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Substituent Effect on the Stability of Benzyl Cation in the Gas Phase

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Chloride ion affinities of substituted benzyl cations in the gas phase have been determined by means of an ICR mass spectrometer. The substituent effect has been analyzed in terms of the LArSR Eq., giving a ρ=13.6 and an r^+=1.31.

For many years we have studied substituent effects on solvolytic reactions of benzylic substrates,1) which have provided valuable evidence for validating our basic concept of varying resonance demand of reaction center as formulated into the LArSR Eq. 1.2) Resonance demand parameter r^+ varies significantly with systems,

$$\log(k/k_o) \text{ or } P-P_o = \rho(\sigma^o + r^+\Delta\bar{\sigma}_R{}^+) \qquad (1)$$

e.g., from 1.00 for 1-methyl-1-phenylethyl chloride solvolysis via 1.17 for 1-phenylethyl chloride to 1.4 for 1-trifluoromethyl-1-phenylethyl tosylate, and the r value appears to be characteristic of the transition state or carbocation intermediate. The substituent effect on solvolysis of benzyl substrates is of particular interest for well-known failure of proper analysis of the substituent effect arising from a mechanistic transition, and in the theoretical view as a reference benzylic system.3) Recent development of experimental techniques makes it possible to determine intrinsic stabilities of carbocations. Cation stabilities in the gas phase are completely free from any mechanistic complexities.4) These data would provide new insight into the nature of transition state of solvolysis of the primary benzyl substrate as well as a basis for studying an essential linear free energy relationship. In this paper, we will discuss the substituent effect on the stability of the primary benzyl cation in comparison with that of tertiary 1-methyl-1-phenylethyl cations.

The intrinsic stabilities of benzyl cations can be estimated by measuring relative chloride affinity based on chloride transfer equilibria (2) in the gas phase.5) The standard free energy changes of chloride transfer equilibria (2) have

$$XC_6H_4CH_2Cl + C_6H_5CH_2{}^+ \rightleftarrows XC_6H_4CH_2{}^+ + C_6H_5CH_2Cl \qquad (2)$$

been determined by means of an ion cyclotron resonance mass spectrometer. Experimental data have been obtained based on overlapping equilibria between carbocations of nearly equivalent chloride affinity strengths.6) The chloride affinities of representative substituted benzyl cations relative to unsubstituted one are summarized in Table 1 together with the corresponding acidity values of 1-methyl-1-phenylethyl cations which were determined based on the proton transfer equilibria.[7,8]

In Fig. 1 the relative chloride affinities of substituted benzyl cations are plotted against the corresponding acidities of 1-methyl-1-phenylethyl cations. The plot is neither simple linear relationship nor monotonic curvature as a whole, but a good linear relationship with a slope of unity is observed as far as meta substituents and para π-acceptor ones are concerned. On the other hand, all para π-donor substituents show significant upward deviations from the line of unity. Deviations of para-π-donors are systematic, and greater stabilization with stronger π-donor substituents may be indicative of enhanced resonance contribution in the benzyl cation system compared with the 1-methyl-1-phenylethyl cation system. The deviation behavior is just what has generally been observed in the σ^{+} plots for benzylic solvolyses. The LArSR theory appears to be equally applicable to the gas phase substituent effects, provided an appropriate set of substituent constants for gas phase reactivities. There seems to be no significant difference between two systems in any particular effects inherent in gas phase data such as polarizability effect.[9] Furthermore, the substituent effect on acidity of 1-methyl-1-phenylethyl

$$-\delta\Delta G^{o}_{Me,Me} = -13.04\ \sigma^{+} \qquad (R=0.998,\ SD=\pm 0.4\ kcal/mol,\ n=15) \tag{3}$$

cations can be described in fact rather unexpectedly well with σ^{+} values in solution except for a few particular solvent-sensitive groups and highly polarizable ones.[11] Detailed examination of Fig. 1 indicates that magnitude of enhanced stabilization by such substituents can be related with resonance effect of respective substituents, $\Delta\bar{\sigma}_{R}^{+}$ values,[1b,2b] in solution by Eq. 4 with excellent precision.

Table 1. Relative Stabilities of Substituted Benzyl Cations and Substituted 1-Methyl-1-phenylethyl Cations in the Gas Phase

	$-\delta\Delta G^{o}$ a)			$-\delta\Delta G^{o}$ a)	
Subst	H,H[b]	Me,Me[c]	Subst	H,H[b]	Me,Me[c]
p-OMe	13.9	10.5[d]	m,m-Me_2	4.3	3.6
m-Cl-p-OMe	11.0	6.7	p-F	1.1	-0.1[d]
m-F-p-OMe	10.6	6.8	m-F	-5.3	-5.1[d]
m-CN-p-OMe	7.1	3.3	p-Cl	0.8	-0.5
p-SMe	13.0	10.0	m-Cl	-3.8	-4.7[d]
m-Cl-p-SMe	9.5	6.2	p-CF_3	-7.2	-7.0
m-CN-p-SMe	5.0	1.5	m-CF_3	-6.9	-6.2
p-Me	5.8	4.1[d]	H	0.0	0.0
m-OMe	2.7	2.1[d]		(0.2)[e,f]	(11.9)[e]
m-Me	2.1	1.8[d]			

a) In kcal/mol, 1 cal=4.184 J. b) For a reaction, $ArCH_2Cl + C_6H_5CH_2^{+} \rightleftarrows ArCH_2^{+} + C_6H_5CH_2Cl$. c) For a reaction, $ArC(Me){=}CH_2 + C_6H_5C(Me)_2^{+} \rightleftarrows ArC(Me)_2^{+} + C_6H_5C(Me){=}CH_2$. d) Ref. 8. e) Relative to t-butyl cation. f) -0.2 kcal/mol(303 K) and 1.2 kcal/mol(300 K) were reported (Refs. 10 and 5b, respectively).

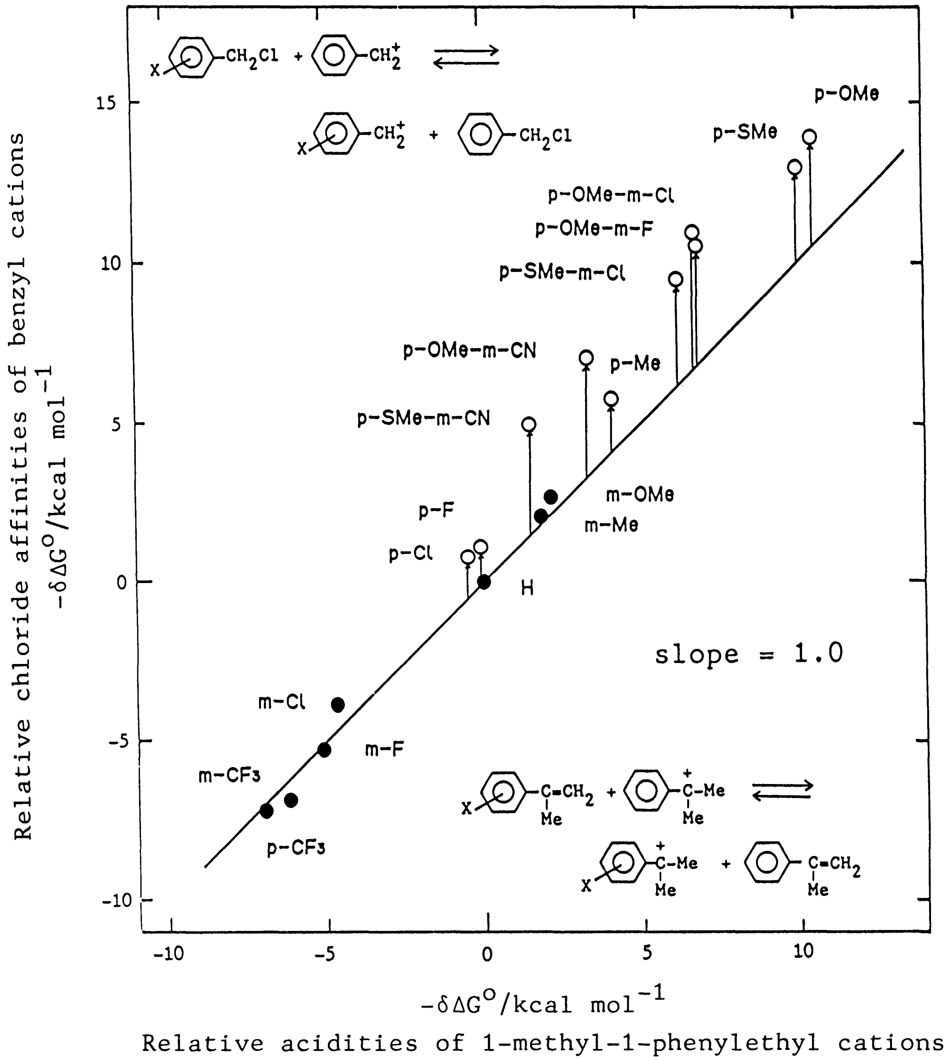

Fig. 1. Plots of relative chloride affinities of substituted benzyl cations against the corresponding acidities of 1-methyl-1-phenylethyl cations.

$$-\delta\Delta G^{o}{}_{H,H} = 1.04(-\delta\Delta G^{o})_{Me,Me} - 4.4\Delta\bar{\sigma}_{R}{}^{+} \qquad (4)$$

(R=0.997, SD=±0.4 kcal/mol, n=18)

The ρ values in both substituent effects are identical regardless of different stability of carbocations. Substituting Eq. 4 into Eq. 3 yields the ordinary LArSR expression (5), as $\sigma^{+}=1.00\sigma^{o} + 1.00\Delta\bar{\sigma}_{R}{}^{+}$ by definition.

$$-\delta\Delta G^{o}{}_{H,H} = -13.6(\sigma^{o} + 1.31\Delta\bar{\sigma}_{R}{}^{+}) \qquad (5)$$

The exalted r^{+} value implies greater resonance demand in the benzyl cation system than in the 1-methyl-1-phenylethyl one (r^{+}=1.00). This may be referred to the fact that the benzyl cation in the gas phase is less stable than the 1-methyl-1-phenylethyl cation by 12.0 kcal/mol.6) The resonance demand varies essentially depending upon inherent stability of parent carbocation. This is consistent with the results of substituent effects on the gas phase basicities of benzoyl series, ArCOY.12)

A detailed analysis of the acetolysis of benzyl tosylates permits a most reasonable estimation of the ρ of -5.4 and r^+ of 1.3 based on a wide variety of electron-donating substituents excluding k_s substrates of mechanistic complexity.13) This r^+ value for the solvolysis is identical in its value with that observed for the gas stability of benzyl cations. Obviously, the enhanced resonance demand obtained for the benzyl solvolysis must be intrinsic one, but not a correlational artifact of the non-linear relation caused from mechanistic complexity. The stabilization of solvolysis intermediates should be proportional, though attenuated, to the intrinsic one in the gas phase cations. The same r^+ value implies that the resonance demand of the solvolysis transition state is essentially determined by the intrinsic demand of the intermediate carbocation. This leads to an important suggestion that the r^+ value for the solvolysis of ordinary endothermic ionization process does not depend significantly upon the shift of transition state relative to the intermediate along the reaction coordinate, and consequently, the Hammond-Leffler postulate should be much more widely applicable to general solvolysis processes.

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