Thermodynamic stabilities of propylenebenzenium ions in the gas phase. Substituent effect of unsymmetrical phenonium ions

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Dedicated to Professor Nouria Al-Awadi

Abstract

The thermodynamic stabilities of the propylenebenzenium (α-methylphenonium) ion and ring-substituted derivatives were determined based on the bromide-transfer equilibria in the gas phase. It has been shown that the α-methylphenonium ion is 4.5 kcal mol^{-1} more stable than the phenonium cation, and that the substituent effect on its stability can be correlated with the Yukawa-Tsuno equation with a ρ value of -12.9 and an r^+ of 0.58. The r^+ value is nearly identical to that for the phenonium ion, regardless of the higher stability of α-methylphenonium ion than phenonium ion, indicating that the resonance demand in the phenonium ion system is less sensitive to a change of stability of the unsubstituted cation. The unique intermediate r^+ value of 0.6 must be an intrinsic property of a bridged structure of the phenonium ion, suggesting that the π-delocalization of positive charge in the bridged structure must be essentially less effective than that in the benzylic carbocation. In addition, it has been shown that the α-methylphenonium ions having a strongly electron-withdrawing substituent have an open cation character. This is supported by the optimized structures at DFT calculations.

Keywords: α-Methylphenonium ions, bromide ion affinities, substituent effects, DFT calculations, Yukawa-Tsuno equation

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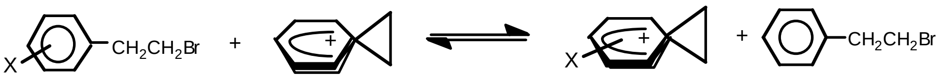
Introduction

Neighboring phenyl-group participation, leading to a bridged phenonium (ethylenebenzenium) ion in the solvolysis of the 2-arylalkyl system, has been a subject of intense investigation since Cram's pioneering work.[1,2] The structural aspects of the phenonium ion were obtained from NMR studies[3] and theoretical calculations,[4-6] revealing a symmetrical σ-bridged structure. Recently, we determined the thermodynamic stabilities of phenonium ions in the gas phase by measuring equilibrium constants of bromide ion transfer reactions (1) of 2-arylethyl bromides and found that the substituent effect on the stability of phenonium ion is characterized by an r^+ of 0.62 and a ρ value of -12.6 from the correlation in terms of the Yukawa-Tsuno equation (2).[7-9]



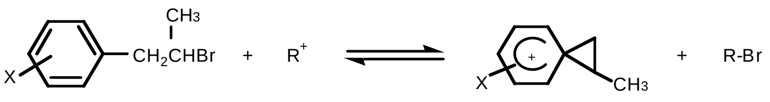
(1)

$$\log K/K_0 = -1000\delta\Delta G^0/2.303RT$$
$$= \rho(\sigma^0 + r^+\Delta\bar{\sigma}^+_R) \qquad (2)$$

where σ^o and $\Delta\bar{\sigma}^+_R$ are the normal substituent constant and the resonance substituent constant, respectively, and r^+ is the resonance demand parameter representing the degree of the π-delocalization of the positive charge into the aryl π-system. In a series of gas-phase benzylic carbocations r^+ decreases as the stability of the unsubstituted carbocation increases,[10,11] *e.g.* 1.53 for 2,2,2-trifluoro-1-phenylethyl cation[10c] to 1.00 for α-cumyl cation.[14] An r^+ value of 0.62 for the phenonium ion is a unique position in a continuous spectrum, and remarkably smaller than that for the stability of the benzenium ion ($r^+ = 1.3$),[13] which has a similar molecular framework. The reduced resonance demand of the phenonium ion was attributed to its high stability compared to the benzenium ion. The same variation of the r^+ value was observed for the substituent effects of the S_N1 solvolysis of the benzylic substrates when the corresponding carbocation intermediates are formed in the rate-determining step.[9] The r^+ value of 0.62 for the phenonium ion is also completely agreement with the r^+ observed for the rate constants of aryl-assisted solvolysis of 2-arylethyl tosylates.[12] On the other hand, the r^+ value for the aryl-assisted solvolysis was nearly constant at 0.5 – 0.6 and independent of the variation of the reactivities of the substrates.[9] These intermediate r^+ values were discussed in terms of less effective π-delocalization by β-aryl-participation than a benzylic π-interaction in transition state. Recently, Okamura and co-workers[15] observed the enhanced r^+ value of 0.77 for the β-aryl-assisted process of the acetolysis of 2-aryl-2-(trifluoromethyl)ethyl *m*-nitrobenzenesulfonates. This is attributed to the reduced stability of the phenonium ion due to electron-withdrawing effect of the CF_3 group. This variation of the r^+ value is consistent with the trend observed for the benzylic cation series, but the degree of reduction of r^+ is significantly small. It is of great interest to investigate how the r^+ value is sensitive to the variation of the stability of the phenonium ion in the gas phase. This would help us to understand the essential nature of this unique bridged ion. In this paper, we report the substituent effect on the stability of methyl substituted phenonium ion (α-methylphenonium ion), which must be stabilized by the electron-releasing effect of the methyl group at the cyclopropane-like moiety.

Results and Discussion

Bromide ion affinities of α-methylphenonium ions have been determined on the basis of bromide ion transfer equilibrium method using an FT-ICR mass spectrometer as described previously.[7] The standard free energy changes of respective bromide ion transfer equilibria (3) are given in Figure 1.



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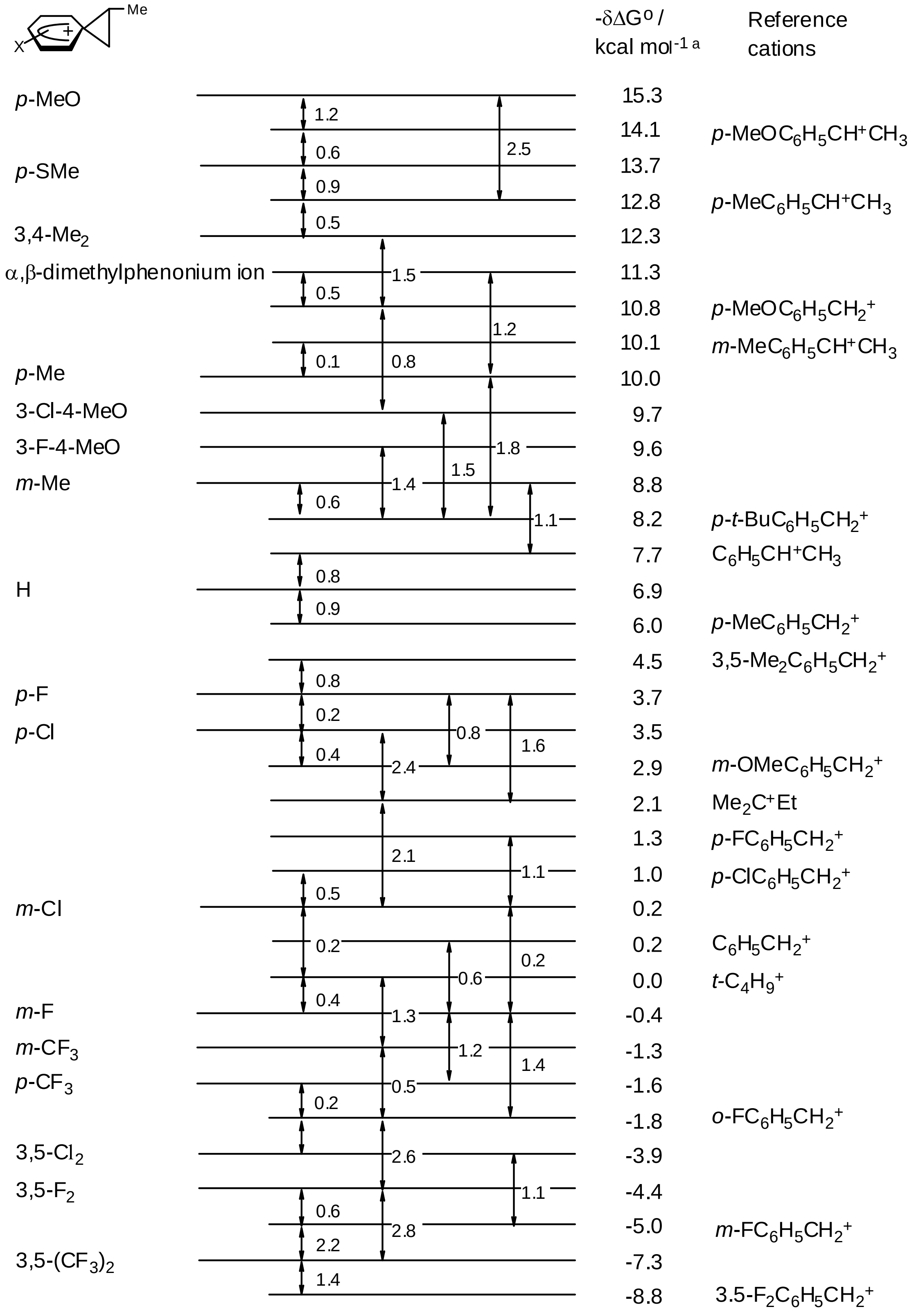
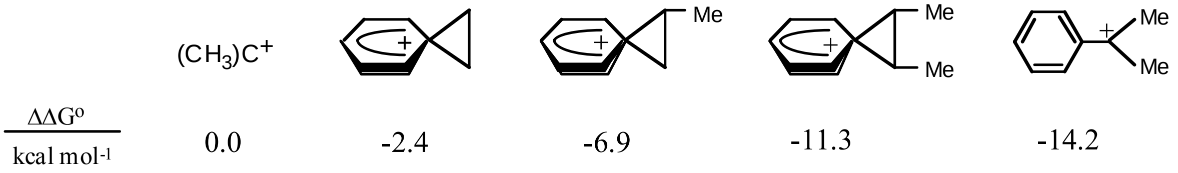


Figure 1. Ladder of ΔG^o values for bromide ion transfer equilibrium measured at 323 K. Bromide ion affinity increases and stability of R^+ decrease from top to bottom. [a]Relative to *t*-butyl cation. The values of reference cations were taken from ref. 7.

Relative stabilities of relevant carbocations are shown in Scheme 1. It is found that α-methylphenonium ion is 7.3 kcal mol^{-1} less stable than α-cumyl cation, indicating that the cation generated from 2-bromo-1-phenylpropane does not undergo rearrangement to give α-cumyl cation. Comparison among phenonium ions shows that α-methylphenonium ion is 4.5 kcal mol^{-1} more stable than the parent phenonium ion, and α,β-dimethylphenonium ion is more stable by another 4.4 kcal mol^{-1}.



Scheme 1. Relative stabilities of relevant carbocations in kcal/mol.[16]

A replacement of a hydrogen of the cyclopropane-like ring by the methyl group enhances significantly the stability of the phenonium ion as expected from the electron-releasing effect of the methyl group. The increment in stability caused by the methyl group seems to be similar to that in the benzylic cation system, where the methyl group directly links to the positive center carbon atom; *e.g.*, 1-phenylethyl cation and α-cumyl cation are by 6.8 and 12.0 kcal mol^{-1} more stable relative to benzyl cation, respectively.[10a]

Table 1. Relative stabilities of α-methylphenonium ions, phenonium ions, and α-cumyl cations

	$-\delta\Delta G^{0}$ [a]		
Subst.	Phenonium ions		α-Cumyl cations [d]
	Me, H [b]	H,H [c]	
p-OMe	8.4	9.2	10.5
p-SMe	6.8	7.4	10.0
3-Cl-4-OMe	2.8	3.3	6.7
3-F-4-OMe	2.8	-	6.7
3,4-Me$_2$	5.4	5.0	6.1
p-Me	3.1	3.6	3.6
m-Me	1.9	2.1	1.8
H	0.0	0.0	0.0
p-F	-3.2	-2.6	-0.1
p-Cl	-3.4	-3.2	-0.4
m-Cl	-6.7	-6.5	-4.7
m-F	-7.3	-6.9	-5.1
m-CF$_3$	-8.2	-8.4	-6.3
p-CF$_3$	-8.5	-9.9	-7.2
3,5-Cl$_2$	-10.8	-	-
3,5-F$_2$	-11.3	-	-8.5
3,5-(CF$_3$)$_2$	-14.3	-	-12.6

[a] Free energy changes for a bromide transfer reaction, in kcal mol^{-1}. [b] α-Methylphenonium ions. [c] Phenonium ions, ref. 7. [d] Relative gas phase basicities of α-methylstyrenes, ref. 14.

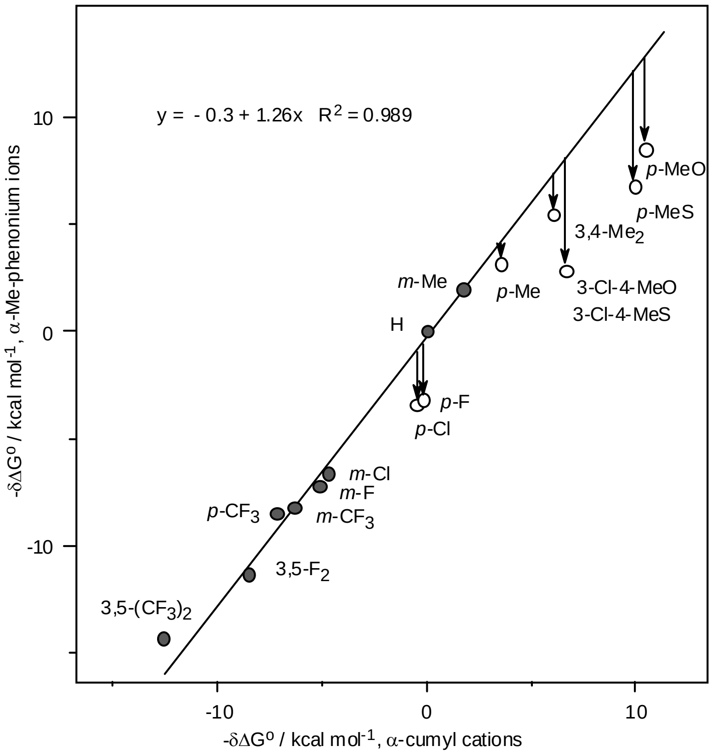


Figure 2. Plot of relative stabilities of α-methylphenonium ions against the corresponding α-cumyl cations.

The relative stabilities of α-methylphenonium ions are summarized in Table 1 along with phenonium ions and α-cumyl cations. Figure 2 shows a plot of the relative stabilities of α-methylphenonium ions against the corresponding values of α-cumyl cations which were evaluated from gas-phase basicities of α-methylstyrenes.[14] Although there is no simple linear relationship for all substitutents, one can find a good linear relationship with a slope of 1.26 for meta substituents and electron-withdrawing substituents except for 3,5-$(CF_3)_2$. With respect to this line, significant negative deviations are observed for para π-donor substituents. The magnitude of the slope of 1.26 clearly indicates higher response of the substituent effect on the stability of α-methylphenonium ion than that of α-cumyl cation. Such a large substituent effect was also observed for the stability of benzenium ions,[17] suggesting that the large substituent effect appears to be characteristic of the benzenium ion structure which bears the positive charge in the ring system itself. This is also supported by the fact that the effects of meta substituents on the stability of the phenonium ion and α-methylphenonium ion are equal to that on the gas phase basicity of pyridine, of which the conjugate acid ion also bears the positive charge within the pyridine-ring. The negative deviations of para π-donor substituents in Figure 2 are systematic, *i.e.*, the substituent having the greater π-donating ability shows the larger negative deviation, suggesting that the resonance effect of the para π-donor involved in this substituent effect is smaller than that for the α-cumyl ion. This figure resembles the corresponding plot observed for phenonium ions vs. α-cumyl cations.[7] In fact, there exists an excellent linear relationship between the stabilities of α-methylphenonium ions and phenonium ions as shown Figure 3; δ ΔG^0[α-methylphenonium ion] = 0.99 (δΔG^0[phenonium ion] + 0.3 ($R^2 = 0.996$), excluding *m*-CF_3 and *p*-CF_3.

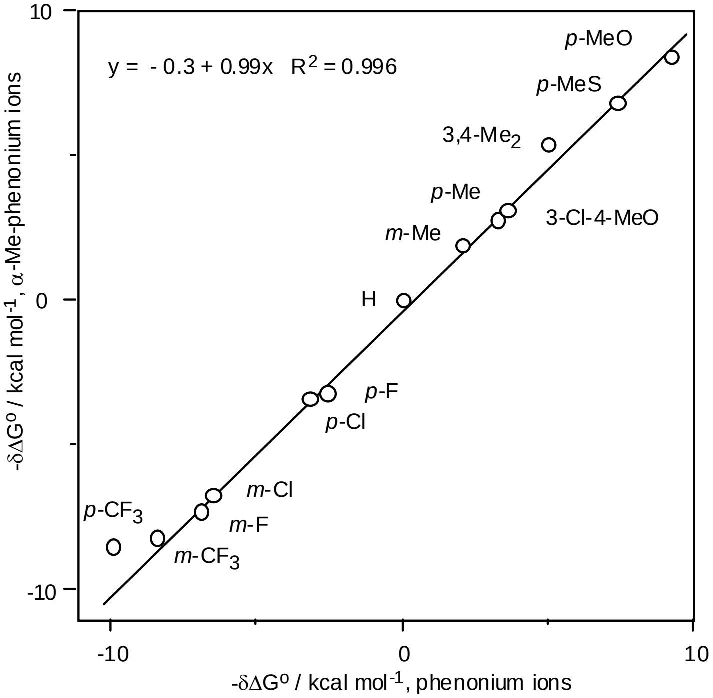


Figure 3. Plot of relative stabilities of α-methylphenonium ions against the corresponding phenonium cations.

This indicates that both systems have the same response to the substituent perturbation and also suggests that there is no significant difference in π-delocalization between both phenonium ions. A careful inspection of this figure indicates that *m*-CF_3 and *p*-CF_3 feasibly deviate upward from the line obtained for a range of the substituents from *m*-F to *p*-MeO. The reduced effects of these two substituents as well as the 3,5-$(CF_3)_2$ group shown in Figure 2 may be indicative of an open cation character for such a highly destabilized α-methylphenonium ion.

Accordingly, the substituent effect on the stability of α-methylphenonium ions having a deactivating substituent stronger than *m*-CF_3 and *p*-CF_3 must be analyzed with caution. Even though such destabilizing substituents are excluded from the correlation analysis, an application of the Yukawa-Tsuno equation (2) provides a good correlation as shown in Figure 4 with a satisfactory precision ($R^2 = 0.990$, n = 12).[18]

$$\begin{aligned}\log K/K_o &= -1000\ \delta\Delta G^o/2.303RT \\ &= -12.9(\sigma^o + 0.58\Delta\overline{\sigma}_R^+) \qquad (4)\end{aligned}$$

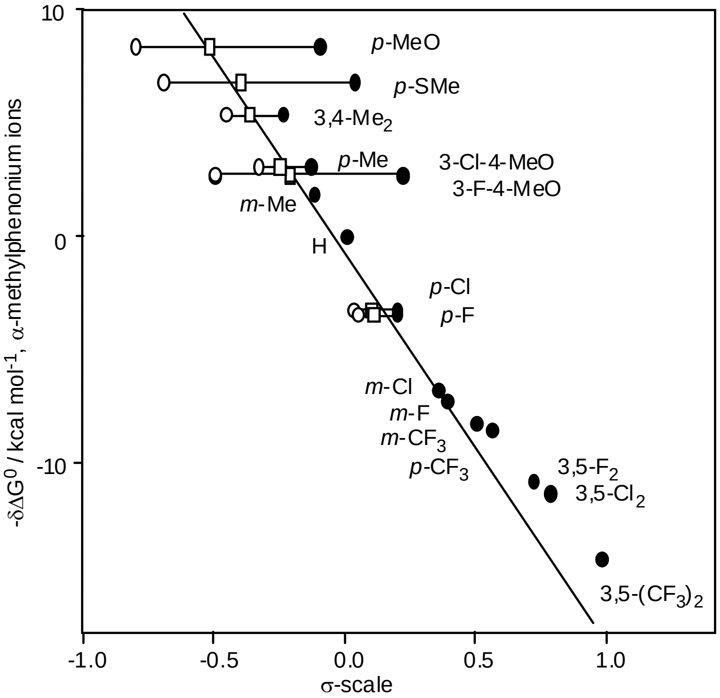
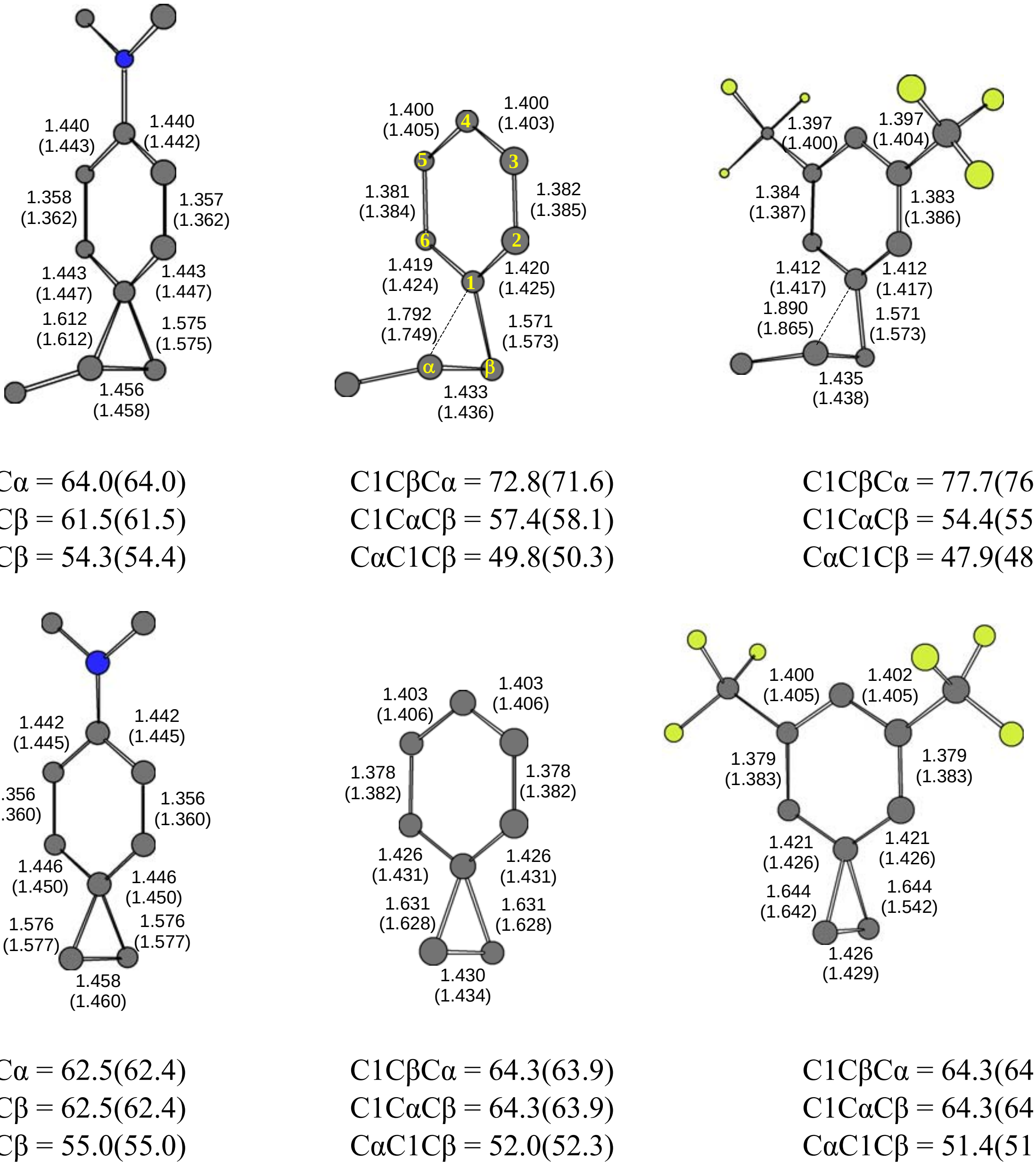


Figure 4. Yukawa-Tsuno plot for the stabilities of α-methylphenonium ions. Closed circles; σ^o, open circles; σ^+, squares; $\overline{\sigma}$ at $r^+ = 0.58$.

The r^+ value is slightly smaller than that for the phenonium ion ($r^+ = 0.62$), being consistent with the general trend that the more stable carbocation system has the smaller resonance demand (r^+).[11] However, the reduction of the r^+ is negligibly small compared to that observed for the benzylic carbocation system, where a replacement of a hydrogen of the benzyl cation by the methyl group results in a decrease of the r^+ value by 0.14 unit.[10,20] It is concluded that the resonance demand in the phenonium ion system is less sensitive to a change of stability of the unsubstituted cation. The present result is consistent with the fact that a nearly constant r^+ value of 0.5 to 0.6 is observed for the aryl-assisted solvolysis of a variety of substrates where a bridged phenonium ion intervenes as an intermediate followed by the rate-determining transition state even though their reactivities vary significantly.[9] Consequently, the unique intermediate r^+ value of 0.6 must be an intrinsic property of a bridged structure of the phenonium ion, suggesting that the π-delocalization of positive charge in this bridged structure must be essentially less effective than that in the benzylic carbocation and transition state.

It should be noted that the α-methylphenonium ions having a deactivating substituent stronger than *m*-CF_3 and *p*-CF_3 deviate consistently from the Y-T correlation line. Although similar curved plots were observed for the substituent effect of the rate constants of the solvolysis of 2-phenylethyl tosylates and 1-phenyl-2-propyl tosylates where non-linear substitutent effects are attributed to varying reaction mechanism from neighboring participation mechanism (k_Δ) via phenonium ions to solvent nucleophilic assistance mechanism (k_s),[9] the present observation is not the case because of no mechanistic complexities in the thermodynamic quantities of carbocations. The curved correlation observed for the destabilized derivatives should result from the intrinsic property of α-methylphenonium ion. These deviations seem to be due to the increased open cation character as mentioned above. Theoretical calculation may provide useful clues for understanding this behavior. We therefore conducted DFT calculations for the α-methylphenonium ions, phenonium ions, and α-cumyl cations for comparison at the same level of theory.

The selected geometric parameters of the optimized structures of a series of phenonium ions, α-methylphenonium ions, and α-cumylcations at the B3LYP/6-311+G** and B3LYP/6-31+G* levels are summarized in Table S4, S5, and S6 (Supporting information). Selected bond distances and angles of representative derivatives are given in Figure 5.



C1CβCα = 64.0(64.0)
C1CαCβ = 61.5(61.5)
CαC1Cβ = 54.3(54.4)

C1CβCα = 72.8(71.6)
C1CαCβ = 57.4(58.1)
CαC1Cβ = 49.8(50.3)

C1CβCα = 77.7(76.4)
C1CαCβ = 54.4(55.1)
CαC1Cβ = 47.9(48.5)

C1CβCα = 62.5(62.4)
C1CαCβ = 62.5(62.4)
CαC1Cβ = 55.0(55.0)

C1CβCα = 64.3(63.9)
C1CαCβ = 64.3(63.9)
CαC1Cβ = 52.0(52.3)

C1CβCα = 64.3(64.2)
C1CαCβ = 64.3(64.2)
CαC1Cβ = 51.4(51.4)

Figure 5. Optimized structures of *p*-NMe_2, H, and 3,5-$(CF_3)_2$ substituted α-methylphenonium ions and the corresponding phenonium ions at B3LYP/6-311+G(d,p). Hydrogens are not shown. Bond distances and angles are given in Angstrom and degree, respectively. The values in parentheses are obtained at B3LYP/6-31+G(d).

Bond distances of C1C2 and C1C6 of phenonium ion and α-methylphenonium ion are longer than the CC bond (1.40 Å) in benzene and C2C3 and C5C6 are shorter. Such behavior of bond distances is consistent with those in the α-cumyl cations, indicating the importance of the contribution of resonance structure in a similar manner to that in α-cumyl cation. Resonance theory predicts further elongation of C1C2(C1C6) and C3C4(C4C5) and shortening of C2C3 (C5C6) with increasing degree of π-delocalization of the positive charge to the substituent. This trend is in fact found when the substituent changes from H to *p*-NMe_2.

The most characteristic feature of α-methylphenonium ion is an unsymmetrically birdged structure; the C1Cα is significantly longer than the C1Cβ, while a phenonium ion has a symmetrical structure regardless of the variation of the substituent. In addition, the C1Cα of the α-methylphenonium ion significantly lengthens with increase of electron-withdrawing ability of the substituent, by 0.28 Å for the change from *p*-NMe_2 to 3,5-$(CF_3)_2$, while the C1Cβ bond is nearly constant as shown in Figure 6.

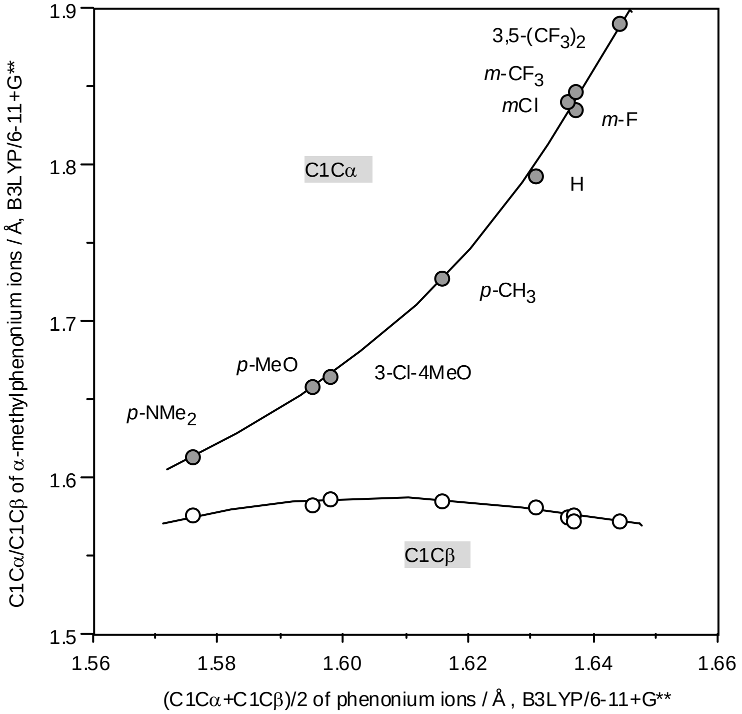


Figure 6. Comparison of C1Cα/C1Cβ between α-methylphenonium ions vs. phenonium ions.

This is also a sharp contrast to the change of the bond distances of a phenonium ion where the C1Cα (C1Cb) lengthens only by 0.07 Å for the same substituent change. Such feature suggests the increase of an open cation character of the α-methylphenonium ion as the substituent on the benzene ring is electron-withdrawing. This is also consistent with the change of the bond angles of C1CβCα; that is, the ∠C1CβCα increases from 64.0° to 77.7° for the change from *p*-NMe_2 to 3,5-$(CF_3)_2$ while in the phenonium ion the ∠C1CβCα varies only by 1.8° for the same change of the subsitutent.

In addition, the natural (NPA) charge variations are useful for deeper understanding of the nature of a bridged ion. The sum of NPA charges in the benzene ring are listed for phenonium ions, α-methylphenonium ions, and α-cumyl cations in Table 2. The NPA charge of unsubstituted phenonium ion shows that a half of the positive charge is distributed in the benzene ring moiety, and this is consistent with results obtained by Sieber *et al.*[5] at MP2/6-31G* level of theory.

Table 2. The sum of NPA charges in the aromatic moiety calculated at B3LYP/6-311+G(d,p) and B3LYP/6-31+G(d)

Subst.	α-Methylphenonium ions	Phenonium ions	α-Cumyl cations
p-NMe_2	0.638	0.665	0.569
	(0.638)	(0.661)	(0.581)
p-MeO	0.565	0.604	0.492
	(0.566)	(0.601)	(0.504)
3-Cl-4-MeO	0.550	0.590	0.476
	(0.550)	(0.587)	(0.489)
p-Me	0.494	0.550	0.431
	(0.499)	(0.550)	(0.446)
H	0.444	0.513	0.391
	(0.450)	(0.516)	(0.407)
m-F	0.405	0.493	0.371
	(0.412)	(0.493)	(0.386)
m-Cl	0.413	0.497	0.375
	(0.420)	(0.498)	(0.391)
m-CF_3	0.402	0.490	0.361
	(0.410)	(0.491)	(0.379)
3,5-$(CF_3)_2$	0.362	0.466	0.345
	(0.370)	(0.468)	(0.354)

Values in parentheses are obtained at B3LYP/6-31+G(d).

The charge distribution to the benzene ring in α-methylphenonium ion is slightly smaller than that of the parent phenonium ion. The charge distribution in α-cumyl cation is further smaller than that for α-methylphenonium ion. This change seems to be related to the stability of the carbocation. Figure 7 shows a plot of the sum of natural charges in the aromatic moiety of phenonium ions and α-methylphenonium ions against the corresponding values of the α-cumyl cations. There is a good linear relationship for the phenonium ion series with a slope of 0.88, suggesting that the charge-transfer interaction between the substituent and the benzene ring is nearly the same in both π-systems. On the other hand, the variation of the charge distribution in the α-methylphenonium ion with the change of substituent differs considerably from that in the α-cumyl cation. That is, the positive charge in the aromatic moiety is reduced significantly when the substituent is a strong electron-withdrawing group while the derivatives having an electron-releasing group behaves in a similar manner as the phenonium ions. The reduced charge in the destabilized α-methylphenonium ions can be interpreted in terms of the increase of an open cation character, and this is consistent with the geometrical features noted above. These results obtained from theoretical calculations may suggest that the stabilities of unsymmetrical α-methylphenonium ions have essentially non-linear substituent effect, strictly speaking. However, the Yukawa-Tsuno equation with an r^+ of 0.58 can describe nicely the substituent effect except for the derivatives having highly electron-withdrawing substituents, which give a smoothly curved correlation. This suggests that the thermodynamic stability of α-methylphenonium ion is less sensitive to the variation in structure. Only in a highly deactivated α-methylphenonium such as 3,5-$(CF_3)_2$ derivative a structural change can make an appreciable change in the energetic aspect. This would be intrinsic nature of a bridged phenonium ion and may be reason for the low response of resonance demand to the stability of a phenonium ion.

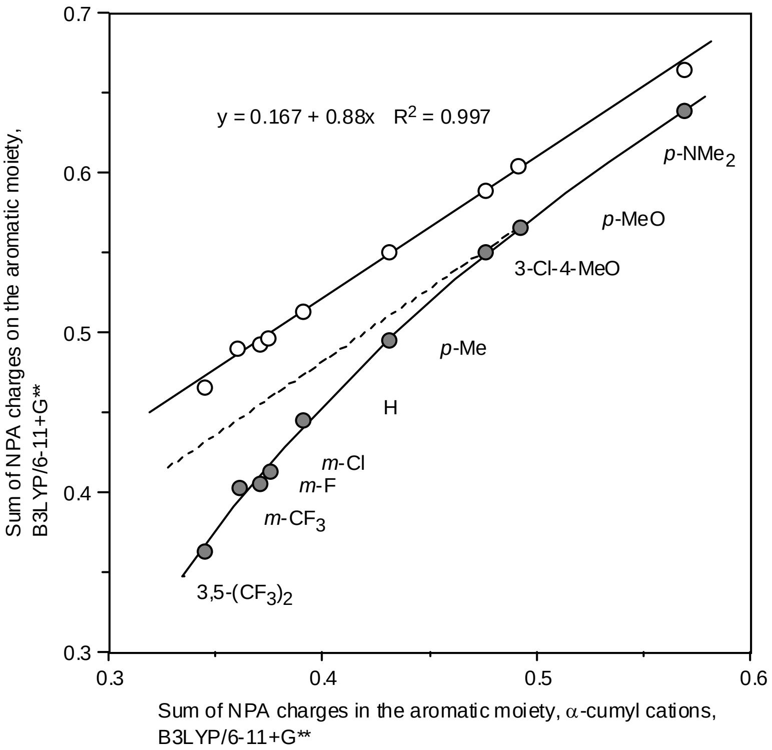


Figure 7. Comparison of the sum of NPA charges in the aromatic moiety, phenonium ions and α-methylphenonium ions vs. α-cumyl cations. Open circles; phenonium ions, closed circles; α-methylphenonium ions.

Conclusions

The substituent effect on the stability of α-methylphenonium ion was characterized by an r^+ of 0.58 and a ρ of -12.9. The r^+ value is identical to that for the phenonium ion, nevertheless the unsubstituted α-methylphenonium ion is more stable than the corresponding phenonium ion by 4.5 kcal mol^{-1}. The resonance demand in the phenonium ion system is less sensitive to a change of stability of the unsubstituted cation in contrast with the results observed for the benzylic carbocation series. The r^+ of 0.6 for phenonium ions indicates that the π-delocalization of positive charge in this bridged structure must be essentially less effective than that in the benzylic carbocation. In addition, it has been shown that the α-methylphenonium ions destabilized by a strongly electron-withdrawing substituent have some open cation character. Theoretical DFT calculations showed that an electron-withdrawing group lengthens significantly the C1Cα bond in the α-methylphenonium ion compared with that in the corresponding phenonium ion while the C1Cβ bond is nearly constant for the variation of the subsitutent. The NPA positive charge in the aromatic moiety decreases significantly when the substituent is a strongly electron-withdrawing group such as 3,5-$(CF_3)_2$. These features are consistent with an open cation character of the α-methylphenonium ions having a strongly electron-withdrawing group.

Experimental Section

General Procedures. 2-Bromo-1-(substituted phenyl)propanes except for commercially available derivatives were prepared from the corresponding alcohols using thionyl bromide. Most of 1-aryl-2-propanols were available from our previous studies.[21] The remaining alcohols were prepared by a Grignard reaction of the corresponding bromobenzenes with propylene oxide in THF.

General procedure for preparation of 1-aryl-2-bromopropane
To 0.05 mol of magnesium in 3 mL of THF was added slowly 0.05 mol of substituted bromobenzene in 40 mL of distilled THF under N_2. After reflux for 1 h, to the solution 1.9 g (0.01 mol) of CuI was added at -30 ^oC. The reaction mixture was allowed to stir for about 10 min, then a mixture of 2.9 g (0.05 mol) propylene oxide and 25 mL of THF was added slowly. Stirring was continued overnight at -30 ^oC. The reaction mixture was quenched with aqueous ammonium chloride solution. The aqueous phase was extracted with ether. The combined organic layer was washed with saturated aqueous NaCl solution, and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave the alcohol quantitatively. The crude alcohols were used for preparation of bromides without further purification. 2-Bromo-1-(substituted phenyl)propanes were prepared according to the procedure in literature.[22] To a mixture of 0.02 mol of 1-aryl-2-propanol and 0.02 mol of pyridine in 30 mL of benzene was added slowly a mixture of 0.02 mol thionyl bromide and 20 mL of dry benzene at -5 ^oC. After stirring overnight at 40 °C, the organic layer was extracted with ether, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude bromides were purified through a silica gel column with hexane eluent and by a recycling preparative HPLC JAI Co., Ltd. (GPC) LC-908 or gas chromatography Hitachi 263-80. All compounds were characterized by NMR and FT-ICR mass spectra. ^1H NMR spectra were measured at 400 MHz in $CDCl_3$ using a JEOL-EX400 spectrometer and the chemical shifts were recorded in ppm (δ) downfield from TMS as internal standard.

2-Bromo-1-(3-chlorophenyl)propane. ^1H NMR δ 1.70 (d, J = 6.5 Hz, 3H), 3.05 (dd, J = 6.5, 14.5 Hz, 1H), 3.17 (dd, J = 7.0, 14.0 Hz, 1H), 4.27 (sextet, J = 7.0 Hz, 1H), 7.09-7.26 (m, 4H).

***2*-Bromo-1-(4-methylthiophenyl)propane.** ^1H NMR δ 1.68 (d, J = 6.83 Hz, 3H), 3.02 (m, 1H), 3.17 (m, 1H), 4.26 (m, 1H), 7.13 (m, 2H), 7.22 (m, 2H). Found: C, 48.82; H, 5.29%. Calcd for $C_{10}H_{13}BrS$: C, 48.99; H, 5.34%.

2-Bromo-1-(3-chloro-4-methoxyphenyl)propane. ^1H NMR δ 1.68 (d, J = 6.83 Hz, 3H), 2.98 (m, 1H), 3.08 (m, 1H), 4.22 (m, 1H), 6.86 (d, 1H), 7.05 (q, 1H), 7.21 (t, 1H), 3.87 (s, 3H). Found: C,45.39; H, 4.56%. Calcd for $C_{10}H_{13}BrClO$: C, 45.57; H, 4.59%.

2-Bromo-1-(3-fluoro-4-methoxyphenyl)propane. ^1H NMR δ1.69 (d, J = 6.83 Hz, 3H), 3.01 (m, 1H), 3.11 (m, 1H), 4.23 (m, 1H), 6.90 (m, 2H), 6.92 (d, 1H), 3.88 (s, 3H). Found: C, 48.86; H, 4.93%. Calcd for $C_{10}H_{12}BrFO$: C, 48.61; H, 4.89%.

2-Bromo-1-(4-methylphenyl)propane. ^{1}H NMR δ 1.69 (d, J = 6.0 Hz, 3H), 2.33 (s, 3H), 3.03 (dd, J = 7.0, 14.2 Hz, 1H), 3.20 (dd, J = 7.5, 14.0 Hz, 1H), 4.28 (sextet, J = 7.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H).

2-Bromo-1-(3-methylphenyl)propane. ^{1}H NMR δ 1.68 (d, J = 6.5 Hz, 3H), 2.34 (s, 3H), 3.01 (dd, J = 7.5, 14.0 Hz, 1H), 3.19 (dd, J = 7.0, 14.0 Hz, 1H), 4.29 (sextet, J = 7.5 Hz, 1H), 4.31 (m, 1H), 6.98-7.23 (m, 4H).

2-Bromo-1-(4-fluorophenyl)propane. ^{1}H NMR δ1.69 (d, J = 6.84Hz, 3H), 3.07 (dd, J = 7.0, 14.0 Hz, 1H), 3.16 (dd, J = 7.0, 14.5 Hz, 1H), 4.26 (sextet, 7.0 Hz, 1H), 6.98-7.00 (m, 2H), 7.26 (d, J_{HF} = 3. 5 Hz, 2H).

2-Bromo-1-(3-fluorophenyl)propane. ^{1}H NMR δ 1.70 (d, J = 6.5 Hz, 3H), 3.07 (dd, J = 6.5, 14.3 Hz, 1H), 3.20 (dd, J = 7.0, 14.5 Hz, 1H), 4.28 (sextet, J = 7.0 Hz, 1H), 6.91-6.99 (m, 4H).

***2*-Bromo-1-(3-trifluoromethylphenyl)propane.** ^{1}H NMR δ1.72 (d, J = 6.5 Hz, 3H), 3.15 (dd, J = 6.5, 14.0 Hz, 1H), 3.23 (dd, J = 7.2, 14.3 Hz, 1H), 4.29 (h, J = 7.5 Hz, 1H), 7.39-7.53 (m, 4H). Found: C, 44.64; H, 3.73%. Calcd for $C_{10}H_{10}BrF_3$: C, 44.97; H, 3.77%.

2-Bromo-1-(3,4-dimethylphenyl)propane. ^{1}H NMR δ 1.68 (d, J = 6.83Hz, 3H), 3.01 (m, 1H), 3.16 (m, 1H), 4.28 (m, 1H), 6.95 (m, 2H), 7.07 (m, 1H), 2.24 (d, J = 6.83 Hz, 6H).

2-Bromo-1-(4-methoxyphenyl)propane. ^{1}H NMR δ 1.68 (d, J = 6.35Hz, 3H), 3.00 1H), 3.16 (m, 1H), 4.25 (m, 1H), 6.86 (t, 2H), 7.13 (t, 2H), 3.79 (s, 3H). Found: C, 52.29; H, 5.72%. Calcd for $C_{10}H_{13}BrO$: C, 52.42; H, 5.72%.

2-Bromo-1-(4-trifluoromethylphenyl)propane. ^{1}H NMR δ1.72 (d, J = 6.35Hz, 3H), 2.77-2.88 (m, 2H), 4.29 (m, 1H), 7.32 (m, 2H), 7.58 (m, 2H). Found: C, 44.79; H, 3.80%. Calcd for $C_{10}H_{10}BrF_3$: C, 44.97; H, 3.77%.

2-Bromo-1-[3,5-bis(trifluoromethyl)phenyl]propane. ^{1}H NMR δ 1.77 (d, J = 6.8 Hz, 3H), 3.07 (q, J = 7.0 Hz, 1H), 3.15 (q, J = 7.5 Hz, 1H), 4.28 (m, 1H), 7.86 (m, 2H), 7.79 (m, 1H). C, 39.51; H, 2.72%. Calcd for $C_{11}H_9BrF_6$: C, 39.43; H, 2.71%.

2-Bromo-1-(3,5-difluorophenyl)propane. ^{1}H NMR δ 1.71 (d, J = 7.0 Hz, 3H), 3.07 (dd, J = 7.0, 14.3 Hz, 1H), 3.15 (dd, J = 7.0, 14.3 Hz, 2H), 4.25 (sextet, J = 7.0 Hz, 1H), 6.69 - 6.75 (m, 3H). Found: C, 45.66; H, 3.86%. Calcd for $C_9H_9BrF_2$: C, 45.99; H, 3.86%.

2-Bromo-1-(3,5-dichlorophenyl)propane. ^{1}H NMR δ 1.72 (d, J = 6.0 Hz, 3H), 3.05 (dd, J = 6.0, 14.3 Hz, 1H), 3.11 (dd, J = 7.5, 14.3 Hz, 1H), 4.24 (sextet, J = 7.0 Hz, 1H), 7.10 (s, 2H), 7.27 (s, 1H).

2-Bromo-1-(4-chlorophenyl)propane. ^{1}H NMR δ 1.69 (d, J = 6.35Hz, 3H), 3.04-3.15 (m, 2H), 4.26 (m, 1H), 7.13 (m, 2H), 7.27 (m, 2H). Found: C, 45.96; H, 4.28%. Calcd for $C_9H_{10}BrCl$: C, 46.29; H, 4.32%.

Each sample was subjected to several freeze-pump-thaw cycles on the ICR inlet system to remove entrapped volatile impurities, and their purities were checked by ICR mass spectra.

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.

$$\mathrm{RBr} + \mathrm{R_0}^+ \rightleftharpoons \mathrm{R}^+ + \mathrm{R_0Br} \tag{5}$$

$$K = [\mathrm{R_0Br}/\mathrm{RBr}]\cdot[\mathrm{R}^+/\mathrm{R_0}^+] \tag{6}$$

$$\Delta G^0 = -RT \ln K \tag{7}$$

The equilibrium constant is expressed by equation (6), where RBr and R_oBr are a given 2-bromo-1-(substituted phenyl)propane 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.[23] The overall pressures of the reagents were maintained at 0.6 to $2x10^{-4}$ Pa by controlled rates through variable leak valves from a parallel inlet manifold into the ICR 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^0 at 300 K, the average uncertainty being ± 0.3 kcal mol^{-1} in most cases.

DFT Calculations. All geometries were fully optimized at the B3LYP/6-31+G* and B3LYP/6-311+G** levels of theory using the Gaussian 03 program[24] suite. The force constant matrices obtained for the stationary points were confirmed to have the correct number of negative eigenvalues (zero for equilibrium structures).

Supplementary Information Available

Detailed results of the calculations, Cartesian coordinates for the optimized structures, selected bond distances, and bond angles, are available in Tables S1 to S6 in Supporting Information.

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