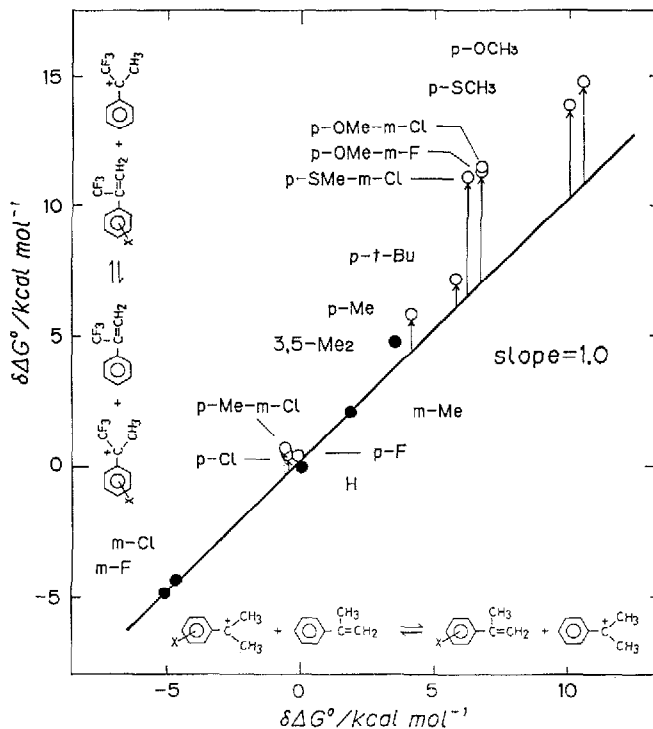


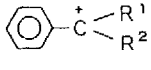
Fig. 2. Plots of gas-phase stabilities of 1-aryl-1-(trifluoromethyl)ethyl cations against the corresponding cumyl cations

carbocations as summarized in Table 2. Clearly, the r value varies with the stability of respective parent benzylic carbocations (ring substituent=H), whereas the ρ value remains surprisingly constant within a series of benzylic carbocations. Most importantly, the r value for gas phase stability of **1** has been found to be identical in magnitude with the r value for the S_N1 solvolysis of the corresponding substrate. This is also the case for other benzylic carbocations.^{6,7} The present results are the strong evidence for our basic concept of varying resonance demand in the LArSR Eq.⁸ The ρ value for the solvolysis is reduced significantly by effective solvation of the cationic transition state compared with that for the corresponding gas phase cation-stability. These findings strongly support that the LArSR Eq. 1 is applicable to the gas phase substituent effects in exactly the same manner as to the solution phase substituent effects.

The identity of r value between the solvolysis and the corresponding gas-phase cation stability may provide quite important information concerning the real picture of the solvolysis transition state. The degree of π -delocalization of the charge into the aryl ring relative to the charge-delocalization by inductive/field effect will remain essentially the same in the gas phase as in solution. The solvation of cation reduces the central charge to lower the response to substituent perturbation, essentially without changing the nature of the intramolecular charge-delocalization. Furthermore, the charge delocalization in the S_N1 transition state in the solvolysis should also be quite close to that of the carbocation intermediate. The Hammond-Leffler postulate¹³ must be strictly applied to all these endothermic processes. The enhanced r value of 1.39 obtained for the solvolysis of

1-aryl-1-(trifluoromethyl)ethyl tosylates must reflect the intrinsic resonance demand characteristic of the parent 1-aryl-1-(trifluoromethyl)ethyl cation itself. The success of LArSR analysis with moderate ρ value implies that remarkably large ρ^+ values emphasized as a characteristic of highly deactivated substrates are simply an artifact of improper σ^+ analysis.

Table 2. Results of LArSR Analysis for Gas-phase Stability of Benzylic Cations and for the Solvolysis of the Corresponding Substrates

		ΔG_{ST}^a	gas-phase stability		solvolysis reactivity	
R ¹	R ²		ρ^b	r	ρ^c	r
CF ₃	Me (1)	-16.2	-14.0(-10.2)	1.40	-6.29 ^f	1.39 ^f
H	H	-12.5	-13.7(-10.0) ^d	1.31 ^d	-5.20 ^g	1.30 ^g
H	Me	-5.2	-13.6(-9.9) ^e	1.14 ^e	-5.45 ^h	1.15 ^h
Me	Me (2)	0.0	-13.0(-9.5)	1.00	-4.59 ⁱ	1.00 ⁱ

a) Relative stability of respective parent carbocations estimated from proton-transfer or chloride-transfer equilibria, in kcal mol⁻¹. b) Values in parentheses are obtained by multiplying the ρ of gas-phase stability by the factor of 1000/2.303RT. c) For log(k/k₀). d) Ref. 9. e) Ref. 12. f) Tosylates in 80% aq. ethanol, refs. 6 and 7. g) Tosylates in acetic acid, ref. 7. h) Chlorides in 80% aq. acetone, ref. 8b. ρ value corrected to 25°C. i) Chlorides in 90% aq. acetone.

References

1. K. T. Liu and C.-F. Shu, *Tetrahedron Lett.*, **21**, 4091 (1980); K. T. Liu, M. Y. Kuo, and C.-F. Shu, *J. Am. Chem. Soc.*, **104**, 211 (1982).
2. 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. Mehrsheikh-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, *ibid.*, **108**, 3470 (1986).
6. Y. Tsuno, A. Murata, M. Goto, and M. Fujio, "Physical Organic Chemistry 1986," ed. by M. Kobayashi, Elsevier, Amsterdam-Tokyo (1987), p. 167; A. Murata, M. Goto, R. Fujiyama, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **16(2)**, 225 (1988).
7. M. Fujio, M. Goto, A. Murata, Y. Tsuji, M. Mishima, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **16(2)**, 271 (1988).
8. a) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.*, **45**, 1198 (1972); b) Y. Tsuno, Y. Kusuyama, M. Sawada, T. Fujii, and Y. Yukawa, *ibid.*, **48**, 3337 (1975); c) Y. Tsuno, W.-Y. Chong, Y. Tairaka, M. Sawada, and Y. Yukawa, *ibid.*, **51**, 596 (1978).
9. M. Mishima, K. Arima, S. Usui, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **15(2)**, 277 (1986); M. Mishima, K. Arima, S. Usui, M. Fujio, and Y. Tsuno, *Chem. Lett.*, **1987**, 1047.
10. M. Mishima, S. Usui, H. Inoue, M. Fujio, and Y. Tsuno, *Nippon Kagaku Kaishi*, submitted.
11. A ρ^+ of -12.6 was reported earlier based on limited substituents; A. G. Harrison, R. Houriet, and T. T. Tidwell, *J. Org. Chem.*, **49**, 1302 (1984).
12. M. Mishima, S. Usui, M. Fujio, and Y. Tsuno, *Nippon Kagaku Kaishi*, submitted.
13. G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955); J. E. Leffler, *Science*, **117**, 340 (1953).

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