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Gas-Phase Substituent Effects in Stabilized Benzylic Carbocations. Basicities of Benzaldehydes, Acetophenones, and Methyl Benzoates in the Gas Phase[1)]

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The gas-phase basicities of a series of aromatic carbonyl compounds (ArCOR; R=OMe, Me, H) were measured based on the proton-transfer equilibrium method using a pulsed ICR mass spectrometer. The effects of ring-substituents on the gas-phase basicities were analyzed in terms of the Yukawa–Tsuno equation. It was shown that the resonance demand parameter (r^+) decreases significantly from 1.06 for the benzaldehyde to 0.50 for the methyl benzoate in increasing order of the electron-donating ability of the R group directly linked to the carbonyl carbon. This indicates that the π-charge formed in the conjugate acid ion is competitively delocalized into an aryl group and an R group. In contrast, the ρ value is nearly constant at -11 (in kcal mol^{-1} per $\bar{\sigma}$ unit) in all series. Most importantly, it was found that the r^+ value in the gas phase is in agreement with that for the basicities in aqueous solution, whereas the ρ value is significantly reduced in aqueous solution. This fact led us to the conclusion that the solvation of a cation reduces the central charge so as to lower the response to substituent perturbation, essentially without changing the nature of the intramolecular charge-delocalization.

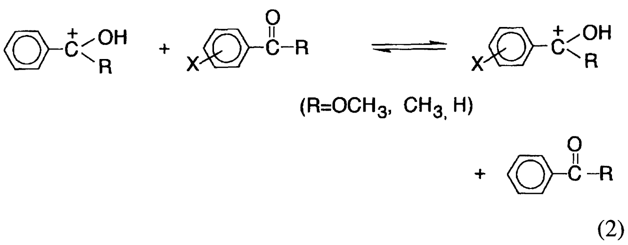
Studies on ion-molecule reactions in the gas phase have played an important role for improving our understanding of organic reactions in solution.[2—4)] Particularly, the thermodynamic stabilities of various ions determined by a measurement of the gas-phase basicity and acidity provided a critical basis for developing the fundamental concept of a structure–reactivity relationship.[5—9)] In our earlier studies,[10—12)] the substituent effects of the gas-phase stability of benzylic carbocations were successfully analyzed using the Yukawa–Tsuno equation (Eq. 1),[13)] which was originally based on the reactivity in solution.

$$-\delta\Delta G^\circ = \rho(\sigma^\circ + r^+\Delta\bar{\sigma}_R^+). \qquad (1)$$

In Eq. 1 σ° and $\Delta\bar{\sigma}_R^+$ are a normal substituent constant and a resonance substituent constant ($=\sigma^+ - \sigma^\circ$), respectively; r^+ is a resonance demand parameter, indicating the degree of the π-interaction between a *para* π-donor substituent and a positive charge, and ρ is a susceptibility parameter of the system.

From this analysis it was found that highly electron-deficient benzylic cations, such as benzyl cation[12)] and 1-phenyl-1-(trifluoromethyl)ethyl cation[11a)] were characterized by unique r^+ values higher than unity for the α-cumyl (1-methyl-1-phenylethyl) cation.[10)] Thus, the r^+ values increased in decreasing order of the intrinsic stability of the unsubstituted member (ring substituent=H) of each carbocation series.[11b)] This suggested that the degree of the π-delocalization of the positive charge into the aryl group varies essentially with the electron-deficiency at the benzylic carbon.

An extension of this study to a stabilized carbocation system is of great importance for further clarifying the intrinsic behavior of charge-delocalization in the benzylic carbocation system and physical significance of the r^+ value. The trend of the r^+ value mentioned above predicts that a stabilized carbocation does not require a large π-delocalization of the positive charge to *para* π-donor substituents, i.e., the r^+ value is smaller than unity for the α-cumyl cation irrespective of the formation of a positive charge at the benzylic position. As such a stabilized carbocation system, we studied the substituent effects on the gas-phase basicities (GB) of aromatic carbonyl compounds (ArCOR), where the positive charge in the conjugate acid ions, ArC$^+$(R)OH, is stabilized by an electron-releasing hydroxyl group linked to the benzylic carbon, and the stability of the ion is regulated by the electronic effect of the R group.



(2)

In this paper, we report on results concerning an analysis of the substituent effects on the gas-phase basicity of methyl benzoate, acetophenone, and benzaldehyde series on the basis of the Yukawa–Tsuno Eq. 1. In addition, the solvent effects on these proton-transfer reactions have been discussed in a comparison of the substituent effects between the gas and aqueous solution phases.[14)]

Although some data concerning these series in the gas phase are available from the literature,[15)] they are not sufficient for a detailed analysis because of the lower accuracy in addition to the limited range of the substituent variation. All of the data used for the present analysis were therefore determined in this study.

Results and Discussion

The gas-phase basicities were determined by measuring the standard free-energy changes of the proton-transfer equilibria using reference bases (B_0) of known basicity. The free-energy changes (ΔG°) for individual equilibrium are given in Tables 1, 2, and 3. The GB values of the reference bases used in these measurements are given in Table 4. The relative basicities ($-\delta\Delta G^\circ$) of each series, which correspond to the free-energy changes of the reaction (Eq. 2), are summarized in Table 5. The uncertainty in the $-\delta\Delta G^\circ$ values may be estimated to be ≤ 0.2 kcal mol^{-1} in most cases. Although the present measurements were carried out at 343 K, selected GB values may be regarded as mean values at 300 K, because the GB values of the reference bases were determined at 300 to 320 K.[16)] In addition, since the entropy changes of the proton-transfer reaction (Eq. 2) are small in the gas phase,[8a)] it is reasonable to assume $-\delta\Delta G^\circ_{(343\ \mathrm{K})} \approx -\delta\Delta G^\circ_{(300\ \mathrm{K})}$.

p-Dimethylamino and *p*-amino derivatives have two basic sites, i.e., the amino nitrogen and the carbonyl oxygen. Since the GB value of *p*-aminoacetophenone (208.7 kcal mol^{-1}) is significantly higher than that of aniline, where protonation occurs at the amino nitrogen, the possibility of protonation at the amino group is precluded. If the protonation of *p*-aminoacetophenone occurred at the amino nitrogen, this should have been less basic than aniline. However, the observed GB is higher than aniline by 6 kcal mol^{-1}. We therefore assume that protonation must occur at the carbonyl oxygen to give a benzylic carbocation. For the same reason, the protonation site of *p*-dimethylaminobenzaldehyde and methyl *p*-aminobenzoate is the carbonyl oxygen. For *p*-methoxycarbonylbenzaldehyde and *p*-methoxycarbonylacetophenone protonation seems to occur at the formyl group and the acetyl group, respectively. No such difficulty in assigning the protonation site exists for the other substituted aromatic carbonyl compounds studied here, because the sub-

Table 1. Standard Free Energy Changes of Proton Transfer Equilibria of Benzaldehydes[a)]

Subst.	Reference base (B_0)	ΔG° [b)]	GB[c)]	Subst.	Reference base (B_0)	ΔG° [b)]	GB[c)]
p-NMe_2	2-Methoxypyridine	0.6	213.2	*m*-OH	Et_2O	−0.9	192.6
	$C_6H_5NMe_2$	2.1			EtOAc	−0.5	
p-OMe	3-Cyanopyridine	−1.1	202.3		Pr_2O	1.2	
	4-Cyanopyridine	−0.1		*p*-F	THF	−1.0	191.5
p-SMe	Acetylacetone	−2.1	201.6		Et_2O	0.2	
	Bu_2S	−0.8		*m*-F	Acetone	−0.2	188.1
	3-Cyanopyridine	−0.4			MeOAc	1.0	
	p-$MeC_6H_4COCH_3$	−0.3		*p*-Cl	THF	−1.0	191.5
	2-Fluoropyridine	1.3			Et_2O	0.1	
3-Cl-4-OMe	*i*-Pr_2O	−1.1	198.9	*m*-Cl	Acetone	−0.9	188.9
	Acetylacetone	0.2			MeOAc	0.2	
3-Cl-4-SMe	Pr_2CO	−3.4	198.5	*p*-CO_2Me	THF	−1.4	191.7
p-OH	*i*-Pr_2O	−1.2	198.9		EtOAc	0.5	
	Acetylacetone	0.3			MeCOEt	−1.2	
p-Me	Pr_2CO	−1.5	196.6	*p*-CHO	*i*-PrCN	−1.7	187.6
	cyclo-PrCOMe	−0.3			Acetone	0.2	
	i-Pr_2O	1.1		*m*-CF_3	*i*-PrCN	−0.8	186.5
p-*t*-Bu	*i*-Pr_2O	−0.2	197.8		C_6H_5CN	1.2	
	Acetylacetone	1.5		*p*-CF_3	1,4-Dioxane	−0.9	186.2
p-Et	*cyclo*-PrCOMe	−0.4	196.8		*i*-PrCN	−0.6	
	i-Pr_2O	0.8		*m*-CN	*i*-PrCHO	−0.5	184.5
p-*i*-Pr	*i*-Pr_2O	−0.2	197.8		PrCN	0.3	
	Acetylacetone	1.5		*p*-CN	PrOH	−2.0	184.0
3,5-Me_2	*cyclo*-PrCOMe	−0.6	196.9		PrCHO	−0.9	
	i-Pr_2O	0.7			*i*-PrCHO	0.2	
m-Me	Pr_2O	−1.0	194.9	*m*-NO_2	EtCN	−0.2	183.7
	Pr_2CO	0.2			*i*-PrCHO	0.3	
m-SMe	Et_2CO	−1.1	193.9	*p*-NO_2	PrOH	−1.7	183.4
	Pr_2O	0.1			PrCHO	−0.3	
m-OMe	Pr_2O	−0.9	194.8	3,5-Me_2-4-NO_2	Acetone	−1.6	189.6
	Pr_2CO	0.3			MeOAc	−0.4	
					THF	0.7	

a) All values in kcal mol^{-1}, 1 cal=4.184 J. b) Standard free energy change for each equilibrium at 343 K. $B+B_0H^+ \rightleftharpoons BH^+ + B_0$. c) Selected GB values.

Table 2. Standard Free Energy Changes of Proton Transfer Equilibria of Acetophenones[a)]

Subst.	Reference base (B_0)	ΔG° [b)]	GB[c)]	Subst.	Reference base (B_0)	ΔG° [b)]	GB[c)]
p-NMe$_2$	$C_6H_5NMe_2$	0.0	215.4	*p*-F	*i*-Pr$_2$CO	−0.8	196.7
	m-MeC$_6$H$_4$NMe$_2$	1.6			PhCOMe	0.7	
p-NH$_2$	$MeCONMe_2$	−0.3	208.7	*m*-Cl	Cyclohexanone	−0.2	194.0
	$PhCH_2NH_2$	0.2			Styrene	0.0	
3-CH$_2$CH$_2$O-4	2-Chloropyridine	−0.6	207.2	*m*-F	PhCHO	−1.2	193.6
	$MeCONMe_2$	1.2			Cyclohexanone	−0.4	
p-OMe	*t*-Bu$_2$S	0.2	205.4		Styrene	0.2	
	2-Chloropyridine	1.1		*p*-COCH$_3$	$C_6H_5CO_2Me$	−0.5	196.1
p-SMe	2-Fluoropyridine	−0.9	203.8		*i*-Pr$_2$CO	0.0	
	$HCONMe_2$	−0.6			*cyclo*-PrCOMe	0.3	
	$(MeO)_3PO$	1.0		*p*-CO$_2$Me	*i*-Pr$_2$CO	0.0	196.1
3-Cl-4-OMe	Bu_2S	−1.8	202.7		*cyclo*-PrCOMe	0.2	
	4-Cyanopyridine	−0.6		*m*-CF$_3$	THF	−1.5	192.0
3-Cl-4-SMe	3-Cyanopyridine	−0.5	201.8		Et_2O	−0.3	
p-OH	4-Cyanopyridine	−0.7	203.7		EtOAc	0.0	
	$HCONMe_2$	0.4		*p*-CF$_3$	Et_2O	0.3	191.5
3,4-Me$_2$	Aniline	0.1	202.4		EtOAc	0.5	
p-*t*-Bu	4-Cyanopyridine	−0.2	202.3	*m*-CN	Acetone	−1.3	189.3
	Aniline	0.2			MeOAc	−0.1	
	$HCONMe_2$	0.7			THF	1.0	
p-Cyclopropyl	Bu_2S	−1.4	202.4	*p*-CN	Acetone	−1.1	189.1
	4-Cyanopyridine	−0.5			MeOAc	0.0	
p-Me	Acetylacetone	−2.1	201.3	*m*-NO$_2$	Acetone	−1.0	188.9
	Bu_2S	−0.5			MeOAc	0.2	
	3-Cyanopyridine	0.1		*p*-NO$_2$	Acetone	−0.6	188.5
	p-SMeC$_6$H$_4$CHO	0.3			MeOAc	0.6	
3,5-Me$_2$	Bu_2S	−0.3	201.2	3,5-(CF$_3$)$_2$	HCO_2Et	−1.9	186.8
m-Me	*i*-Pr$_2$O	−1.2	199.0		1,4-Dioxane	−1.2	
	Acetylacetone	0.2			*i*-PrCN	−1.1	
m-SMe	*i*-Pr$_2$O	−1.0	198.6		C_6H_5CN	0.8	
	Acetylacetone	0.6		3,5-Me$_2$-4-NO$_2$	EtOAc	−2.6	194.7
m-OMe	*m*-Fluoroaniline	−1.0	200.0		Pr_2O	−1.0	
	Acetylacetone	−0.5		3,5-Me$_2$-4-OH	$(MeO)_3PO$	−1.4	206.4
	3-Cyanopyridine	1.2			2-Chloropyridine	0.2	
m-OH	*i*-Pr$_2$O	−0.3	198.0	3-Me-4-OH	2-Fluoropyridine	−1.6	204.5
	Acetylacetone	1.2			$(MeO)_3PO$	0.4	
p-Cl	$PhCO_2Me$	−1.5	196.7				
	i-Pr$_2$CO	−0.6					
	PhCOMe	0.6					

See footnotes of Table 1.

stituents are less basic than the carbonyl group. These assignments of the protonation site are consistent with the results of the substituent effect analysis discussed below.

Gas Phase Substituent Effects. The relative GB values of benzaldehydes are plotted in Fig. 1 against those of the corresponding α-methylstyrenes, which measure the relative stabilities of the formed α-cumyl cations. Since there exists an excellent linear relationship for the gas-phase stabilities of the α-cumyl cations against the ordinary σ^+ values in solution,[10a)] there is no difficulty in defining a gas-phase σ^+ scale based on the stabilities of these cations. Thus, the $-\delta\Delta G^{\circ}$ vs. $-\delta\Delta G^{\circ}$ plot of the substituted benzaldehydes agains α-methylstyrenes corresponds to a σ^+-plot in the gas phase. This figure shows that there is a good linear relationship between both systems, indicating that the stabilities of α-hydroxybenzyl cations can be described by σ^+ substituent constants. The slope of 0.9 suggests that the response of the stability of the cation to the ring-substituents is somewhat reduced in the α-hydroxybenzyl cation system compared with that in the α-cumyl cation.

In contrast, the plot of the relative GB values of methyl benzoates versus α-methylstyrenes (Fig. 2) shows no simple linear relationship for the whole set of substituents. If limited only to non-conjugated substituents, *meta* substituents and *para* π-electron acceptors, there exists a good linear relationship. All *para* π-donors show negative deviations from this line. Similar situations of these π-donors are observed for a mutual comparison between the benzoyl series, as shown in Fig. 3. The deviations of the *para* π-donors in these figures are systematic, i.e., the stronger *para* π-donor substituent shows a greater deviation, suggesting that the resonance-stabilization effects due to the *para* π-donor substituents vary with the system. The deviations of the *p*-*t*-butyl and 3,5-dimethyl groups shown in Fig. 3 cannot be explained in terms

Table 3. Standard Free Energy Changes of Proton Transfer Equilibria of Methyl Benzoates[a)]

Subst.	Reference base (B_0)	ΔG° [b)]	GB[c)]	Subst.	Reference base (B_0)	ΔG° [b)]	GB[c)]
p-NMe$_2$	*m*-FC$_6$H$_4$NMe$_2$	−0.8	212.4	*p*-F	Et$_2$O	−2.0	193.5
	p-FC$_6$H$_4$NMe$_2$	0.8			EtOAc	−1.0	
p-NH$_2$	3-Cyanopyridine	−2.0	203.6		Et$_2$CO	−0.5	
	4-Cyanopyridine	−1.4			C$_6$H$_5$CH=CH$_2$	0.4	
	Aniline	−1.1			Pr$_2$O	0.4	
	HCONMe$_2$	−0.7			Cyclohexanone	0.6	
	(MeO)$_3$PO	1.3		*p*-Cl	Et$_2$CO	−0.8	193.6
p-OMe	Acetylacetone	−1.2	200.5		Pr$_2$O	0.2	
	2-Cyanopyridine	−0.5			Cyclohexanone	0.5	
	3-Cyanopyridine	0.7		*m*-Cl	THF	−2.0	192.1
p-SMe	*i*-Pr$_2$O	−1.5	199.1		Et$_2$O	−0.4	
	Acetylacetone	0.3			EtOAc	−0.1	
	2-Cyanopyridine	0.7		*m*-F	THF	−1.1	191.5
3-Cl-4-OMe	*cyclo*-PrCOMe	−1.2	197.6		Et$_2$O	0.0	
	i-Pr$_2$O	0.0			EtOAc	0.7	
3-Cl-4-SMe	*i*-Pr$_2$CO	−1.1	197.1	*m*-CF$_3$	MeOAc	−1.2	190.3
	cyclo-PrCOMe	−0.8			THF	0.2	
p-OH	*i*-Pr$_2$O	−1.1	198.7	*p*-CF$_3$	MeOAc	−0.9	190.0
p-*t*-Bu	Acetylacetone	−0.6	199.8		THF	0.5	
	p-Fluoroaniline	0.6		*p*-CO$_2$Me	Pr$_2$O	−0.9	194.7
3,4-Me$_2$	Acetylacetone	−0.4	199.6		Cyclohexanone	−0.7	
	2-Cyanopyridine	0.4		*m*-CN	*i*-PrCN	−2.3	187.8
p-Me	*i*-Pr$_2$O	−0.4	198.0		Acetone	0.2	
3,5-Me$_2$	*i*-Pr$_2$O	−0.9	198.5	*p*-CN	*i*-PrCN	−1.8	187.5
	Acetylacetone	0.7			C$_6$H$_5$CN	0.1	
m-Me	*cyclo*-PrCOMe	−0.7	197.1	*m*-NO$_2$	Acetone	0.6	187.3
	i-Pr$_2$O	0.5		*p*-NO$_2$	*i*-PrCN	−1.0	186.7
m-OH	*i*-Pr$_2$CO	0.5	195.6		Acetone	1.1	
m-OMe	*cyclo*-PrCOMe	−0.9	197.2	3,5-(CF$_3$)$_2$	PrCN	−1.0	185.4
	i-Pr$_2$O	0.4			1,4-Dioxane	−0.2	
m-SMe	*i*-Pr$_2$CO	−0.4	196.4	3,5-Me$_2$-4-NO$_2$	THF	−1.3	191.8
	cyclo-PrCOMe	−0.1			EtOAc	0.2	
H	Pr$_2$O	−1.8	195.7				
	i-Pr$_2$CO	0.3					

See footnotes of Table 1.

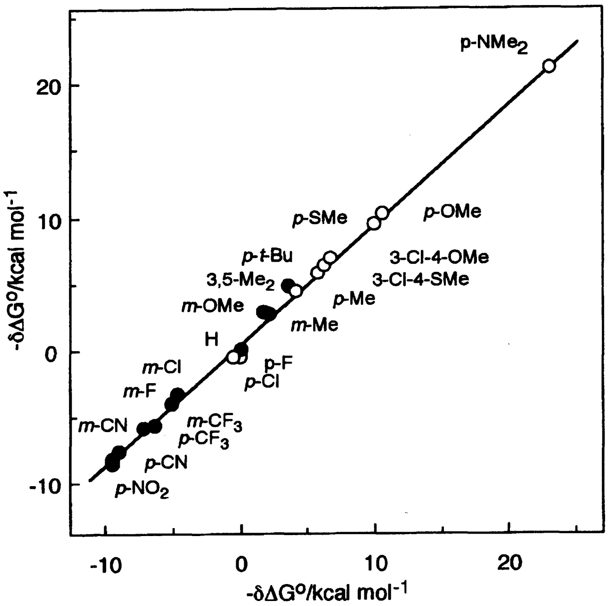


Fig. 1. Plot of gas phase basicities of benzaldehydes against relative stabilities of α-cumyl cations.

of a different contribution of the resonance effect between the two series. Taft et al. recently pointed out the importance of the polarizability effect in the gas-phase substituent effect (as discussed later), and found that the contribution of this effect was large in the electron-deficient carbocation system compared with that in relatively stable carbocation.[8)] The deviations of the *p*-*t*-butyl and 3,5-dimethyl groups may be explained by this effect, because the benzylic carbon in the α-hydroxybenzyl cation is more electron-deficient than that in the 1-hydroxy-1-methoxybenzyl cation. A similar trend was observed for *m*-methyl, *m*-methoxyl, and *m*-methylthio groups, and was probably due to the same cause.

Excluding these particular substituents, the deviations of the *para*-π-donor substituents are satisfactorily related to the resonance substituent constant, $\Delta\bar{\sigma}^+_{\mathrm{R}}$ ($=\sigma^+-\sigma^\circ$). For example, the $-\delta\Delta G^\circ$ values of the 1-hydroxy-1-methoxybenzyl cations are nicely described by Eq. 3.

$$-\delta\Delta G^\circ_{(\text{1-hydroxy-1-methoxybenzyl cation})} = -0.86\delta\Delta G^\circ_{(\alpha\text{-cumyl cation})} + 5.1\Delta\bar{\sigma}^+_{\mathrm{R}} \qquad (3)$$

This relation can be converted into the form of the

Table 4. Gas Phase Basicities of Reference Bases Used in This Study

Bases	GB	Bases	GB
m-MeC$_6$H$_4$NMe$_2$	217.0	i-Pr$_2$CO	196.1
C$_6$H$_5$NMe$_2$	215.4	C$_6$H$_5$CO$_2$Me	195.7
2-Methoxypyridine	213.7	Pr$_2$CO	195.1
p-FC$_6$H$_4$NMe$_2$	213.2	Cyclohexanone	194.0
m-FC$_6$H$_4$NMe$_2$	211.6	Styrene	193.9
MeCONMe$_2$	208.4	Pr$_2$O	193.9
PhCH$_2$NH$_2$	208.8	Et$_2$CO	192.8
2-Chloropyridine	206.6	PhCHO	192.1
t-Bu$_2$S	205.6	EtOAc	192.0
(MeO)$_3$PO	204.9	Et$_2$O	191.7
2-Pyrorridone	204.3	EtCOMe	190.8
HCONMe$_2$	203.0	THF	190.4
2-Fluoropyridine	202.9	MeOAc	189.2
Aniline	202.5	Acetone	187.9
4-Cyanopyridine	202.1	C$_6$H$_5$CN	187.6
3-Cyanopyridine	201.3	i-PrCN	185.7
Bu$_2$S	200.9	1,4-Dioxane	185.1
p-Fluoroaniline	200.2	PrCN	184.9
2-Cyanopyridine	200.0	HCO$_2$Et	184.6
Acetylacetone	199.3	i-PrCHO	184.0
m-Fluoroaniline	199.1	EtCN	183.6
i-Pr$_2$O	197.6	PrCHO	183.0
PhCOMe	197.3	PrOH	182.0
$cyclo$-PrCOMe	196.3		

All values in kcal mol^{-1}. Taken from Ref. 16 and private communication from R. W. Taft.

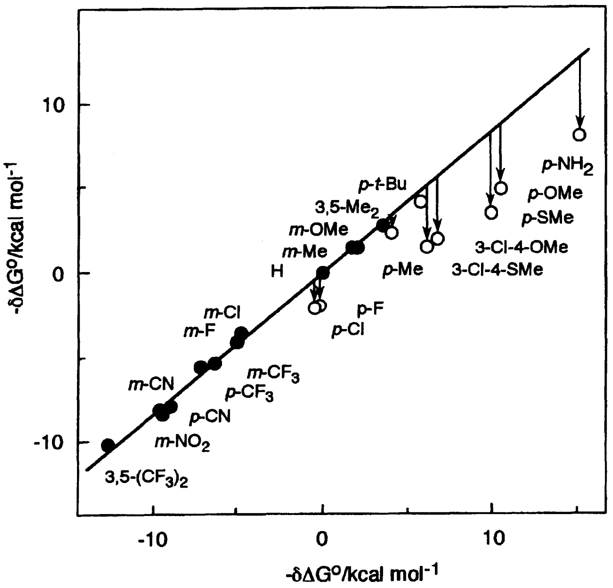


Fig. 2. Plot of gas phase basicities of methyl benzoates against relative stabilities of α-cumyl cations.

Table 5. Relative Gas Phase Basicities ($-\delta\Delta G^\circ$)[a] of Substituted Methyl Benzoates, Acetophenones, and Benzaldehydes

Subst.	$-\delta\Delta G^\circ$/kcal mol^{-1}		
	Methyl benzoates	Acetophenones	Benzaldehydes
p-NMe$_2$	c)	18.1	21.1
p-NH$_2$	7.9	11.4	—
3-CH$_2$CH$_2$O-4	—	9.9	—
p-OMe	4.8	8.1	10.2
p-SMe	3.4	6.5	9.5
3-Cl-4-OMe	1.9	5.4	6.8
3-Cl-4-SMe	1.4	4.5	6.4
p-OH	3.0	5.4	6.8
p-t-Bu	4.1	5.0	5.7
3,4-Me$_2$	3.9	5.1	—
p-Me	2.3	4.0	4.5
p-Et	—	—	4.7
p-i-Pr	—	—	5.7
p-$cyclo$-Pr	—	5.1	—
3,5-Me$_2$	2.8	3.9	4.8
m-Me	1.4	1.7	2.8
m-OMe	1.5	2.7	2.7
m-SMe	0.8	1.3	1.8
m-OH	−0.1	0.7	0.5
p-Cl	−2.1	−0.6	−0.6
p-F	−2.2	−0.6	−0.6
m-Cl	−3.6	−3.3	−3.2
m-F	−4.2	−3.7	−4.0
p-CO$_2$Me	−1.5[b]	−1.2	−1.0
p-COMe	c)	−1.7[b]	—
p-CHO	c)	—	−5.0[b]
m-CF$_3$	−5.4	−5.3	−5.6
p-CF$_3$	−5.7	−5.8	−5.9
m-CN	−7.9	−8.0	−7.6
p-CN	−8.2	−8.2	−8.1
m-NO$_2$	−8.4	−8.4	−8.4
p-NO$_2$	−9.0	−8.8	−8.7
3,5-(CF$_3$)$_2$	−10.3	−10.5	—
H	(195.7)[d]	(197.3)[d]	(192.1)[d]
3,5-Me$_2$-4-NO$_2$	−6.7[e]	−6.5[e]	−7.3[e]

a) In kcal mol^{-1}, a positive sign denotes greater basicity. b) Applied with a statistical correction. c) Protonation occurs at the substituent. d) Absolute GB values. e) Relative to 3,5-Me$_2$ derivatives of respective series.

Yukawa–Tsuno Eq. 1, because the $-\delta\Delta G^\circ{}_{\alpha\text{-cumyl cation}}$ is described by σ^+ ($=1.00\sigma^\circ+1.00\Delta\bar{\sigma}^+_R$).[13] In fact, the application of Eq. 1 to these substituent effects using the gas-phase substituent constants listed in Table 6 provided excellent correlations, as shown Figs. 4, 5, and 6. Figure 4 clearly demonstrates that the substituent effect on the stability of the 1-hydroxy-1-methoxybenzyl cation cannot be described in terms of a single set of ordinary substituent constants, either σ^+ or σ°, referred to as $r^+=1.00$ or 0.00, respectively. The r^+ value of 0.50 is reasonably attributed to the large stabilization of the positive charge in the 1-hydroxy-1-methoxybenzyl cation by the hydroxyl and methoxyl groups linked to the positive center carbon. The r^+ value of the α-hydroxybenzyl cation, having a single electron-donating substituent at the α-position, is the largest among the present three series, and is even larger than that of the α-cumyl cation. Thus, the r^+ value seems to decrease in the increasing order of electron-donating ability of the R group(s). This trend is qualitatively consistent with that observed for the ordinary benzylic carbocation system, PhC$^+$(R^1)R^2, where

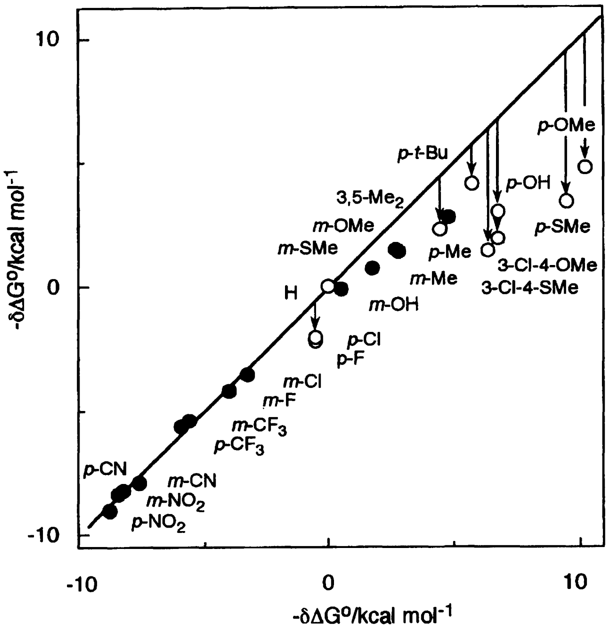


Fig. 3. Plot of gas phase basicities of methyl benzoates against those of benzaldehydes.

Table 6. Substituent Constants Used for Analysis of Gas Phase Substituent Effects

Subst.	$\sigma^{\circ}_{(g)}$	$\Delta\bar{\sigma}^{+}_{R(g)}$	Subst.	$\sigma^{\circ}_{(g)}$	$\Delta\bar{\sigma}^{+}_{R(g)}$
p-NMe_2	−0.43	−1.30	m-F	0.39	0.00
p-NH_2	−0.19	−1.00	m-Cl	0.36	0.00
3-CH_2CH_2O-4	−0.19	−0.75	p-$COCH_3$	0.17	0.00
p-OMe	−0.10	−0.70	p-CO_2Me	0.14	0.00
3-Cl-4-OMe	0.22	−0.72	p-CHO	0.43	0.00
p-SMe	0.04	−0.73	m-CF_3	0.50	0.00
3-Cl-4-SMe	0.25	−0.73	p-CF_3	0.56	0.00
p-OH	−0.05	−0.50	m-CN	0.69	0.00
p-t-Bu	−0.27	−0.17	p-CN	0.73	0.00
p-Me	−0.13	−0.20	m-NO_2	0.73	0.00
m-Me	−0.12	0.00	p-NO_2	0.80	0.00
p-F	0.20	−0.17	3,5-$(CF_3)_2$	0.98	0.00
p-Cl	0.20	−0.15	H	0.00	0.00

Taken from Ref. 12b.

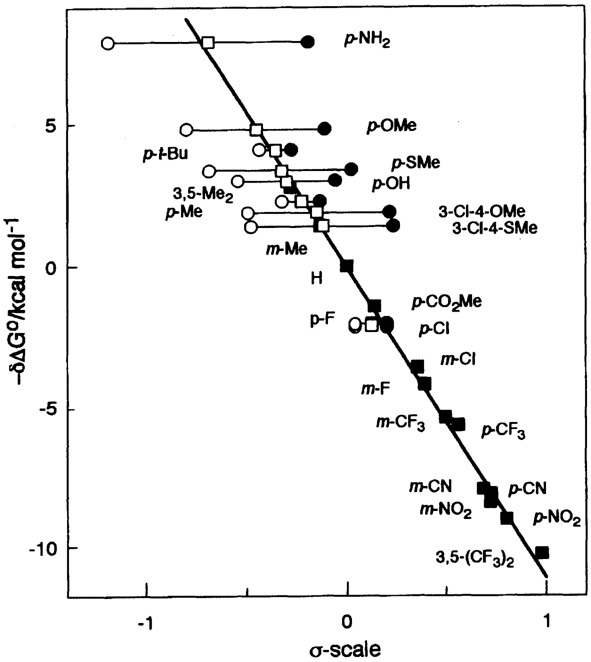


Fig. 4. The Hammett plot of gas phase basicities of methyl benzoates. ● and ■; σ°, ○; σ^{+}, □; $\bar{\sigma}$ (r^{+}=0.50).

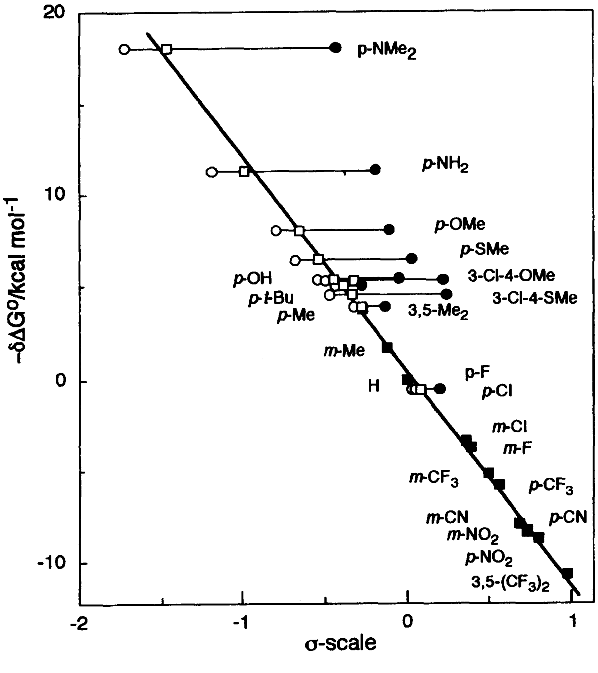


Fig. 5. The Hammett plot of gas phase basicities of acetophenones. ● and ■; σ°, ○; σ^{+}, □; $\bar{\sigma}$ (r^{+}=0.82).

R^1 and R^2=H, Me, CF_3.11) While the r^+ values in the latter system correlated linearly with the intrinsic stability of the unsubstituted member (ring substituent=H) of the respective series, in the $PhC^+(OH)R$ system there is no simple linear relationship between the r^+ values and the relative stabilities of the parent cation, which were estimated from the GB values of the unsubstituted derivatives (Table 7). This means that the effect of the R group on the r^+ value differs somewhat from the effect on the stability of the parent carbocation. It is likely that the thermodynamic stability of the parent carbocation is affected not only by electronic effects, such as the resonance and inductive effects of the R group, but also by electronegativity and polarizability effects, whereas the r^+ value depends mainly on the electronic effects. Since the variation of the R group in the $PhC^+(R^1)R^2$ system is limited to within a relatively narrow range, it appears that both the stability of the parent cation and the r^+ value are similarly influenced by the R group, and hence give a linear relationship between these quantities. Further studies may be necessary to verify this explanation.

Furthermore, an alternative linear relationship was observed when the r^+ values were plotted against the differential GB values between PhCOR and HCOR, which may be

Table 7. Correlation Results of Gas Phase Basicities by Eq. 1

ArCOR	$-\rho$ a)	r^+	SD b)	R c)	n d)	ΔGB e)	$\Delta\bar{\sigma}_R^+$ f)	ΔSE_{Ph} g)
R=OMe	11.1±0.2	0.50±0.03	±0.26	0.998	19 h)	3.6	−0.70	14.8
Me	11.5±0.2	0.82±0.04	±0.31	0.999	24 i)	5.2	−0.20	19.3
H	11.6±0.2	1.06±0.04	±0.30	0.999	20 j)	0.0	0.00	27.8

a) In kcal mol^{-1} $\bar{\sigma}^{-1}$ unit. b) Standard deviations. c) Correlation coefficient. d) Number of substituents used for regression calculations. e) GB values of the parent benzoyl compounds relative to benzaldehyde in kcal mol^{-1}. f) Resonance substituent constant of R in the gas phase, Ref. 12b. g) Stabilization effect of the phenyl group given by [$GB_{(PhCOR)}-GB_{(HCOR)}$], in kcal mol^{-1}. GB values of HCOR were taken from Ref. 16a. h) Excluded *p*-Cl and *p*-F. i) Excluded 3-Cl-4-OMe. j) Excluded *p*-Cl, *p*-F, and *m*-Me.

regarded as a measure of the stabilization effects of the phenyl group on the stability of a cation, $HC^+(OH)R$, (Fig. 7). This result is consistent with our basic concept that the r^+value is a measure of the π-interaction between a positive charge and the phenyl ring. In conclusion, the π-charge formed at the benzylic position by the addition of a proton is stabilized through competitive π-delocalization by the aryl group and the R group.

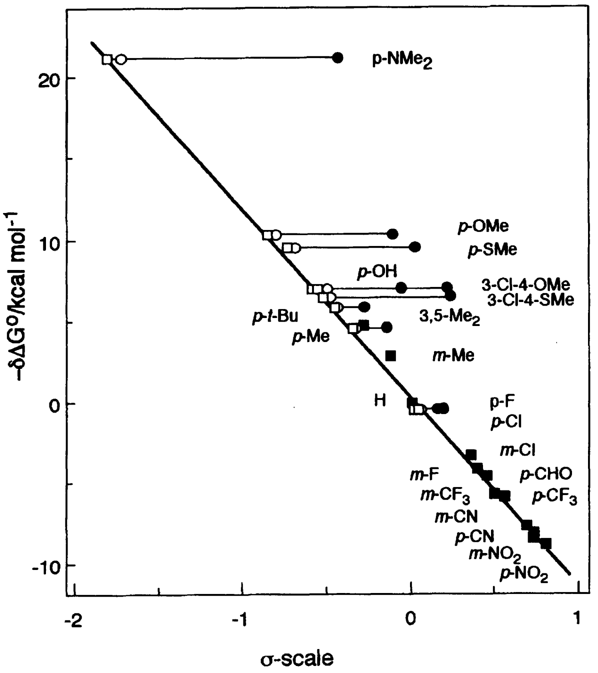


Fig. 6. The Hammett plot of gas phase basicities of benzaldehydes. ● and ■; σ°, ○; σ^+, □; $\bar{\sigma}$ (r^+=1.06).

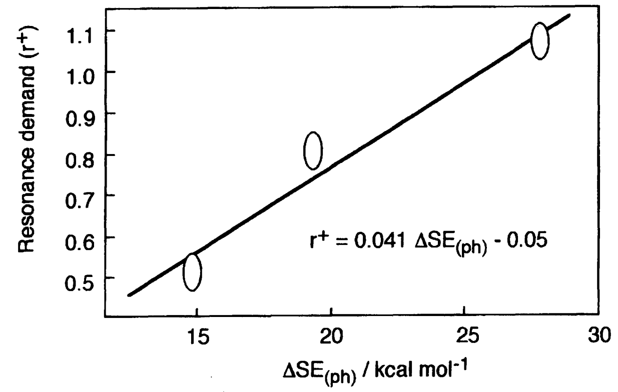


Fig. 7. Linear relationship between the ρ^+ value and the stabilization effect of the phenyl group.

In contrast to the high response of the r^+ value to the variation of the R group, the ρ values are nearly constant in this system. Such constancy of the ρ value was also observed for a series of substituent effects on the GB of the α-substituted styrene system, $PhC(R)$=CH_2, though the ρ values are somewhat larger than those of the benzoyl system.[10—12] The identical ρ value within the homologous series suggests that the response of the stability of a cation to the polar effect of substituents is primarily determined by the distance between the charge and a substituent. The cause for the result that the ρ value of the benzoyl system is about 10% smaller than that of the styrene system is not clear. This trend, however, is consistent with theoretical calculations showing that relative proton affinities for benzaldehydes having non-conjugative substituents are consistently smaller than the corresponding values of α-methylstyrenes to give a ρ ratio of 0.88.[17]

Comparison with Taft's Treatments. It is necessary to discuss Taft's treatment for the gas-phase substituent effects because Taft and Topsom recently analyzed the gas-phase substituent effects of the present aromatic carbonyl system based on a new equation (Eq. 4) using our preliminary data,[8b)]

$$-\,\delta\Delta G^\circ = \rho_F\sigma_F + \rho\sigma_R^+ + \rho_\alpha\sigma_\alpha. \qquad (4)$$

In this equation, σ_F, σ_R^+, and σ_α are substituent constants representing the field effect, resonance effect, and polarizability effect, respectively. ρ_F, ρ_R, and ρ_α are the susceptibility parameters for the respective effects. From this analysis they pointed out several features of the substituent effects of the present system: (1) The ρ_R^{para} values are a strong function of the σ_R^+ value of R and are satisfactorily correlated by the positive π-charge for the unsubstituted member (X=H) of that series at the carbon atom to which the R substituents are bonded. (2) The ρ_α^{para} value is quite small compared with both ρ_F and ρ_R, and decreases in the order H>Me>OMe. (3) The ratio $\rho_F^{para}/\rho_F^{meta}$ is essentially constant for all the series at 1.1, indicating that the inherent field effects of a substituent are closely equivalent at the *meta* and *para* positions.

The most important feature of the present system elucidated by our analysis that the contribution of resonance effect involved in these substituent effects decreases in increasing order of electron-donating ability of R is equivalent to the conclusion (1) derived from Taft's analysis. Although in our analysis the polarizability effect is neglected, this does not practically cause any serious conflict with Taft's conclusion, because its contribution is small for most substituents. In addition, the precision of the correlations given by both treatments satisfies the minimum requirement of the correlation analysis.

There is, however, a severe difference in the fundamental concepts concerning the substituent effect analysis. In our analysis, the effects of π-electron-withdrawing substituents can be described by σ°, which involves both inductive/field and resonance effects, $\sigma^\circ=1.00\sigma_I+1.00\sigma_\pi$,[18] whereas in the analysis based on Eq. 4, $\sigma_R^+=0.00$ is assumed to all π-electron-withdrawing substituents in the reactions with a strongly electron-deficient reaction center. This assumption does not appear to be well confirmed, although they pointed out as evidence that the contribution of a resonance effect evaluated by $-\delta\Delta G^\circ -\rho_F\sigma_F-\rho_\alpha\sigma_\alpha$ is zero for the π-electron-withdrawing substituents. It is thus necessary to examine from a different point of view whether the assumption is valid or not. A steric inhibition of the resonance effect would provide a decisive criterion for evaluating the contribution of the resonance effect involved in the substituent effect.[19] For example, the nitro group is well-known to be twisted by introducting two methyl groups at a position ortho to the nitro group, hence resulting in a reduced resonance effect.[20] We therefore measured the gas-phase basicities of 3,5-dimethyl-4-nitrobenzaldehyde, 3,5-dimethyl-4-nitroacetophenone, and methyl 3,5-dimethyl-4-nitrobenzoate. The effects of the nitro group in the 3,5-dimethyl system are given as follows: benzaldehyde, −7.3; acetophenone, −6.5; methyl benzoate, −6.7 kcal mol^{-1}. These $-\delta\Delta G^\circ$ values of the twisted nitro group are apparently smaller than those of the planar nitro group. This reduction is reasonably attributed to a steric inhibition of the resonance effect as a first approximation, because the hydroxyl group, which is not sterically twisted, does not show such a reduced effect in the 3,5-dimethyl system (see Table 2). A similar reduced effect of the twisted nitro group was observed for the gas-phase acidities of benzoic acids,[21] of which the substituent effect was correlated with σ°.[22] These results lead to the conclusion that the π-electron-withdrawing substituents have appreciable resonance effects, even in a strongly electron-deficient reaction system. Accordingly, the assumption that $\sigma_R^+=0.00$ for all +R groups appears to be oversimplified for describing such substituent effects, even though the correlations are given with high precision.[21] Since the *para* +R derivatives have consistently lower basicities than do the corresponding *meta* derivatives, this improper assumption would also be the cause for the ratio $\rho_F^{para}/\rho_F^{meta}>1.0$, which is not readily explained in terms of the transmission model of the field/inductive effect.[23]

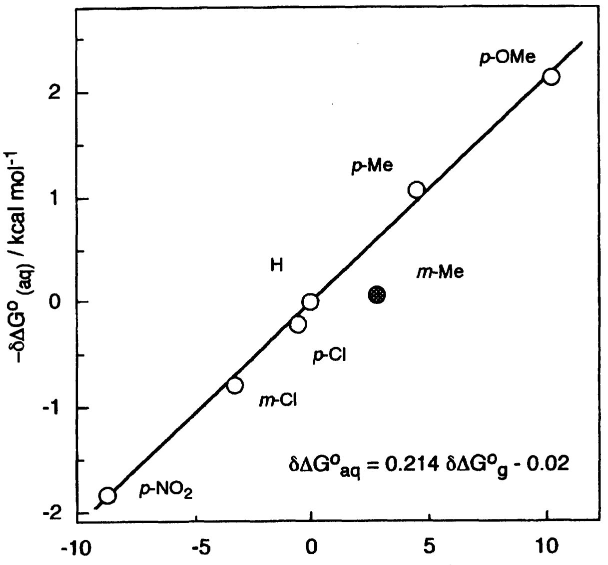


Fig. 8. Aqueous solution versus gas phase basicities of benzaldehydes.

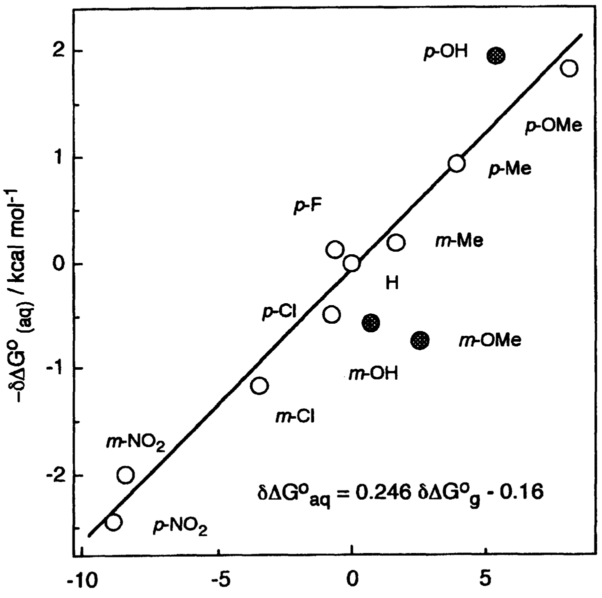


Fig. 9. Aqueous solution versus gas phase basicities of acetophenones.

Solvent Effects. The relative basicities of the benzaldehydes[14a)] and acetophenones[14b)] in aqueous solution are plotted against the corresponding values in the gas phase in Figs. 8 and 9, respectively. In an analysis of the solvent effects, it may be convenient to separate the solvent effects into two classes, i.e., common solvent effects on a whole system and specific solvent effects arising from a specific interaction with the particular substituent. Since the latter solvent effects correspond to solvent-modifications of the substituents, in order to explore the solvent effects on a whole system it would be reasonable to exclude particular substituents, such as the hydroxyl group, from a comparative analysis, $-\delta\Delta G^\circ_{aq}$ versus $-\delta\Delta G^\circ_{gas}$. In fact, by excluding these substituents we can find a good linear relationship in both Figs. 8 and 9. The deviation of the *m*-methyl group in Fig. 8 may again be explained in terms of a larger contribution of the polarizability

Table 8. Correlation Results of Basicities in Aqueous Solution by Eq. 1[a)]

	Benzoic acid	Acetophenone	Benzaldehyde
$-\rho$[b)]	1.56	2.99	2.37
r^+	0.55	0.76	1.16

a) Taken from Ref. 13a. b) In kcal mol^{-1} per $\overline{\sigma}$ unit.

effect in the gas phase than that in solution. Although the *m*-methyl group in Fig. 9 does not show such a large deviation, this is not surprising because the polarizability effect tends to be more significant in the electron-deficient α-hydroxybenzyl cation compared with that in the relatively stable 1-hydroxy-1-phenylethyl cation (as mentioned above). The deviation of the *m*-methoxyl group in Fig. 9 may be attributed to an increased inductive effect in aqueous solution due to a hydrogen-bonding interaction between the oxygen atom of the substituent and the solvent.[24,25)]

The existence of such a linear relationship between gas and aqueous solution phases suggests that there is a common set of substituent constants for the respective series in both phases. One of the authors had analyzed many years ago these substituent effects in aqueous solution, including a larger number of substituents than that of the present comparative analysis, $-\delta\Delta G^\circ_{\text{aq}}$ versus $-\delta\Delta G^\circ_{\text{gas}}$.[13a)] The results given in Table 8 show that the r^+ values of the benzaldehyde and acetophenone series in aqueous solution indeed agree with those for the corresponding gas-phase basicities, being consistent with the graphical analysis described above. The r^+ value of the benzoic acid series in aqueous solution is comparable to that of methyl benzoates in the gas phase. Considering the similarity of the electron-donating ability between the hydroxyl and methoxyl groups, we can assume that the r^+ value of the benzoic acid series in aqueous solution is also identical to that in the gas phase. Consequently, it appears more likely that the r^+ value is essentially the same in aqueous solution and gas phases. That is, the degree of stabilization of the positive charge through π-delocalization into the aryl ring relative to that by an inductive/field effect is independent of the solvation of the cation, and the r^+ value is a function of the structure of the ion. This conclusion is consistent with our previous observation that the r^+ values of ordinary benzylic carbocation system, $PhC^+(R^1)R^2$, in the gas phase are in complete agreement with those of the S_N1 solvolysis of the corresponding precursors.[11)] Accordingly, the ρ value is regarded as being the only probe of solvent effects on the whole system of proton-transfer equilibria. Indeed, the ρ values of the solution basicities are remarkably smaller than those of the gas-phase basicities. This is easily explained by the effective dispersion of the positive charge of the ion to solvent molecules. In conclusion, the solvation of a cation reduces the central charge so as to lower the response to substituent perturbation, essentially without changing the nature of the intramolecular charge-delocalization.

Experimental

Chemicals. The majority of chemicals used in this work were obtained from commercial sources. The remaining compounds were prepared according to general procedures. The identity of all chemicals prepared in this study was confirmed by their NMR and IR spectra. Purification of all compounds was performed just before use by distillation, recrystalization, or sublimation. Their purities were checked by ICR mass spectra. Each liquid sample was subjected to several freeze-pump-thaw cycles on the ICR inlet system to remove any entrapped volatile impurities.

Measurements. The equilibrium-constant measurements were performed on a homemade pulsed ion cyclotron resonance mass spectrometer equipped with a capacitance-bridge detector.[26)] An Extrel FTMS-2001 was also used for several measurements. Details concerning the experimental techniques used for the measurements of the equilibrium constants (*K*) of the proton-transfer reaction (5), where B refers to a given benzoyl compounds and B_0 is a reference base, were described previously.[10)]

$$B + B_0H^+ \rightleftharpoons BH^+ + B_0, \tag{5}$$

$$K = [B_0/B]\cdot[BH^+/B_0H^+], \tag{6}$$

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

All measurements were performed at 70 °C at a constant magnet field strength of 1.3 Tesla (or at 3.0 Tesla on the Extrel FTMS-2001). The pressures of the neutral reactants were measured by means of a Bayard–Alpert type ionization gauge with appropriate correction factors being applied in order to correct the gauge readings for the different ionization cross sections of the various compounds.[27,28)] The overall pressures of the reagents were maintained at 1 to 3×10^{-4} Pa by controlled rates through leak valves (Anelva) from a parallel inlet manifold into the vacuum chamber. After a reaction period of several hundred ms to 1 s, depending upon the reactant, equilibrium was attained and the relative abundance of BH^+ and B_0H^+ was 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-mean values of *K* from Eq. 6 were used to calculate ΔG° at 343 K (Eq. 7) with an average uncertainty of ±0.2 kcal mol^{-1}. More than two reference compounds were used in most cases in order to ensure the internal consistency of the data. The GB values for the reference compounds were taken from the literature.[8a,16)]

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