Selected Papers

Gas-Phase Acidities of α - and α , α -SO₂CF₃-Substituted Toluenes. Varying Resonance Demand in the Electron-Rich System

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The gas-phase acidities (GA) of aryl(trifluoromethylsulfonyl)methanes (ArCH₂SO₂CF₃; **1**) and arylbis(trifluoromethylsulfonyl)methanes (ArCH(SO₂CF₃)₂; **2**) were determined by measuring proton-transfer equilibria. Substituent effects for acidities of a series of ArCH(R¹)R² including **1** and **2** have been analyzed successfully in terms of the Yukawa– Tsuno equation. The resonance demand parameter r^- value was found to decrease linearly with increasing acidity of the GA values of the unsubstituted parent carbon acids, and the change of the r^- value was correlated with the acidifying effect of the phenyl group (R = Ph) in the RCH₂(R¹)R². In addition, the geometric features and natural charges of the conjugate anions calculated at B3LYP/6-311+G(d,p) were found to be correlated linearly with the r^- values. Such behavior of the resonance demand parameter in the electron-rich system, ArC⁻(R¹)R², is completely consistent with that observed for the electron-deficient system, ArC⁺(R¹)R², revealing that the resonance demand is contingent upon the structure of carbanions and carbocations. Furthermore, it was found that the ρ values also decreased with increasing acidity of the GA values of the unsubstituted parent carbon acids. This would be related to the distribution of the charge between the aromatic moiety and the C(R¹)R² moiety.

Gas-phase proton-transfer experiments have played a key role for separating structural effects from medium effects on organic reactivity, providing new insights into the intrinsic nature of the resonance demand in the substituent effect which is one of the most important concepts in physical organic chemistry.^{1–5} The substituent effects on the thermodynamic stability (ΔG° in kcal mol⁻¹) of benzylic carbocation, XC₆H₄C⁺(R¹)R², were found to be described in terms of the Yukawa–Tsuno eq 1 using a gas-phase set of substituent constants of which values differ slightly from the standard values determined in aqueous solution.^{6–11}

$$-\delta\Delta G^{\circ} = \rho(\sigma^{\circ} + r^{+}\Delta\bar{\sigma}_{\rm R}^{+}) \tag{1}$$

where σ° 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. These correlation results revealed that the resonance demand parameter (r^{+}) varies significantly with the stability of the unsubstituted parent carbocations (X = H), i.e., the r^{+} value is correlated linearly as the following eq 2.¹¹

$$r^{+} = 0.026 \Delta \Delta G^{\circ}_{(\mathrm{X}=\mathrm{H})} + 1.00 \tag{2}$$

where $\Delta\Delta G^{\circ}_{(X=H)}$ is the stability of the unsubstituted parent benzylic carbocation relative to α -cumyl cation. Furthermore, the r^+ value was described in terms of substituent constants for fixed substituents, R¹ and R²,

$$r^{+} = 0.45\Sigma\sigma^{\circ} + 0.40\Sigma\Delta\bar{\sigma}_{\rm R}^{+} + 1.28\tag{3}$$

where $\Sigma \sigma^{\circ}$ and $\Sigma \Delta \bar{\sigma}_{R}^{+}$ are sums for σ° and $\Delta \bar{\sigma}_{R}^{+}$ of R¹ and R², respectively, indicating that the change of the r^+ value can be related quantitatively with both field/inductive and resonance effects of R¹ and R² substituents. These results suggest that the degree of π -delocalization in the benzylic carbocation is determined by the intrinsic properties of the structure of the unsubstituted parent carbocation. Similar correlations were observed for the gas-phase basicities of benzoyl compounds, ArCOR,¹² and arylacetylenes, ArC=CR,¹³⁻¹⁵ of which the conjugate acids are benzylic carbocations, ArC⁺(OH)R and ArC⁺=CHR, respectively. In addition, similar relationships were observed for the substituent effects of electron affinities of aromatic compounds, XC6H4R where R is a fixed substituent.^{16,17} Therefore, it is interesting to study whether the resonance demand parameter in the substituent effect shows similar behavior for the electron-rich system in which the π -delocalization effect of *para*- π -acceptor should be exalted. The gas-phase substituent effects in such electron-rich systems themselves are important for understanding the intrinsic nature of resonance effects because strong π -acceptors such as NO₂, NO, and CHO groups at para-position in solution are significantly influenced by specific hydrogen-bonding solvation, i.e., substituent solvation assisted resonance (SSAR) effects as noted by Taft et al.²⁻⁴ We thus decided to examine the effects of α -substituents on the resonance demand for the gas-phase acidity of α , α -substituted toluene derivatives, ArCH(R¹)R², as a measure of the thermodynamic stabilities of benzylic carbanions. The gas-phase acidity values are known for several series of benzylic carbon acids.^{18,19} In this study, the gas-phase acidities of aryl(trifluoromethylsulfonyl)methanes 1 and arylbis(trifluoromethylsulfonyl)methanes 2 (Chart 1) have been determined to cover enough range of variation of the stability of benzylic carbanions by measuring proton-transfer equilibria.

Results and Discussion

Table 1 presents the gas-phase acidity (GA) values (kcal mol⁻¹) derived from ΔG° values for the proton-transfer equilibria between benzylic carbon acids 1 and 2 of interest and

(1)
$$R^{1} = H$$
, $R^{2} = SO_{2}CF_{3}$
(2) $R^{1} = R^{2} = SO_{2}CF_{3}$
(2) $R^{1} = R^{2} = SO_{2}CF_{3}$

Chart 1.

an appropriate reference conjugate anion (A^-) of which acidity is known.

$$A-H + A_o^{-} \rightleftharpoons A^{-} + A_o H \tag{4}$$

It was found that **1** is $45.6 \text{ kcal mol}^{-1}$ stronger acid than toluene (GA = $373.7 \text{ kcal mol}^{-122}$) and 16 kcal mol^{-1} stronger than phenylacetone (344.5^{22}) and benzylnitrile (344.1^{22}), being consistent with the order of the electron-withdrawing ability of the α -substituent. That the gas-phase acidity of **2** is 73.7 kcal mol⁻¹ stronger than toluene indicates that the effect of a second substitution by the SO₂CF₃ group on the acidity is somewhat reduced compared to the first substitution. Such nonadditive effects of second substitution on gas-phase acidities were generally observed for multisubstituted methane derivatives.¹⁹

The gas-phase acidity of **2** was found to strengthen from 300.0 to 292.7 kcal mol⁻¹ as the substituent changes from H

Table 1. GA Values (kcal mol⁻¹) Derived from ΔG° Values for the Proton-Transfer Equilibria between the Indicated Acid-Conjugate Base^{a)}

Acid	ΔG°	$GA/kcal mol^{-1}$	Acid	ΔG°	GA/kcal mol ⁻¹
p-CF ₃ C ₆ H ₄ OH	•	— 330.1 ^{b)}	C ₆ H ₅ CHTf ₂		- 300.0 ^{g)}
CH ₂ (CN) ₂	2.0	— 328.9 ^{b)}		1.7	- 200 0
C ₆ H ₅ CH ₂ Tf		- 328.1	(CF ₃) ₅ 0 ₆ 0H	0.9	299.0
p-FC ₆ H ₄ CH ₂ Tf	2.6	- 326.1	m-FC ₆ H ₄ CHTf ₂	1.5 2.8	- 298.1
p-CF ₃ C ₆ H₄CO ₂ H -	4.0	— 325.3 ^{c)}	m-CF ₃ C ₆ H ₄ CHTf ₂	¥ ¥	- 296.4
p-CIC ₆ H ₄ CH ₂ Tf	0.5	324.9	C ₆ F ₅ SO ₂ NHC ₆ H ₄ CI-p	2.1	– 296.0 ^{g)}
<i>m</i> -FC ₆ H ₄ CH ₂ Tf	0.0	- 324.9	p-CF ₂ C ₂ H ₄ CHTf ₂		- 295.8
(CF ₃) ₃ COH	1.0	— 324.0 ^{d)}	р 0. 306. 40. 22 СН ₃	1.0 1.2 3.1	200.0
m-CIC ₆ H ₄ CH ₂ Tf	0.2	— 323.6	н ₃ с — Он		- 294.8
CF3COCH2COCH3 -	1.6	— 322.0 ^{e)}	CH ₂ CHTf ₂	Ĩ↓	
m-CF ₃ C ₆ H ₄ CH ₂ Tf	0.5	— 321.3	3,5-(CF ₃) ₂ C ₆ H ₃ CHTf ₂	3.5	- 292.7
C ₆ F ₅ OH	0.4	— 320.8 ^{e)}		2.5	- 001.0
p-CF ₃ C ₆ H ₄ CH ₂ Tf	2.3	— 318.5			291.5
m-CNC ₆ H ₄ CH ₂ Tf	1.0	— 317.5	Tf ₂ CHCH ₂ CHTf ₂		- 290.2
3,5-(CF ₃) ₂ C ₆ H ₃ CO ₂ H -		— 317.4 ^{f)}			
C ₆ F ₅ CO ₂ H		— 316.6 ^{e)}			
CF ₃ CO ₂ H	0.4	— 316.3 ^{e)}			
m-NO ₂ C ₆ H ₄ CH ₂ Tf -	1.3	316.2			
p-CNC ₆ H ₄ CH ₂ Tf	3.3	— 315.1			
C ₄ F ₉ SO ₂ NH ₂	1.8	— 315.1 ^{e)}			
3,5-(CF) ₃ C ₆ H ₃ CH ₂ Tf -	<u>↓</u> ↓	— 313.3			
p-NO ₂ C ₆ H ₄ CH ₂ Tf	0.6	312.6			
CH ₂ (COCF ₃) ₂	2.3	— 310.3 ^{e)}			

a) Tf: SO₂CF₃. 1 cal = 4.184 J. b) Ref. 3. c) Ref. 2. d) Ref. 20, see also Ref. 22. e) Ref. 19. f) Ref. 21. g) Ref. 18.

Subst in An	R^1 , R^2 in ArCH(R^1) R^2 , $-\delta\Delta G^\circ$ /kcal mol ⁻¹							
Subst. III AI	H, H ^{a)}	H, CN ^{b)}	CN, CN ^{c)}	CF ₃ , CF ₃ ^{d)}	Cl, CF ₃ ^{d)}	H, T _f ^{e)}	T _f , T _f ^{e)}	
<i>p</i> -NO ₂	28.5 ^{b)}	20.8	14.8		19.0	15.5		
$m-NO_2$	15.7 ^f)	13.2	11.3			11.9		
<i>p</i> -CN	20.4 ^{b)}	16.2			14.6	13.0		
<i>m</i> -CN		11.8	9.9			10.6		
$3,5-(CF_3)_2$	19.5 ^{b)}				16.3	14.8	7.3	
p-CF ₃	13.9	11.2			11.3	9.6	4.2	
<i>m</i> -CF ₃	11.7	8.8	7.3	8.5	8.6	6.8	3.6	
<i>p</i> -Cl	6.9	5.6	5.3	3.9	4.5	3.2		
<i>m</i> -Cl	6.8	6.6	5.5	5.3		4.5		
<i>m</i> -F	5.5			3.8	4.1	3.2	1.9	
<i>p</i> -F	1.3	1.7				2.0		
<i>m</i> -Me	-0.2	-0.1		-1.0				
<i>p</i> -Me	-1.1	-0.9	-1.4	-1.7				
Н	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
(GA)	$(373.7)^{a)}$	$(344.1)^{a)}$	$(314.3)^{a),c)}$	$(335.3)^{d}$	$(348.7)^{d}$	(328.1) ^{e)}	$(300.0)^{g)}$	

 Table 2. Relative Acidities of Benzylic Carbon Acids with Typical Substituents

a) Ref. 22. b) Ref. 23. c) Ref. 19. d) Ref. 24. e) This work. f) Ref. 2. g) Ref. 18.

to $3,5-(CF_3)_2$ while the corresponding change of **1** was 14.8 kcal mol⁻¹ from 328.1 to 313.3 kcal mol⁻¹, indicating that the magnitude of the substituent effect in **2** is significantly smaller than **1**. The relative gas-phase acidities of **1** and **2** are given in Table 2 along with those for a series of benzylic carbon acids, $ArCH(R^1)R^2$, which are available in the literature.^{2,18,19,22-24}

$$\underbrace{ -\tilde{c} <_{R^2}^{R^1} + }_{R^2} \underbrace{ -\tilde{c} <_{R^2}^{R^1}}_{R^2}$$

$$\underbrace{ \delta \Delta G }_{R^2} \underbrace{ -\tilde{c} <_{R^2}^{R^1} + }_{R^2} \underbrace{ -\tilde{c} <_{R^2}^{R^1} (5) }_{R^2}$$

The gas-phase substituent constants, σ° and $\Delta \bar{\sigma}_{R}^{-}$, for typical substituents are given in Table 3. Although the gas-phase substituent effect is considered to be affected by substituent polarizability in addition to the conventional resonance and field/inductive effects,^{2,25,26} the polarizability effect is not significant in the benzylic system because this effect is sharply attenuated with a distance between the charged center and the substituent.⁵ Therefore, we analyzed a series of substituent effects for acidities of ArCH(R¹)R², in terms of the Y–T equation without polarizability effect in a similar manner to that applied to the stabilities of benzylic carbocations in the gas phase.^{7–15} Since *para*- π -acceptors are conjugated to the anionic centers in the electron rich system, $\Delta \bar{\sigma}_{R}^{-}$ instead of $\Delta \bar{\sigma}_{R}^{+}$ was used for the present systems.

$$-\delta\Delta G^{\circ} = \rho(\sigma^{\circ} + r^{-}\Delta\bar{\sigma}_{\rm R}^{-}) \tag{6}$$

where $\Delta \bar{\sigma}_{R}^{-}$ is the resonance substituent constant for π -acceptor. The typical correlations are illustrated for $R^{1} = R^{2} = H$ and $R^{1} = H$, $R^{2} = SO_{2}CF_{3}$ in Figures 1 and 2, respectively. Figure 1 shows that the substituent effect for acidities of toluenes is not correlated with σ° (closed circles) and σ^{-} (open circles) but is excellently correlated with $\bar{\sigma}$ with an r^{-} of 1.86 (squares). The r^{-} of 1.86 reveals a remarkably exalted π -delocalization of the negative charge at the benzylic carbon atom of benzyl anion compared with that for phenoxide in gas-phase ($r^{-} = 1.00$ by definition). Similarly, the best correlation

Table 3. Gas-Phase Substituent Constants Used for Correlation Analysis Based on Yukawa–Tsuno Equation

Subst.	$\sigma^{\circ\mathrm{a})}$	$\Delta ar{\sigma}_{ m R}^{-{ m b})}$	Subst.	$\sigma^{\circ\mathrm{a})}$	$\Delta \bar{\sigma}_{ m R}^{-{ m b})}$
p-SO ₂ CF ₃	1.08	0.265	<i>m</i> -CN	0.67	_
p-NO ₂	0.81	0.288	m-SCF ₃	0.59	_
<i>p</i> -NO	0.77	0.294	$3,5-(CF_3)_2$	0.98	_
<i>p</i> -COCH ₃	0.40	0.269	3,5-Cl ₂	0.77	_
<i>p</i> -CO ₂ Me	0.36	0.252	3,5-F ₂	0.54	_
<i>p</i> -CHO	0.49	0.293	<i>m</i> -CF ₃	0.50	_
<i>p</i> -CN	0.70	0.135	<i>m</i> -Cl	0.36	_
<i>p</i> -SO ₂ Me	0.69	0.204	<i>p</i> -Cl	0.30	_
p-SOMe	0.49	0.103	<i>m</i> -F	0.26	_
p-SCF ₃	0.63	0.089	<i>p</i> -F	0.10	
p-CF ₃	0.56	0.057	<i>m</i> -Me	-0.04	_
m-SO ₂ CF ₃	0.99	_	<i>p</i> -Me	-0.07	_
m-NO ₂	0.73	_	<i>p</i> -OMe	-0.09	_
<i>m</i> -COCH ₃	0.33		<i>m</i> -OMe	0.05	_
m-CHO	0.42		Н	0.00	0.00

a) Refs. 7 and 12. b) Determined from $\sigma_{\rm p}^{-}{}_{({\rm g})} - \sigma^{\circ}{}_{({\rm g})}$. The $\sigma_{\rm p}^{-}{}_{({\rm g})}$ values were derived from gas-phase acidities of phenols where $r^{-} = 1.00$ by definition. The $\Delta \bar{\sigma}_{\rm R}^{-}$ values for *meta* substituents and *para*- π -donors are zero because of no direct resonance interaction with the negative charge at the reaction site.

for the acidities of 1 is observed against $\bar{\sigma}$ with an r^- of 0.74 (squares, in Figure 2), indicating a somewhat smaller π -delocalization than that of phenol acidity.

The correlation parameters, ρ and r^- , for a series of benzylic carbon acids are summarized in Table 4. The r^- value varies significantly with the system from 1.86 for $R^1 = R^2 = H$ to 0.16 for $R^1 = R^2 = SO_2CF_3$, indicating obviously that a degree of π -delocalization of the negative charge formed at the benzylic carbon atom into the aromatic π -system decreases when R^1 and R^2 change to stronger electron-withdrawing groups, i.e., the increasing acidity of the unsubstituted parent carbon acid. Indeed, the r^- values are correlated linearly with



Figure 1. Y–T plot for gas-phase acidities of toluenes $(R^1 = R^2 = H)$, closed circle; σ° , open circle; σ^{-} , square; $\bar{\sigma}$ at $r^- = 1.86$.



Figure 2. Y–T plot for gas-phase acidities of α -SO₂CF₃substituted toluenes (R¹ = H, R² = SO₂CF₃), closed circle; σ° , open circle; σ^{-} , square; $\bar{\sigma}$ at $r^{-} = 0.74$.

the GA values of the unsubstituted parent benzylic compounds as shown in Figure 3.

$$r^{-} = 0.023 \Delta \text{GA} - 6.57 \ (R = 0.984)$$
 (7)

This linear relationship indicates that the degree of the π -delocalization of the negative charge formed at the benzylic carbon atom into the aryl π -system decreases with the increasing stability of the carbanions. In addition, it is found that the r^- values are correlated linearly with the acidifying effect of the phenyl group ($\Delta\Delta G^{\circ}_{\rm Ph}$) that is given by the difference in GA values between unsubstituted parent benzylic carbon acid, PhCH(R¹)R², and the corresponding methane derivative, CH₂(R¹)R² (Table 5 and Figure 4).

$$r^{-} = 0.050 \Delta \Delta G^{\circ}_{\rm Ph} + 0.11 \ (R = 0.971) \tag{8}$$

 Table 4.
 Y-T Correlation Results for Substituent Effects of Gas-Phase Acidities

Carbon acids	$ ho^{\mathrm{a})}$	r^{-}	R	SD	п
ArCH ₃	20.9 ± 0.6	1.86 ± 0.11	0.997	± 0.3	22 ^{d)}
ArCH(CF ₃) ₂	16.3 ± 1.1	b)	0.987	± 0.3	8
ArCH(Cl)CF ₃	16.8 ± 0.7	1.18 ± 0.16	0.998	± 0.5	9 ^{e)}
ArCH ₂ CN	17.1 ± 0.2	1.36 ± 0.08	0.999	± 0.2	14 ^{f)}
ArCH ₂ SO ₂ CF ₃	15.7 ± 0.8	0.74 ± 0.19	0.996	± 0.6	12
ArCH(CN) ₂	15.0 ± 0.5	0.60 ± 0.13	0.999	± 0.4	9 ^{g)}
ArCH(SO ₂ CF ₃) ₂	7.4 ± 0.1	$0.16\pm0.19^{\rm c)}$	0.999	± 0.1	5

a) In kcal mol⁻¹ $\bar{\sigma}^{-1}$ unit. b) No available data to determine the r^{-} value. c) Less reliable because of a limited data. d) Included nine substituents other than data listed in Table 3, p-SO₂CF₃; 33.0, p-NO; 28.6, p-CHO; 21.3, p-COCH₃; 18.8, p-CO₂CH₃; 18.3, p-COC₆H₅; 20.4, p-SO₂CH₃; 21.6, p-SOCH₃; 14.4, m-CHO; 9.6, taken from Refs. 2 and 23. e) Included 3,5-F₂; 8.2. f) Included m-OCH₃; 1.4, p-OCH₃; -0.9. g) Included p-OCH₃; -1.1.



Figure 3. Plot of the resonance demand parameter (r^{-}) against gas-phase acidities of unsubstituted parent carbonacids, $C_6H_5CH(R^1)R^2$.

Since the acidifying effect of the phenyl group can be regarded as a measure of the degree of the π -delocalization of the negative charge formed at the benzylic carbon atom into the phenyl group, the existence of such a linear relationship between both quantities suggests again that the negative charge formed at the benzylic carbon atom is stabilized competitively by the aryl group and α -substituents. In fact, the stabilization effect of the phenyl substitution in the strongest acid, RCH(SO₂CF₃)₂, is nearly zero, being consistent with a negligibly small r^- value of 0.16. In conclusion, the effect of the aryl group on the stability of the carbanion is compensated with the electronic effects of R¹ and R².

Such changes of the r^- values are expected to relate to the geometric features and the charge distributions of their conjugate anions. Therefore, theoretical calculations have been conducted for the conjugate anions of the unsubstituted parent carbon acids, $C_6H_5C^-(R^1)R^2$, at the B3LYP/6-311+G(d,p) level of theory. The results are given in Table 5 (also Table S1).

\mathbb{R}^1	D 2	GA/kca	$1 \mathrm{mol}^{-1}$	$\Delta \Delta C^{\circ}$ a)	$\nabla_{\alpha}(\mathbf{D}\mathbf{b})\mathbf{b}$	C1C7/Å ^{c)}
	K	$PhCH(R^1)R^2$	$CH_2(R^1)R^2$	$-\Delta\Delta O_{\rm ph}^{\prime\prime}$	$\Sigma q(FII)^{\circ}$	
Н	Н	373.7 ^{d)}	409.9 ^{d)}	36.2	-0.618	1.391
Cl	CF ₃	348.7 ^{e)}	—	—	-0.377	1.416
Н	CN	344.1 ^{d)}	365.2 ^{d)}	21.1	-0.362	1.421
CF ₃	CF ₃	335.3 ^{e)}	348.7 ^f)	13.4	-0.241	1.454
Н	SO ₂ CF ₃	328.1 ^{g)}	339.8 ^{h)}	11.7	-0.223	1.441
CN	CN	314.3 ^{h)}	328.9 ^d)	14.6	-0.197	1.452
SO ₂ CF ₃	SO ₂ CF ₃	300.0 ⁱ⁾	300.6 ⁱ⁾	0.6	-0.035	1.490

Table 5. Gas-Phase Acidities of $PhCH(R^1)R^2$ and $CH_2(R^1)R^2$, Acidifying Effects of the Phenyl Group, Natural Charges of the Phenyl Group, and Selected Bond Distance of the Conjugate Anions

a) $\Delta\Delta G^{\circ}_{ph} = GA[CH_2(R^1)R^2] - GA[PhCH(R^1)R^2]$. b) Group natural charges of the phenyl moiety obtained by natural population analysis at B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p). c) Bond length of C1C7. Numbering of atoms given in Table S1. d) Ref. 22. e) Ref. 24. f) Determined in this study, 1.0 kcal mol⁻¹ stronger than nitromethane (GA = 349.7 kcal mol^{-1d}) and 1.0 kcal mol⁻¹ weaker than 1,1,1,2,3,3,3-heptafluoropropane (GA = 347.8 kcal mol⁻¹, unpublished). g) This work. h) Ref. 19. i) Ref. 18.



Figure 4. Plot of the resonance demand parameter (r^{-}) against the stabilization effect of the phenyl group. $\Delta\Delta G^{\circ}_{Ph} = GA[CH_2(R^1)R^2] - GA[C_6H_5CH(R^1)R^2].$

As expected, as the acidity of the unsubstituted parent carbon acids increases, the bond distance C1C7 lengthens and the sum of the natural charges in the phenyl moiety obtained by natural population analysis decreases, revealing the weakened π interaction between the phenyl group and the negative charge at the benzylic carbon atom. The r^- values are indeed correlated linearly with the bond length of the C1C7 and with the natural charge of the phenyl moiety of the corresponding carbanion, $\Sigma q_{\rm Ph}$ in PhC⁻(R¹)R², following eqs 9 and 10, respectively (Figures S1 and S2).

$$r^{-} = -17.8d(C1C7) + 26.5 \ (R = 0.981) \tag{9}$$

$$\bar{q} = -3.03\Sigma q_{\rm Ph} + 0.062 \quad (R = 0.990)$$
(10)

These results suggest that the resonance demand parameter is an intrinsic property of molecular structure. The present results on the resonance demand in the electron-rich system are completely consistent with that observed for the effects on the resonance demand parameter r^+ for π -donor substituents in the electron-deficient, benzylic carbocations.^{11,12,15}

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Figure 5. Plot of the ρ values against gas-phase acidities of unsubstituted parent carbonacids, $C_6H_5CH(R^1)R^2$.

Furthermore, it is interesting to note that a slope of 0.023 in Figure 3 is surprisingly similar to that of 0.026 observed for the benzylic carbocation system though this agreement may be accidental. This similarity suggest that $\Delta \bar{\sigma}_{\rm R}^+$ and $\Delta \bar{\sigma}_{\rm R}^-$ values may have a common scale in the degree of π -delocalization although both parameters are determined by different definitions, $\Delta \bar{\sigma}_{\rm R}^+ = \sigma^+ - \sigma^\circ$ and $\Delta \bar{\sigma}_{\rm R}^- = \sigma^- - \sigma^\circ$.

It is also noteworthy that the magnitude of ρ value as a measure of electron demand of the system also tends to decrease with the increasing acidity of the unsubstituted parent carbon acid. Excluding $R^1 = R^2 = SO_2CF_3$, the ρ values are correlated linearly with the GA values of the unsubstituted parent acids as shown Figure 5.

$$\rho = 0.098 \Delta \text{GA}_{(\text{X}=\text{H})} - 16.3 \ (R = 0.956) \tag{11}$$

This result suggests that the ρ value is also influenced by the electronic effect of R¹ and R². On the other hand, until now we did not pay much attention to the ρ value for the carbocation system, ArC⁺(R¹)R², because the variation in ρ caused by R¹

and R² substituents is very small, i.e., -13.0 for R¹ = R² = Me to -14.5 for R¹ = H, R² = CF₃. The present obtained ρ values for the electron-rich system forces us to reexamine the previous results for a series of benzylic carbocations for a comparison with the present observation. A careful examination reveals that the ρ value for the benzylic carbocation tends to decrease with the increasing stability of a carbocation. The ρ values are correlated linearly with the stability of the unsubstituted parent benzylic carbocation in a similar manner to the present benzylic carbanion system (Figure S3),²⁷ indicating that the ρ value for the carbocation system is also dependent on the thermodynamic stability of unsubstituted parent cabocation.

$$\rho = -0.069 \Delta \Delta G^{\circ}_{(X=H)} - 13.1 \ (R = 0.975)$$
(12)

where $\Delta\Delta G^{\circ}_{(X=H)}$ is the thermodynamic stability of benzylic carbocation, $C_6H_5CH^+(R^1)R^2$, relative to that of α -cumyl cation ($R^1 = R^2 = CH_3$). Such variation of the ρ value would be interpreted by the charge distribution in a molecular framework of interest. In the thermodynamically more stable carbanions with strong electron-withdrawing groups R^1 and R^2 , the negative charges formed at the benzylic carbon atom by deprotonation are located at the $C(R^1)R^2$ moiety rather than the aromatic moiety. For example, in the conjugate anion of 2 a total natural charge of the phenyl moiety is only -0.035 and the rest of the charge is localized at the $C(SO_2CF_3)_2$ moiety while in the benzyl anion $(R^1 = R^2 = H)$ the group natural charges of the phenyl moiety is -0.618 as seen in Table 5. That is, the center of the charge would be far from the substituent on the benzene ring in the conjugate anion of 2, resulting in a small ρ value. The same situation must be held in the benzylic carbocations.

Finally, it should be noted that the ρ value of 7.4 for **2** is remarkably smaller than the expected value from the linear relationship shown in Figure 5. The reason for the small ρ value is not clear at the present stage. Similar small ρ values as well as the r^+ value were observed for the solvolysis of α, α di-*t*-butylbenzyl *p*-nitrobenzoates²⁸ and 4-methylbenzo[2.2.2]bicycloocten-1-yl triflates²⁹ in which the vacant p-orbital of carbocation intermediates is significantly twisted from the benzene π -orbital plane.³⁰ The calculated geometry of the conjugate anion of **2** shows that the S–C–S plane of the C⁻(SO₂CF₃) moiety is also twisted from the benzene plane by 61.3°, suggesting that there may be some common reasons for a reduced ρ value in a highly congested system. Further study is obviously needed to answer this question.

Conclusion

Substituent effects for acidities of a series of ArCH(\mathbb{R}^1) \mathbb{R}^2 , have been analyzed successfully in terms of the Y–T equation using substituent parameters in gas the phase. The resultant resonance demand parameter r^- value decreased linearly with increasing acidity of the GA values of the unsubstituted parent carbon acids, and the change of the r^- value was found to be related with the geometric parameters and natural charges of the conjugate carbanions calculated at B3LYP/6-311+G(d,p). Such behavior of the resonance demand in the electronrich system, ArC⁻(\mathbb{R}^1) \mathbb{R}^2 , is completely consistent with that observed for the electron-deficient system, ArC⁺(\mathbb{R}^1) \mathbb{R}^2 , suggesting that the resonance demand must be determined by the intrinsic properties arising from the structure of carbanions or carbocations. In addition, it was found that the ρ values also decreased with increasing acidity of the GA values of the unsubstituted parent carbon acids. This would be due to the varying distribution of the charge in the molecuar skeleton caused by the R¹ and R² groups.

Experimental

Melting points were measured on a YanaCO MP-J3 apparatus and are reported uncorrected. The NMR spectra were recorded on a JEOL JNM-EX400 or ECA-500 FT-NMR spectrometer in CDCl₃ and chemical shifts are reported in δ value downfield from the internal standard tetramethylsilane (TMS).

Chemicals. Preparation of (*m*,*p*-substituted phenyl)methyl trifluoromethyl sulfones (1).³¹ General procedure: A mixture of benzylic halide (10 mmol) and CF₃SO₂Na (2.0 g, 13 mmol) in propionitrile (30 mL) was heated at reflux temperature. While disappearance of the starting halide was monitored by TLC, the mixture was cooled, the salts were removed by filtration and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using a linear EtOAc gradient in hexane to give the targeted products 1 as solids. Phenylmethyl trifluoromethyl sulfone: mp 81-83 °C. ¹H NMR (CDCl₃): δ 4.48 (s, 2H), 7.38–7.46 (m, 5H). 3-Fluorophenylmethyl trifluoromethyl sulfone: mp 88–89 °C. ¹H NMR (CDCl₃): & 4.47 (s, 2H), 7.16–7.46 (m, 4H). 4-Fluorophenylmethyl trifluoromethyl sulfone: mp 103-105 °C. ¹H NMR (CDCl₃): δ 4.46 (s, 2H), 7.13–7.16 (m, 2H), 7.40–7.43 (m, 2H). 3-Trifluoromethylphenylmethyl trifluoromethyl sulfone: mp 80–81 °C. ¹H NMR (CDCl₃): δ 4.54 (s, 2H), 7.59–7.76 (m, 4H). Anal. Calcd for C₉H₆F₆O₂S: C, 36.99; H, 2.07%. Found: C, 36.45; H, 2.21%. 4-Trifluoromethylphenylmethyl trifluoromethyl sulfone: mp 110–112 °C. ¹H NMR (CDCl₃): δ 4.54 (s, 2H), 7.58 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H). 3-Nitrophenylmethyl trifluoromethyl sulfone: mp 84–85 °C. ¹H NMR (CDCl₃): δ 4.59 (s, 2H), 7.67–7.82 (m, 2H), 8.33– 8.37 (m, 2H). Anal. Calcd for C₈H₆F₃NO₄S: C, 35.69; H, 2.25; N, 5.20%. Found: C, 36.45; H, 2.21; N, 5.47%. 4-Nitrophenylmethyl trifluoromethyl sulfone: mp 101-102 °C. ¹H NMR (CDCl₃): δ 4.58 (s, 2H), 7.66 (d, J = 8.0 Hz, 2H), 8.32 (d, J = 8.8 Hz, 2H). Anal. Calcd for C₈H₆F₃NO₄S: C, 35.69; H, 2.23; N, 5.20%. Found: C, 35.85; H, 2.20; N, 5.37%. 3-Chlorophenylmethyl trifluoromethyl sulfone: mp 88-89 °C. ¹HNMR (CDCl₃): δ 4.45 (s, 2H), 7.23–7.47 (m, 4H). Anal. Calcd for C₈H₆ClF₃O₂S: C, 37.14; H, 2.32%. Found: C, 37.01; H, 2.32%. 4-Chlorophenylmethyl trifluoromethyl sulfone: mp 103–105 °C. ¹H NMR (CDCl₃): δ 4.45 (s, 2H), 7.39 (d, J =8.4 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H). 3-Cyanophenylmethyl trifluoromethyl sulfone: mp 75–77 °C. ¹H NMR (CDCl₃): δ 4.41 (s, 2H), 7.58–7.79 (m, 4H); 13 C NMR (CDCl₃): δ 55.17, 113.85, 117.58, 120.89, 125.07, 130.23, 133.64, 134.56, 135.47. Anal. Calcd for C₉H₆NF₃O₂S: C, 43.37; H, 2.41; N, 5.62%. Found: C, 43.44; H, 2.36; N, 5.87%. 4-Cyanophenylmethyl trifluoromethyl sulfone: mp 123-125 °C. 1HNMR (CDCl₃): δ 4.53 (s, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H). 3,5-Bis(triluoromethyl)phenylmethyl trifluoromethyl sulfone: mp 86–87 °C. ¹H NMR (CDCl₃): δ 4.60 (s, 2H), 7.91 (s, 2H), 8.00 (s, 1H).

Preparation of substituted arylbis(triflyl)methanes.³¹ General procedure: To a solution of 1 (0.5 mmol) in dry diethyl ether (3 mL) was added t-BuLi (0.34 mL, 0.55 mmol, 1.6 M solution in hexane) dropwise at -78 °C, and the resulting mixture was stirred for 20 min. Triflic anhydride (92 mL, 0.28 mmol) was then added, and the resulting mixture was allowed to warm to room temperature over a period of 1 h. After the reaction mixture was cooled to -78 °C, t-BuLi (0.34 mL, 0.55 mmol, 1.6 M in hexane) was added dropwise, and the resulting mixture was stirred for 20 min. Triflic anhydride (0.28 mmol) was then added, and the resulting mixture was allowed to reach room temperature over a period of 1 h before the reaction was quenched with water. The resultant mixture was neutralized and washed with hexane. The aqueous phase was acidified with 4 M aqueous HCl and extracted with ether twice. The organic lavers were dried over magnesium sulfate, filtered and concentrated under reduced pressure. The residue was recrystallized using 2:1 hexane to ethylacetate to give desired products 2. 3-Fluorophenylbis(triflyl)methane: mp 51–53 °C. ¹H NMR (CDCl₃): δ 5.87 (s, 1H), 7.21–7.58 (m, 4H). MS (FAB): Calcd for [M]⁺ $C_9H_5O_4F_7S_2$: m/z 373.9518. Found: m/z 373.9518. 3-Trifluoromethylphenylbis(triflyl)methane: mp 60–61 °C. ¹H NMR (CDCl₃): δ 5.97 (s, 1H), 7.74–7.95 (m, 4H). MS (FAB): Calcd for $[M]^-$ C₁₀H₄O₄F₉S₂: m/z 422.9407. Found m/z422.9411. 4-Trifluoromethylphenylbis(triflyl)methane: mp 76-77 °C. ¹H NMR (CDCl₃): δ 5.97 (s, 1H), 7.83–7.85 (m, 4H). MS (FAB): Calcd for $[M]^-$ C₁₀H₄O₄F₉S₂: m/z 422.9407. Found: m/z 422.9434. 3,5-Bis(trifluoromethyl)phenylbis(triflyl)methane: mp 71–73 °C. ¹H NMR (CDCl₃): δ 6.04 (s, 1H), 7.91-8.18 (m, 3H). MS (FAB): Calcd for [M]⁻ C₁₁H₃O₄F₁₂S₂: *m*/*z* 490.9281. Found: *m*/*z* 490.9276.

Gas-Phase Acidity Measurement. The gas-phase acidity measurements were performed on an Extrel FTMS 2001 Fourier transform ICR spectrometer equipped with an IonSpec Data station. Most of the experimental techniques used for the measurements of the equilibrium constants of the proton-transfer reactions (eq 16) are the same as the general procedures in the literature.^{3,32} Equations 13–16 describe the sequence of reactions which occur in a typical experiment, where AH and A_oH are the measured acid and the reference acid, respectively.

$$MeONO + e^{-} \rightarrow MeO^{-} + NO$$
(13)

$$MeO^- + A_0H \rightarrow A_0^- + MeOH$$
 (14)

 $MeO^- + AH \rightarrow A^- + MeOH$ (15)

$$A_o^- + AH \rightleftharpoons A^- + A_oH \tag{16}$$

An experiment is initiated by a 5-ms pulse of a low-energy electron beam (0.3 to 0.5 eV) through the ICR cell. The electrons are captured by methyl nitrite at a partial pressure of $1-2 \times 10^{-7}$ Torr and CH₃O⁻ is produced (eq 13). The acids AH and A_oH react with CH₃O⁻ to yield M – 1 negative ions (eqs 14 and 15). For the measurements of arylbis(trifluoro-methylsulfonyl)methanes methyl nitrite was not needed because strongly acidic substrates were deprotonated easily only by electron-ionization. The partial pressures of the neutrals were maintained at lower than 4×10^{-7} Torr. The equilibrium constant *K* for reaction (eq 16) was evaluated from the expression $K = [A_o^-/A^-][AH/A_oH]$. The relative abundances of ions A⁻ and A_o⁻ were determined by the relative intensities of ICR mass spectra signals when the equilibrium was attained. The

time for the establishment of equilibrium was between 500 ms and 50 s, depending upon the pressure and molecular structure of neutrals. In the case of highly delocalized carbanions, the achievement of equilibrium took a very long time ca. 30-50 s. Each measurement was performed at several ratios of partial pressures and at different overall pressures. The pressures of the neutral reactants were measured by means of a Bayard-Alpert ionization gauge with appropriate correction factors being applied to convert the gauge readings to relative intensities of the various compounds.^{33,34} A solid probe equipped with a small glass vessel was also used for some strong acids which were easily decomposed on the surface of a stainless steel inlet tube. Arithmetic mean values of K were used to calculate $\delta \Delta G^{\circ}$ $(=-RT\ln K)$ with an average uncertainty of ± 0.2 kcal mol⁻¹ in most cases. Ion-eject experiments were also carried out to ensure that proton-transfer reactions occurred. The gas-phase acidity values for the reference compounds were taken from the literature.¹⁸⁻²⁰ Although the measurement of each protontransfer equilibrium was carried out at 323 K, the acidity values obtained can be regarded as the values at 298 K, because the entropy term is relatively small in proton-transfer equilibria in the gas phase and because the acidities of reference compounds are compiled at 298 K.

Calculations. DFT calculations were carried out using the Gaussian 09 program.³⁵ The geometries were fully optimized at the B3LYP/6-311+G(d,p) level of theory. Vibrational normal mode analyses were performed at the same level to ensure that each optimized structure was a true minimum on the potential energy surface. Natural population analysis was also carried out to compute the charges.

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Supporting Information

Optimized geometries, plots of the r^- vs. the bond length C1C7 and natural charge of aromatic moiety, and plot of the ρ vs. the relative stability of the unsubstituted benzylic carbocations. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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