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Thermodynamic Stabilities of Phenonium Ions Based on Bromide-Transfer Equilibria in the Gas Phase[1)]

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The thermodynamic stabilities of the phenonium (ethylenebenzenium) ion and ring-substituted derivatives were determined based on the bromide-transfer equilibria in the gas phase. It has been shown that the phenonium ion is 2.4 kcal mol^{-1} more stable than the *t*-butyl cation, and that the substituent effect on its stability can be correlated with the Yukawa–Tsuno equation with a ρ value of -12.6 and an r^+ of 0.62. An r^+ value smaller than unity of the α-cumyl(1-methyl-1-phenylethyl) cation suggested that π-delocalization in the phenonium ion is essentially less effective than through a benzylic π-interaction. On the other hand, the ρ value of -12.6 is distinctly larger than that for the ordinary benzylic carbocation systems, but is comparable to that of the benzenium ion. In addition, it has been found that the r^+ value of the phenonium ions in the gas phase is in complete agreement with that for the aryl-assisted process in the acetolysis of 2-arylethyl toluenesulfonates. This suggests that the degree of π-delocalization of the positive charge is the same in the transition state and the intermediate cation. It is concluded that an r^+ value of 0.6, which is ranked at a unique position in the continuous spectrum of the resonance demand, is characteristic of the bridged structure of the phenonium ion intermediate and the transition state.

Neighboring phenyl-group participation, leading to a bridged phenonium (ethylenebenzenium) ion in the solvolysis of the 2-arylalkyl system, was a matter of intense investigation since Cram's pioneer work.[2,3)] The structural aspects of the phenonium ion were obtained from NMR studies[4)] and theoretical calculations,[5)] revealing a symmetrical σ-bridged structure. The substituent effect is a useful tool for exploring of mechanistic hypotheses in a variety of reactions, giving information regarding the energetic properties of the transition state and the intermediate.[6)] Most solvolyses of 2-arylalkyl sulfonates, however, show nonlinear substituent effects because of a concurring solvent-assisted process. The observed solvolysis rate (k_t) should be the sum of two competing processes, the aryl-assisted (k_Δ) and unassisted (k_s) processes (Scheme 1).[7)]

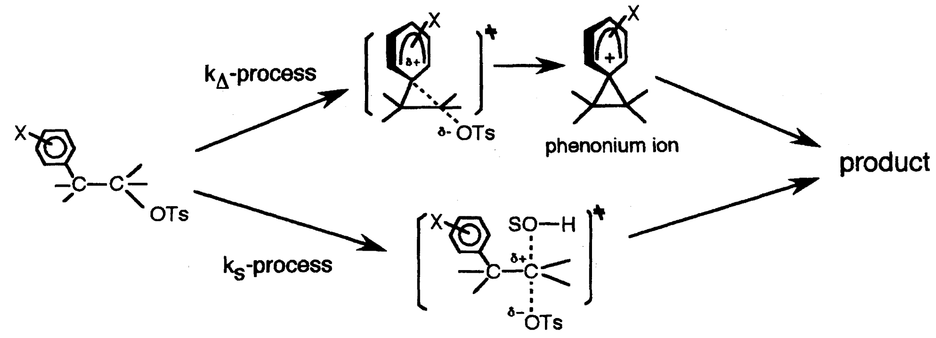
Both processes would independently be described in terms of the Yukawa–Tsuno (Y–T) Equation 1[8)] in the same manner as the substituent effects of the solvolysis of the ordinary benzylic substrates,

$$\log(k/k_\circ) = \rho(\sigma^\circ + r^+\Delta\overline{\sigma}_R^+), \qquad (1)$$

where σ° is a normal substituent constant and $\Delta\overline{\sigma}_R^+$ is a resonance substituent constant ($\Delta\overline{\sigma}_R^+ = \sigma^+ - \sigma^\circ$); r^+ is a resonance demand parameter representing the degree of the π-interaction between a *para* π-donor substituent and a positive charge at the reaction center. The apparent substituent effect described by the Y–T correlation (2) was, in practice, analyzed by using a nonlinear least squares method,[9—11)]

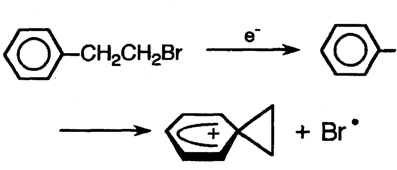
$$\log k/k_\circ = \rho_\Delta(\sigma^\circ + r_\Delta^+\Delta\overline{\sigma}_R^+) + \rho s(\sigma^\circ + r_s^+\Delta\overline{\sigma}_R^+). \qquad (2)$$

In this analysis the $r_s^+ = 0$ was applied for an unassisted process for simplification. In this way, we obtained a ρ value of -3.87 and an r^+ value of 0.63 for the aryl-assisted (k_Δ) process in the acetolysis of 2-arylethyl tosylates.[9)] In addition, the r^+ values of 0.5—0.6 were observed for the k_Δ solvolyses of various 2-arylalkyl substrates.[10,11)] For ordinary benzylic solvolysis, a trend was found that the r^+ value increases as the positive charge formed at the transition state is destabilized by the substituents linked to the benzylic carbon. These results gave a continuous spectrum of the r^+ value from 1.00 for α-cumyl chlorides (1-methyl-1-phenylethyl chlorides), via 1.29 for benzyl tosylates, to ≥ 1.5 for extremely electron-deficient carbocation systems, such as 1-phenyl-2,2,2-trifluoroethyl tosylates.[8c)] Thus, the r^+ values of 0.5—0.6 obtained for the aryl-assisted solvolyses are ranked at a unique position in the continuous spectrum of the r^+ value, and must be a characteristic feature of their unique transition structures. In order to interpret the intermediate r^+ value in connection with the reaction mechanisms and the transition structures of the 2-aryl-assisted solvolyses, the resonance demand of intermediate cations, phenonium ions, would be the most suitable reference, because the magnitude of the r^+ value depends on an inherent nature of the structure of a given carbocation.[12)] The substituent effects on the thermodynamic stabilities of carbocation in the gas phase should be the best model for the behavior of solvolysis intermediates in solution. This is also a critical test for the validity of the dissection of the apparent substituent effect into two competing processes, the aryl-assisted and unassisted processes. The gas-phase stability of the phenonium ion may be determined



Scheme 1. Solvolysis of 2-arylalkyl tosylates.

by the bromide-transfer equilibria of 2-arylethyl bromides, because early mass spectrometric studies suggested that the most plausible structure of the $C_8H_9^+$ ion produced from 2-phenylethyl bromide and 2-phenylethyl iodide by an electron-impact ionization at low electron energies should be the phenonium ion.[13]



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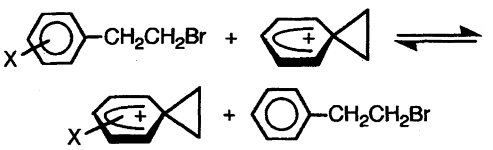
In this paper we report on the thermodynamic stabilities of *m,p*-substituted phenonium ions determined on the basis of the bromide ion-transfer equilibria (4) in the gas phase and the results of an analysis of the substituent effect.



(4)

Resucts and Discussion

The standard free-energy change of bromide-transfer equilibria was determined by measuring the equilibrium constants using the ion cyclotron resonance mass spectrometer. Electron-impact ionization of a binary mixture of 2-phenylethyl bromide and *t*-butyl bromide produced $C_8H_9^+$, $C_7H_7^+$, and $C_4H_9^+$ ions as major abundant ions (Fig. 1a). The abundance of the *t*-butyl cation was found to significantly decrease with time, and $C_8H_9^+$ in turn increased. This suggests that the reaction (5) proceeds from left to right, i.e., an exothermic reaction,

$$\mathrm{PhCH_2CH_2Br} + t\text{-}\mathrm{C_4H_9^+} \rightleftharpoons \mathrm{C_8H_9^+} + t\text{-}\mathrm{C_4H_9Br}. \qquad (5)$$

The direction of the bromide-transfer reaction was confirmed by an ion-ejection experiment using the stored-waveform inverse Fourier-transform (SWIFT^{TM}) technique,[14] i.e., no signal other than *t*-Bu$^+$ was observed just after all ions, except for *t*-Bu$^+$, were ejected from the ICR cell (Fig. 1b), and the signal of the $C_8H_9^+$ ion appeared and gradually increased with time, as shown in Figs. 1c—1f. This result means that the $C_8H_9^+$ ion is evidently generated by a bromide-transfer from 2-phenylethyl bromide to *t*-Bu$^+$. In addition, no $C_7H_7^+$ ion was observed after an ion-ejection pulse was supplied,

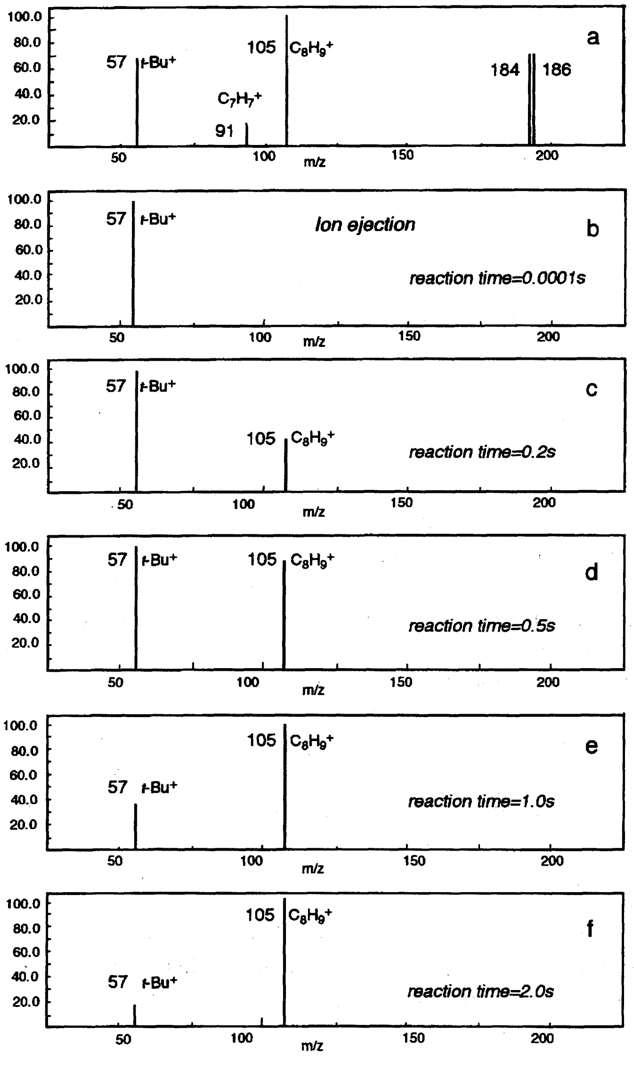


Fig. 1. FT-ICR mass spectra of a binary mixture of 2-phenylethyl bromide (3.5×10^{-7} Torr, 1 Torr=133.322 Pa) and *t*-butyl bromide (14.8×10^{-7} Torr) by electron-impact ionization at the electron energy of 10 eV; (a) no ion-ejection. (b)—(f) at different reaction time under ion-ejection conditions.

indicating that the $C_7H_7^+$ ion is unreactive toward neutral bromides and/or ions. Clearly, reaction (5) is the dominant process occurring in the ion-trapped ICR cell. The relative peak height of the signals of $C_8H_9^+$ to $C_4H_9^+$ became constant for a reaction time longer than 2 s. This means that after the equilibrium condition is attained the equilibrium constant value can be obtained. Thus, the standard free energy changes were determined for the bromide-transfer equilibria between various cations. The results are illustrated in Fig. 2. The internal consistency of data may be low compared to that reported for the proton-transfer equilibrium based on the same technique, because the bromide ion transfer reaction is slower than the proton-transfer reaction. The ladder in Fig. 2 shows that the $C_8H_9^+$ ion is 2.4 kcal mol^{-1} more stable than the *t*-butyl cation. This result easily rules out the possibility of an open (primary) cation for the $C_8H_9^+$ ion.

The combined results with relative stabilities of the relevant carbocations are illustrated in Fig. 3.[16] One scale of the stabilities of carbocations is based on the relative chloride/bromide ion affinity. The other scale is the relative basicities (proton affinities) of olefins. From these data, two points clearly emerge: (1) the $C_8H_9^+$ is 5 kcal mol^{-1} less stable than the 1-phenylethyl cation given by the addition of a proton to styrene or by the loss of a chloride ion from 1-phenylethyl chloride, indicating that the long-lived $C_8H_9^+$ ion in the ICR cell is not the isomerized 1-phenylethyl cation. Therefore, the $C_8H_9^+$ ion must be the phenonium ion, being consistent with the conclusion given by the early mass-spectrometric studies.[13] (2) The gas-phase basicities (proton affinities) of benzene and isobutene indicate that the benzenium ion, which has a similar molecular framework, is less stable than the *t*-butyl cation, while the phenonium ion is more stable than the *t*-butyl cation. A direct comparison between the phenonium ion and the benzenium ion is impossible, because there is no common thermodynamic quantity reflecting the difference in the stability between these two ions. That the stability of the phenonium ion is higher than that of the *t*-butyl cation may be attributed to a strong electron-releasing effect of the cyclopropane-like group, the extended π-delocalized system.

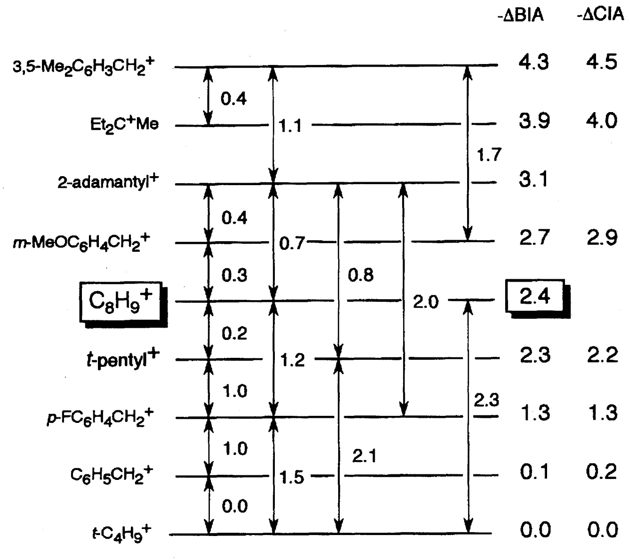


Fig. 2. Ladder of ΔG° values for bromide-transfer equilibria measured at 300 K, in kcal mol^{-1}. Bromide ion affinity (BIA) decreases and stability of R$^+$ increases from bottom to top. ΔCIA means relative chloride ion affnities of the corresponding cations, Ref. 15.

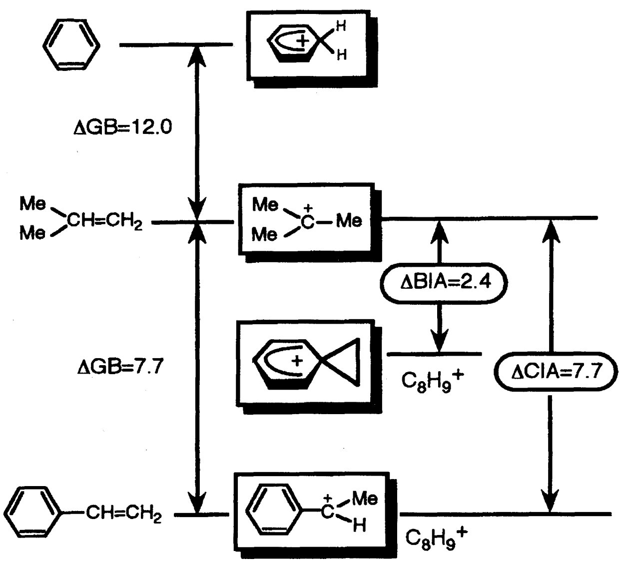


Fig. 3. Free-energy changes of proton-, chloride-, and bromide-transfer equilibria for relevant carbocations. ΔGB and ΔCIA values were taken from Refs. 15 and 16, respectively.

Substituent Effect. To determine the relative stabilities of a series of phenonium ions it is necessary to construct a complete scale covering a wide range of bromide ion affinity (BIA) because of a lack of bromide-ion affinity values for reference carbocations. The relative chloride-ion affinity (CIA) values, however, are in agreement with the corresponding bromide-ion affinities within experimental error, as shown in Fig. 2. This reveals that the chloride-ion affinities and the bromide-ion affinities of carbocations have an identical response to substituent perturbation. Both scales will therefore be equally referred to the relative stabilities of carbocations in the gas phase. Theoretical calculations also suggest that the ranking of the stabilities of carbocations is independent of the nature of a leaving group.[17] These facts allow us to use relative chloride-ion affinity values of reference carbocations as anchored values of their relative stabilities. In this way, the free-energy changes were measured for a series of phenonium ions, as shown in Fig. 4. Although the bromide-ion affinity values of some derivatives having a strongly electron-withdrawing group could not be determined because of the formation of the adduct ion, $(RBrR')^+$, the values summarized in Table 1 cover a sufficiently wide range to analyze the substituent effect in detail.

Figure 5 shows a plot of the relative stabilities of phenonium ions against those of the corresponding α-cumyl cations determined based on the gas-phase basicities of α-methylstyrenes. Although there is no simple linear relationship, one can find a good linear relationship with a slope of 1.3

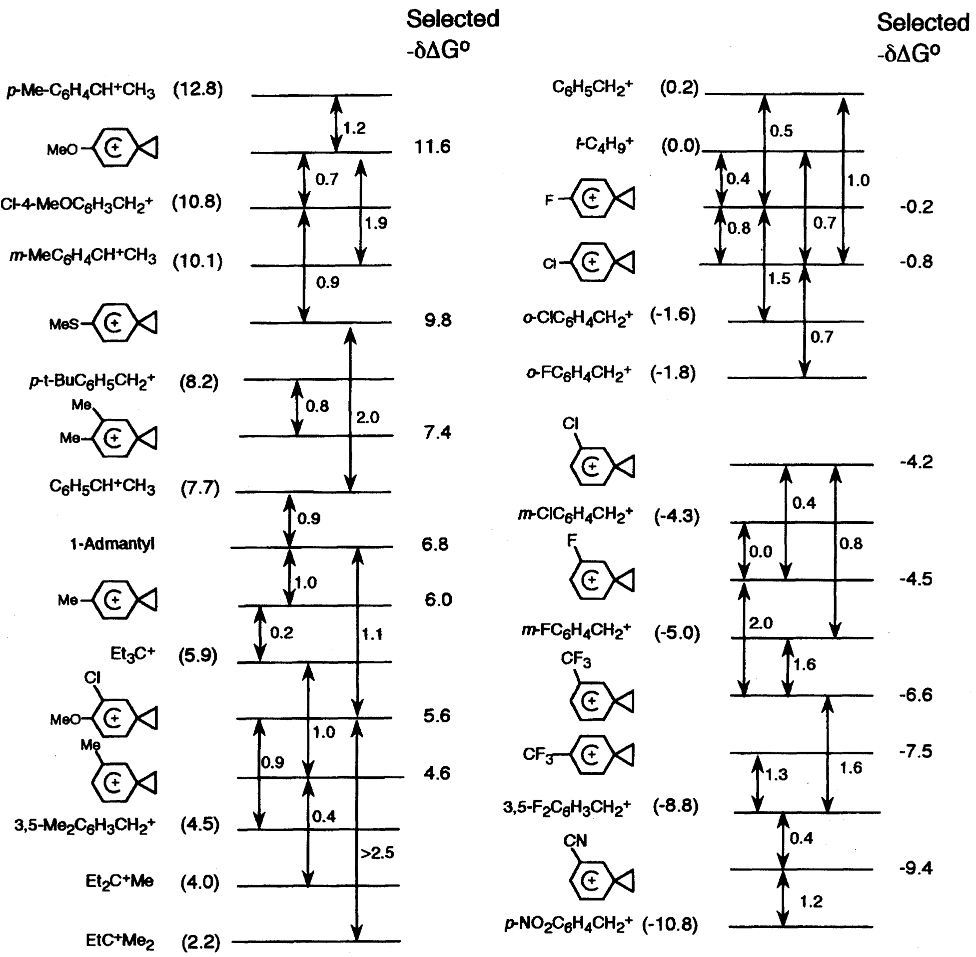


Fig. 4. Free-energy changes for respective bromide transfer equilibria and relative values to *t*-butyl cation (in kcal mol^{-1}). Values in parentheses are $-\Delta$CIA relative to *t*-butyl cation, Ref. 15.

Table 1. Relative Stabilities of Phenonium Ions and the Corresponding α-Cumyl Cations

Subst.	Phenonium ion $-\delta\Delta G^\circ$ [a)]	α-Cumyl cation ΔGB[b)]
p-OMe	9.2	10.5
p-SMe	7.4	10.0
3-Cl-4-OMe	3.2	6.7
3,4-Me$_2$	5.0	6.1
p-Me	3.6	3.6
m-Me	2.2	1.8
H	0.0	0.0
p-F	−2.6	−0.1
p-Cl	−3.2	−0.4
m-Cl	−6.6	−4.7
m-F	−6.9	−5.1
m-CF$_3$	−9.0	−6.3
p-CF$_3$	−9.9	−7.2
m-CN	−11.8	−9.0

a) Free-energy changes for a reaction (4), in kcal mol^{-1}. Positive value denotes greater stability relative to unsubstituted derivative. b) Relative gas-phase basicities of α-methylstyrenes, in kcal mol^{-1}. Taken from Ref. 18.

for *meta* substituents. The magnitude of the slope indicates a higher response of the substituent effect on the stability of the phenonium ion than that of the α-cumyl cation. All *para* π-donor substituents significantly deviate downward from the *meta*-line. This plot corresponds to a gas-phase σ^+-plot, because the substituent effect on the stability of the α-cumyl cation was found to be linearly correlated with σ^+.[18)] In addition, deviations observed for the *para* π-donor substituents are systematic, i.e., the substituent having a strong π-donating ability shows a larger downward deviation. This trend suggests that the resonance effect of the *para* π-donor involved in the substituent effect of the phenonium ion is smaller than that in σ^+. Such a pattern of deviations is indeed what is observed for a system where the contribution of the resonance effect of the π-donor is reduced.[19)]

The application of the Y–T Equation 1 to the substituent effect on the stability of the phenonium ion gave an excellent linear correlation, as shown in Fig. 6. A ρ value of -12.59 and an r^+ of 0.62 were obtained by the least-squares method ($R = 0.998$, SD $= \pm 0.3$, $n = 13$).[20)]

$$\begin{aligned}\log K/K_\text{o} &= -1000\delta\Delta G^\circ/2.303RT\\ &= -12.59(\sigma^\circ + 0.62\Delta + \overline{\sigma}_\text{R}^{+}). \qquad (6)\end{aligned}$$

Table 2 also summarizes the correlation results for the relevant systems. The r^+ value of 0.62 clearly indicates that

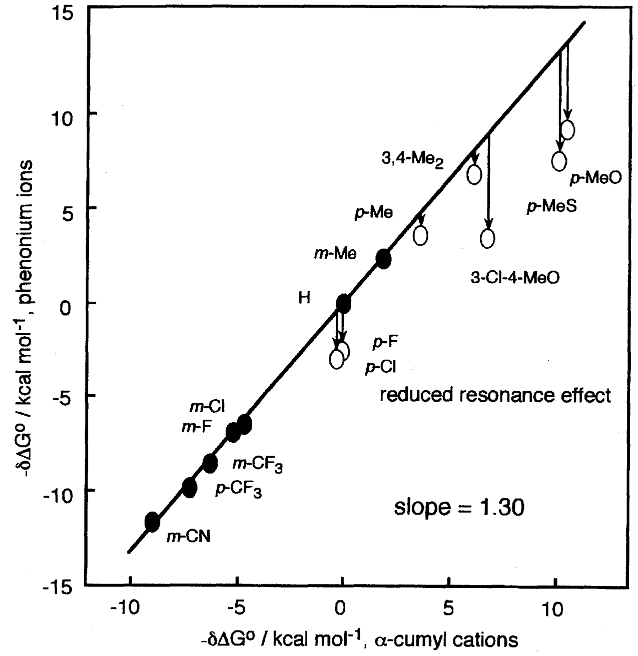


Fig. 5. Plot of the relative stabilities of phenonium ions against the corresponding α-cumyl cations.

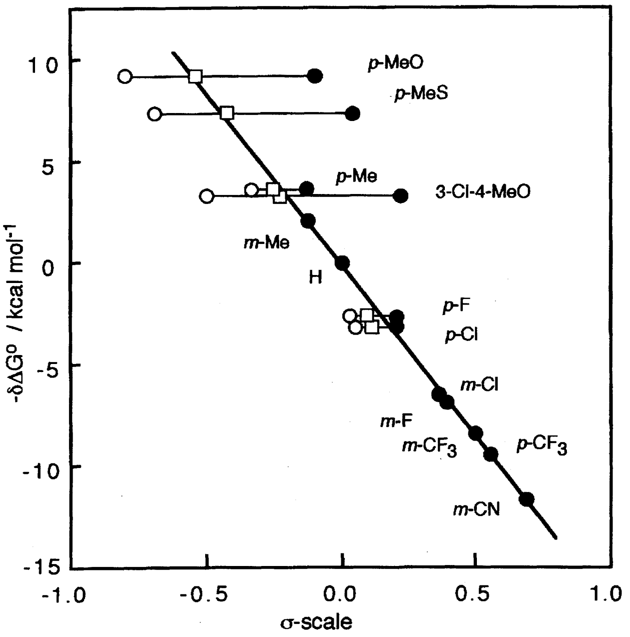


Fig. 6. The Y–T plot for the stabilities of phenonium ions. Closed circles; σ°, open circles; σ^{+}, squares; $\bar{\sigma}$ at r^{+}=0.62.

Table 2. Correlation Results for Gas-phase Carbocation Stabilities and for the Solvolyses of the Corresponding Systems Based on Yukawa–Tsuno Equation

System	ρ	r^{+}
Cation stability		
Phenonium ion	−12.6	0.62
Benzenium ion[a]	−13.1	1.30
$ArC^{+}Me_2$[b]	−9.5	1.00
$ArC^{+}(CF_3)Me$[c]	−10.0	1.41
Solvolysis		
$ArCH_2CH_2OTs$[d]	−3.87	0.63
$ArCMe_2Cl$[e]	−4.59	1.00
$ArC(CF_3)MeOTs$[f]	−6.29	1.39

a) Ref. 21. b) Ref. 18. c) Ref. 12a. d) For the k_{Δ} process, in AcOH at 115 °C, Ref. 10. e) 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). f) In 80% aq ethanol at 25 °C: A. Murata, M. Goto, R. Fujiyama, M. Mishima, M. Fujio, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **63**, 1129 (1990).

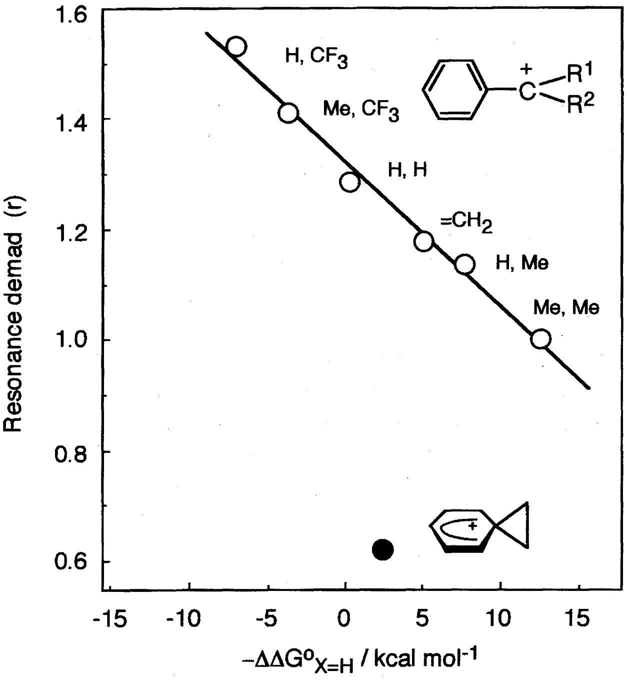


Fig. 7. Plot of the r^{+} values against the relative stabilities of the unsubstituted member of respective series.

although the positive charge in a cation is stabilized by the π-delocalization into *para* π-donor substituents, its magnitude is significantly smaller than that of the benzenium ion (r^{+}=1.3).[21] The r^{+} value in the benzylic carbocation system tends to decrease as the stability of the unsubstituted member of respective series increases.[12] However, the r^{+} value of the phenonium ion is remarkably smaller than that expected from the linear correlation between the r^{+} values of the benzylic carbocations and the stability of the unsubstituted member of the respective series (Fig. 7). This suggests that π-delocalization in the phenonium ion is essentially less effective than through a benzylic π-interaction. This may be interpreted by the orbital interactions in the phenonium ion, as proposed by Yamabe and Tanaka.[5c] They regarded the phenonium ion as being a charge-transfer complex between C_2H_4 and $C_6H_5^{+}$ based on its optimized structure, based on ab initio MO calculation. In this model the charge transfer from C_2H_4 to $XC_6H_4^{+}$ occurs through an orbital interaction between the HOMO of C_2H_4 and the LUMO of $XC_6H_4^{+}$. The resonance effect of the *para* π-donor substituent (X) in $XC_6H_4^{+}$ cannot efficiently affect this orbital interaction, because the LUMO of $XC_6H_4^+$ is perpendiculat to the π-orbital of the benzene ring. On the other hand, the orbital interaction between LUMO of C_2H_4 and HOMO of $XC_6H_4^+$ is strengthened by the the *para* π-donor substituent. This orbital interaction is, however, weaker than the former because of a large energy gap between LUMO of C_2H_4 and HOMO of $XC_6H_4^+$. This would result in a reduced r^+ value compared to that of the ordinary benzylic cation system.

The ρ value of -12.6 is remarkably larger than that observed for ordinary benzylic carbocation systems, e.g., -9.5 for the α-cumyl cation, and is comparable to that of the benzenium ion. Such a large ρ value appears to be a characteristic of the benzenium ion structure, in which most of the positive charge is located in the benzene ring. This is also supported by the fact that the effect of *meta* substituents on the stability of the phenonium ion is equal to that on the gas-phase basicity of pyridine,[22] of which the conjugate acid ion bears a positive charge within the pyridine ring.

$$-\delta\Delta G^\circ_{(\text{meta})} = 1.01\Delta \text{GB}_{(3\text{-X-pyridine})} - 0.01$$
$$(R = 0.999, n = 6) \qquad (7)$$

Comparison with the Results for the k_Δ Solvolysis. Table 2 summarizes the results of the Y–T analysis for the logarithms of the rate constants for the k_Δ process separated from the observed rate constants of the acetolysis of 2-arylethyl tosylates together with the results of the relevant benzylic substrates. It is clear that the r^+ value of 0.62 obtained for the stability of phenonium ions in the gas phase is in complete agreement with the value for k_Δ solvolysis. Such an agreement of the r^+ value was also observed for a series of benzylic cation systems.[12] Because the stabilities of the carbocation in the gas phase should be the best model for the behavior of solvolysis intermediates in solution, the identity of the r^+ value leads to the conclusion that the positive charge developed in the transition state is delocalized into the benzene π-system in the same manner as that of the phenonium ion intermediate. Its degree is characterized by an intermediate r^+ value of 0.6. The identity of the r^+ value also supports the validity of the dissection of concerning the apparent substituent effect on the acetolysis of 2-arylethyl tosylates into the effects on the aryl-assisted and solvent-assisted processes. That is, two competing processes can be independently described in terms of the Yukawa–Tsuno equation, as shown in Eq. 2.

The ρ of -3.87 for the k_Δ process is remarkably smaller than that of -12.6 for the gas-phase cation stability. Such a reduced ρ value in the solvolysis is generally attributed to solvent stabilization of the transition state and an intermediate cation, and in part to an incomplete development of the charge at the transition state. Although a similar reduction of the ρ value was observed for ordinary benzylic cation systems, such as the α-cumyl cation (Table 2),[8c] the degree of the reduction is appreciably small compared with that for the phenonium ion system. The difference in the ρ values between the carbocation stability and solvolysis for the α-cumyl system is 5, while the corresponding value is 8 for the phenonium ion system (Table 2). The phenonium ion and the benzenium ion have essentially a larger ρ value than that of benzylic cation, as mentioned above. Nevertheless, the ρ value of the k_Δ solvolysis is comparable to, or even smaller than, that for the solvolysis of benzylic substrates. Although the magnitude of the ρ value on the reactivity in solution depends on many factors, such as the solvent, temperature, and so on, it is unlikely that a small ρ value for k_Δ solvolysis can be explained by these factors, because there is no reason to consider that the solvent stabilization is remarkably effective in the aryl-assisted process compared with that in the ordinary S_N1 ionizing process of the benzylic substrates. Accordingly, such a large reduction of the ρ value in the aryl-assisted solvolysis of the 2-arylethyl system suggests a relatively small development of the positive charge at the reaction center, early transition state relative to an intermediate along a reaction coordinate, compared with that in the benzylic solvolysis. It is inferred further from this result that the resonance demand is less sensitive to the position of the transition state along the reaction coordinate than the ρ value, as long as the transition structure is similar to that of an intermediate cation.

Thus, the thermodynamic properties of an ion can provide a useful clue not only for characterizing the structure of a carbocation, but also for characterizing of the rate-determining transition state.

Experimental

Materials. 2-Arylethyl bromides were prepared by general procedures from the corresponding alcohols, which were available from our previous studies.[9] All 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-thaw cycles on the ICR inlet system in order to remove entrapped volatile impurities.

ICR Measurements. The equilibrium constant measurements of the bromide-ion transfer reactions were performed on an Extrel FTMS 2001 spectrometer equipped with a 3.0 T superconducting magnet and with a modified inlet system. Several data were also recorded on a homemade pulsed-ion cyclotron resonance mass spectrometer.[23]

$$\text{R–Br} + \text{R}_\circ{}^+ \rightleftharpoons \text{R}^+ + \text{R}_\circ\text{Br} \qquad (8)$$

$$K = [\text{R}_\circ\text{–Br}]/[\text{R–Br}]\cdot[\text{R}^+]/[\text{R}_\circ{}^+] \qquad (9)$$

$$\Delta G^\circ = -RT\ln K \qquad (10)$$

The equilibrium constant is expressed by Eq. 9, where R–Br and $\text{R}_\circ$–Br are a given substituted 2-arylethyl bromide and a reference bromide, 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.[24] The overall pressures of the reagents were maintained at 0.6 to 2×10^{-4} Pa by controlled rates through variable-leak valves from a parallel inlet manifold into the vacuum chamber. After a reaction period of several 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 300 K, the average uncertainty being ± 0.3 kcal mol^{-1} in most cases.

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