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Thermodynamic Stabilities of Phenonium Ions in the Gas Phase

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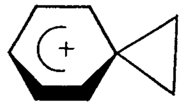
Gas phase stabilities of substituted phenonium (ethylenearenium) ions have been determined based on bromide transfer equilibria. The phenonium ion has been found to be stable even more than *t*-butyl cation, and the substituent effect on its stability has been analyzed based on the LArSR Eq., giving a ρ value of -17.5 and an r of 0.60.

Neighboring phenyl group participation leading to an intermediate phenonium (ethylenebenzenium) ion in the solvolysis of 2-arylethyl systems has been a matter of intense investigation since Cram's pioneer work.[1,2] Much attention has been concentrated on the characterization of the intermediate ion.[3-7] Under the stable ion conditions such as the superacid media the phenonium ion could be generated from 2-phenylethyl chloride, and was found to be a symmetrically bridged structure by means of the ^{13}C and proton NMR spectroscopy in accord with theoretical calculations.[4,7] On the contrary, the quantitative assessment of the energetics of the phenonium ion is not established well.[4,8] For a few past years we have been investigating proton-transfer and halide-transfer equilibria in the gas phase by means of the ion cyclotron resonance (ICR) spectrometry[9] to establish intrinsic stabilities of various benzylic carbocations.[10] This technique may be applicable to the determination of the thermodynamic stability of the phenonium ion relative to relevant carbocations. Recent studies on collisional activation mass spectra of a large number of compounds leading to the $C_8H_9^+$ ion suggested that the phenonium ion was generated from 2-phenylethyl bromide by electron impact ionization at low energies.[11] In this study, we have therefore examined bromide transfer equilibria of 2-arylethyl bromides using the pulsed ICR spectrometer.



$$C_6H_5CH_2CH_2Br + (CH_3)_3C^+ \rightleftharpoons C_8H_9^+ + (CH_3)_3CBr \qquad (1)$$

Electron impact ionization of a binary mixture of 2-phenylethyl bromide and *t*-butyl bromide produced $C_8H_9^+$, $C_7H_7^+$, and $C_4H_9^+$ as major ions. Following the short electron beam pulse (10 ms), the abundance of *t*-butyl cation decreased significantly with time, suggesting that the reaction (1) proceeds from the left to the right, i.e., exothermic reaction. The inferred direction of the bromide transfer was confirmed by ion ejection experiments using double resonance techniques,12) and also $C_7H_7^+$ ion was found to be unreactive toward neutral bromides or alternative ions.13) Consequently, reaction (1) is the dominant process occurring in the ion-trapped ICR cell. The measured free energy change of Eq. 1 is -2 kcal mol^{-1} or more at 300 K. This ΔG^o value may be less accurate because of the slow bromide transfer of the reaction (1) compared with that for simple alkyl bromides. In order to check reliability of this value and to confirm the scale of relative bromide ion affinity, we have examined the equilibria between various bromides including 2-phenylethyl bromide. In Fig. 1 are illustrated the measured free energy changes for bromide transfer equilibria denoted by arrows, indicating good internal consistency of the data. This figure also shows an important fact that the relative bromide affinity values are in agreement with the corresponding chloride affinities determined from chloride transfer equilibria within experimental errors. This means that relative bromide affinity value is predictable from the corresponding chloride affinity value, and vice versa, when experimental difficulties preclude their direct measurements. Thus, we have arrived at an average value of -2.4 kcal mol^{-1} for the phenonium ion relative to *t*-butyl cation, i.e., the phenonium ion is undoubtedly more stable than *t*-butyl cation. On the contrary, the stability of the benzenium cation of which structure is analogous to the phenonium ion is estimated to be ca. 14 kcal mol^{-1} lower than *t*-butyl cation from proton affinity values of

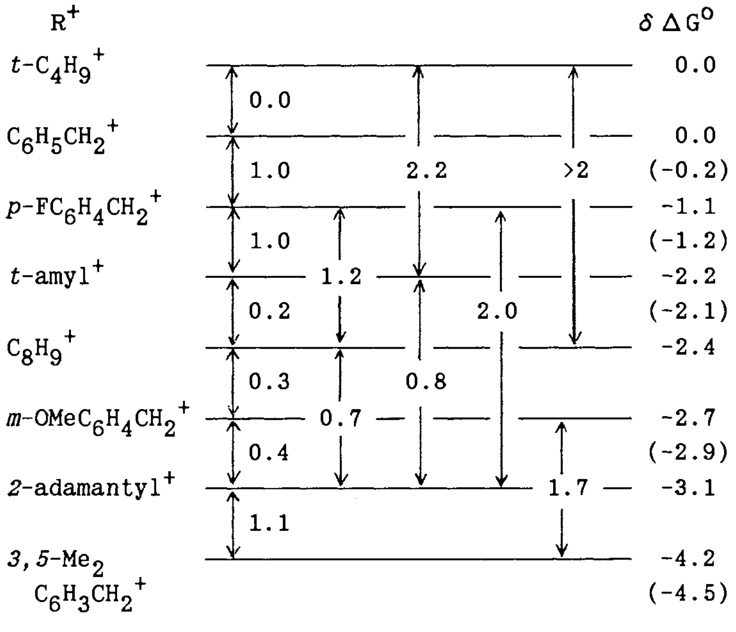


Fig. 1. Ladder of ΔG^o values for bromide transfer equilibria measured at 300 K, in kcal mol^{-1} (1 cal = 4.184 J. Bromide affinity (BIA) decreases and stability of R^+ increases from top to bottom. Values in parentheses are the corresponding chloride affinities.10a)

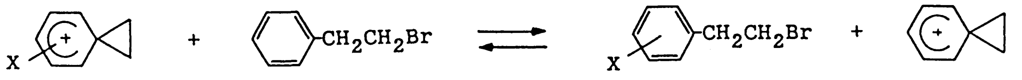
Table 1. Relative Bromide Affinities of Phenonium Ions

Subst.	-ΔBIA a)
p-OMe	8.3
p-SMe	7.4
3-Cl-*4*-OMe	3.5
p-Me	3.6
m-Me	2.1
H	0.0
p-F	-2.6
m-Cl	-6.6
m-F	-7.3
m-CF_3	-9.3

a) Free energy changes for a reaction (2), in kcal mol^{-1}. Positive value denotes greater stability relative to unsubstituted derivative.

benzene and 2-methyl-propene.[14)] The higher stability of the phenonium ion than benzenium ion may be attributed to strong electron releasing effect of the cyclopropane-like group. We found in previous study that 1-phenylethyl cation, an isomer of the phenonium ion, was more stable by 7 kcal mol^{-1} than *t*-butyl cation.[10a,14)] From this result the phenonium ion is inferred to be ca. 5 kcal mol^{-1} less stable than 1-phenylethyl cation. This also is evidence for that the long-lived $C_8H_9^+$ ion generated from 2-phenylethyl bromide by electron impact ionization at low energies is not the isomerized 1-phenylethyl cation.

To clarify further energetic properties of the phenonium ion, we have examined the substituent effect on its stability. Bromide affinities of ring substituted phenonium ions have similarly been determined on the basis of the ladder method using suitable reference compounds. The relative bromide affinities are summarized in Table 1. Application of the LArSR Eq. 3, which has been proved to be applicable to gas phase substituent effects,[10)] to these data gives a ρ value of -17.5 (kcal mol^{-1} $\bar{\sigma}^{-1}$ unit) and an *r* of 0.60 with an excellent precision as shown in Fig. 2.[15)] This ρ value is significantly larger than those observed for ordinary benzylic carbocation systems, e.g., -13 for α-cumyl cation,[10c)] but is in accord with a ρ value for the stabilities of benzenium ions (=proton affinities of substituted benzenes).[16)] Such a large ρ value appears to be characteristic of the benzenium ion structure which bears the positive charge in the ring system itself. The most important fact is that the *r* value is not zero but 0.60, indicating clearly that the positive charge in a cation is stabilized by the π-delocalization into para π-donor substituents in the same manner as the benzenium ion though the degree of the π-delocalization in the present system is significantly smaller than in the benzenium ion



(2)

$$\Delta G^o = -\Delta BIA = \rho(\sigma^o + r\Delta\bar{\sigma}^+_R) \qquad (3)$$

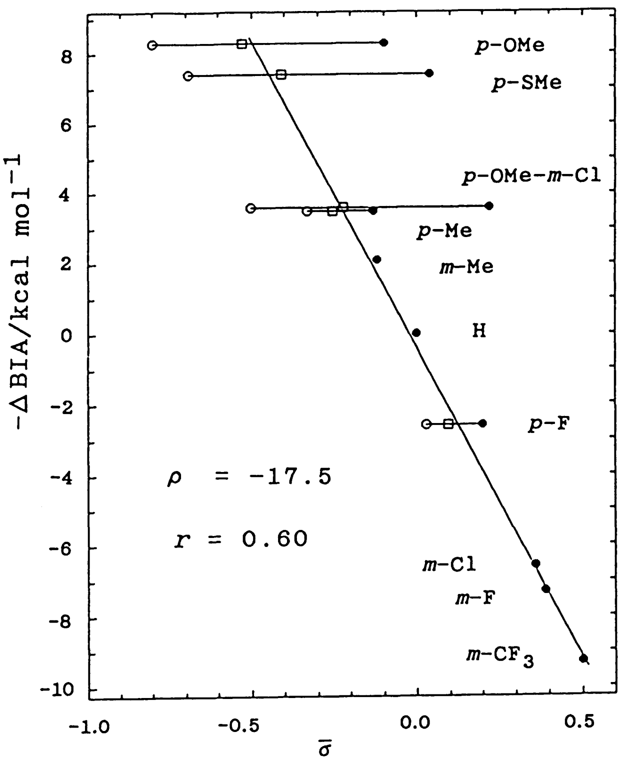


Fig. 2. LArSR correlation for the stabilities of phenonium ions. Closed circles; σ^o, open circles; σ^+, squares; $\bar{\sigma}$ at *r*=0.60.

(r=1.3).16) This reduction of resonance demand in the present system may be attributed to its high stability due to strong electron releasing effect of the cyclopropane ring. The trend of the resonance demand is consistent with previous observations for the benzylic carbocation system.10d,10e,17) Furthermore, the r value of 0.60 is in complete agreement with the value observed for the corresponding solvolysis via an intermediate phenonium ion.18) The agreement of the r value has generally been observed for the benzylic cation systems.10) It is concluded that the phenonium ion is characterized by an intermediate r value of 0.6. This also is strong evidence for that it is the phenonium ion which is actually being observed in the ICR spectrometer. Such thermodynamic properties of an ion would provide useful clue for characterization of the ion structure although mass spectrum itself does not provide direct information on the structure of an observed ion in the gas phase.

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